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Dielectric constant and phase transition sequence in betaine calcium chloride dihydrate (BCCD)

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Abstract. BCCD exhibits a sequence of structural phase transitions from a high-symmetry orthorhombic phase to different commensurate or incommensurate phases modulated along [001]. This work reports a study of the dielectric constant at a constant frequency of 10 kHz as a function of temperature. The results are discussed within the scope of Landau theory and reveal the existence of new intermediate high-order commensurate phases, in agreement with recent pyroelectric measurements.

1. Introduction

Betaine calcium chloride dihydrate (BCCD) exhibits a sequence of structural phase transitions from a high-symmetry orthorhombic phase ($Pnma$) to different commensurate or incommensurate phases modulated along [001] [1, 2].

According to x-ray [2], Raman [3] and EPR [4] studies, there are at least six distinct modulated phases, four of which are commensurate. The modulation wavevectors $\boldsymbol{q} = \delta(T)\boldsymbol{c}^*$ characterising the commensurate phases are $\delta = 2/7$ (127 K > T > 125 K), $\delta = 1/4$ (116 K > T > 75 K), $\delta = 1/5$ (75 K > T > 56 K) and $\delta = 1/6$ (56 K > T > 47 K). The two incommensurate phases occur between 164 K and 127 K (INC1) and between 125 K and 116 K (INC2).

Below $T = 47$ K the phase transition sequence is not well established (see table 1). According to x-ray measurements [2] the satellite reflections associated with the phase $\delta = 1/6$ disappear between 47 K and 43 K but are observed again below this temperature. This re-entrance of the phase $\delta = 1/6$ below the onset of a non-modulated phase is not confirmed, however, by EPR [4] or Raman scattering [3] measurements. According to these later studies [4], a very narrow higher-order commensurate phase and a non-modulated phase ($\delta = 0$) are observed respectively at 45.4 K < T < 46.4 K and T < 45.4 K.

An interesting feature of the phase transition sequence in this material concerns the polar properties of the different commensurate phases. As shown by pyroelectric [5] and hysteresis loops measurements [6] BCCD exhibits spontaneous electrical polarisations along [010] between 125 K and 127 K (phase $\delta = 2/7$) and below 48 K or along [100] in the temperature ranges corresponding to the phases $\delta = 1/4$ and $\delta = 1/6$. In a recent work Perez Mato has shown, by assuming for the phase transition sequence a

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Table 1. The critical temperatures and the possible phase transition sequence in BCCD suggested by the present measurements of the dielectric constants $\varepsilon_{[010]}$ and $\varepsilon_{[100]}$ are compared with the values of the critical temperatures and phase transition sequence reported by x-ray [2] and Raman scattering [3] measurements. The temperatures are expressed in kelvin and each phase is identified by the corresponding values of δ ($\boldsymbol{q} = \delta(T)\boldsymbol{c}^*$).

	T_8	T_7	$T_{6'}$	T_6	$T_{5'}$	T_5	$T_{4''}$	$T_{4'}$	T_4	T_3	T_2	T_1
$\varepsilon_{[010]}$	47	51	55	56.5	76.5	77.5	—	115	116	124	126	164
$\varepsilon_{[100]}$	—	—	—	—	—	—	114	—	—	—	—	—
	1/∞ ↕ ?	? ↕ 1/6	1/6 ↕ 2/11	2/11 ↕ 1/5	1/5 ↕ 2/9	2/9 ↕ 1/4	1/4 ↕ ?	? ↕ 4/15	4/15 ↕ INC2	INC2 ↕ 2/7	2/7 ↕ INC1	INC1 ↕ P*nma*
[2]	43 1/6 ↕ 1/∞	47 1/∞ ↕ 1/6	56 1/6 ↕ 1/5		75 1/5 ↕ 1/4			116 1/4 ↕ INC2		125 INC2 ↕ 2/7	127 2/7 ↕ INC1	164 INC1 ↕ P*nma*
[3]	45.4 1/∞ ↕ ?	46.4 ? ↕ 1/6	52.5 1/6 ↕ 1/5		75 1/5 ↕ 1/4			116 1/4 ↕ INC2		125 INC2 ↕ 2/7	127 2/7 ↕ INC1	164 INC1 ↕ P*nma*

single set of irreducible order parameters with a common small representation, that in general a commensurate phase is polar if δ = even/odd ($P\|[010]$) or if δ = odd/even ($P\|[100]$) and non-polar if δ = odd/odd. [7].

The definite polar character of the different commensurate phases allows the use of pyroelectric or dielectric constant measurements for the study of some fine details of the phase transition sequence. Taking advantage of this situation we have shown in another work [8] that detailed pyroelectric measurements reveal the existence of three additional phases polar along [010] and occurring in narrow temperature ranges centred at about 116 K, 75 K and 56 K.

The aim of the present work is to establish a correlation between the phase transition sequence and the dielectric behaviour of BCCD and to show that the existence of the three additional phases referred to above can explain some details of the temperature dependence of the dielectric constant.

2. Theory

The experimental results reported will be discussed within the scope of Landau theory, using for each phase transition between modulated phases, local $d = 2$ complex conjugated primary order parameters and considering the electrical polarisation P_x and P_y as possible secondary order parameters.

The general form of the Landau free energy density for a given modulated phase in BCCD must verify the same symmetry constraints as in the incommensurate systems of the Rb_2ZnCl_4 family. As in these materials, the modulation wavevector in BCCD lies in a symmetry line [$\boldsymbol{q} = \delta(T)\boldsymbol{c}^*$] of the Brillouin zone for which the star of the vector $\boldsymbol{q}$ contains only two non-equivalent vectors $\{\boldsymbol{q}, -\boldsymbol{q}\}$ and the primary order parameter must be transformed according to one of the four physically irreducible representations (IR) of the group *Pnma* generated by each of the four IR of the point group of the vector $\boldsymbol{q}$ (C_{2v}). Writing the components of the primary order parameter as $Q = \rho\, e^{i\varphi}$ and $Q^* = \rho\, e^{-i\varphi}$ ($\varphi = 2\pi t/n$) we have therefore the following expression for the free energy density [9–11]

$$f_1(x) = \tfrac{1}{2}\alpha\rho^2 + \tfrac{1}{4}\beta\rho^4 - \gamma\rho^{2n}\cos(2n\varphi) - \delta\rho^2(\partial\varphi/\partial x) + \tfrac{1}{2}\kappa[\rho^2(\partial\varphi/\partial x)^2 + (\partial\rho/\partial x)^2]. \quad (1)$$

In this equation $\alpha = \alpha_0(T - T_0)$ and $\alpha_0, \beta, \gamma, \delta$ and κ are positive constants. In order to study the behaviour of the dielectric constant at a given transition point we need to investigate, in addition, the possible coupling between the primary order parameter and an electric polarisation P for each modulated commensurate phase.

A mixed invariant linear on an electric polarisation P must involve a translational invariant polynomial on the primary order parameter components that is transformed exactly like P under the space group operations of the reference phase. For a given commensurate phase $\delta = t/n$, a general translational invariant of degree n, can be obtained as a linear combination of the basic independent translational invariants ρ^n, $\rho^n\sin(n\varphi)$ and $\rho^n\cos(n\varphi)$ [12]. As the symmetry of the order parameter is known to correspond to irreducible representation Λ_3 of C_{2v} $\{\chi(\sigma_y) = \chi(C_{2z}) = -1\}$ [7], it is possible to verify that, from these three independent translational invariants, only $\rho^n\sin(n\varphi)$ is transformed as P_x if δ = odd/even or as P_y if δ = even/odd. In consequence, the possible invariants linear on a dielectric polarisation are of the form $P_x\rho^n\sin(n\varphi)$ if t/n = odd/even or $P_y\rho^n\sin(n\varphi)$ if t/n = even/odd. For the phases of the type δ = odd/odd it is found, in agreement with [7], that no coupling between the primary order parameter and a polarisation is possible since, in this case, the possible translational invariants are transformed according to non-polar irreducible representations.

From the above considerations we can conclude that only the dielectric constants measured along the directions [100] and [010] are expected to be sensitive to some of the phase transitions displayed by the material. As observed experimentally [13], the dielectric constant along [001] cannot exhibit any critical behaviour since the coupling between P_z and the primary order parameter is not allowed by symmetry.

For the commensurate phases δ = odd/even or δ = even/odd we must consider in (1) additional terms respectively on the electrical polarisations P_x or P_y. Up to second order and in the presence of an applied electric field E, these additional terms can be written as

$$f_2 = 2\xi p^n P\sin(n\varphi) + \Omega P^2\rho^2 + (1/2\chi_0)P^2 - PE. \quad (2)$$

From the free energy density $f = f_1 + f_2$, we can now calculate the behaviour of the dielectric constant (ε) at zero applied field, in the vicinity of a transition from an INC phase to a polar commensurate phase. Assuming a constant amplitude approximation and following Prelovsek [11], we obtain

$$\varepsilon = \bar{\chi}_0 + [\bar{\chi}_0^2\xi^2/(\bar{\chi}_0\xi^2 - \gamma)]\{[E(m)/(1-m)^2K(m)] - 1\} \quad (3)$$

where $\bar{\chi}_0 = \chi_0/(2\Omega\rho_0^2\chi_0 + 1)$ represents a renormalised electrical susceptibility. $K(m)$ and $E(m)$ stand respectively for the complete elliptic integrals of first and second kind, defined according to [14]. The parameter m is real and is defined in the interval [0, 1].

If the temperature dependence of the amplitude of the order parameter is assumed to be $\rho^2(T) = [\alpha_0/\beta]|T - T_I|$ (imposed amplitude approximation) then the temperature dependence of the dielectric constant in (3) is only defined by the parameter m. Con-

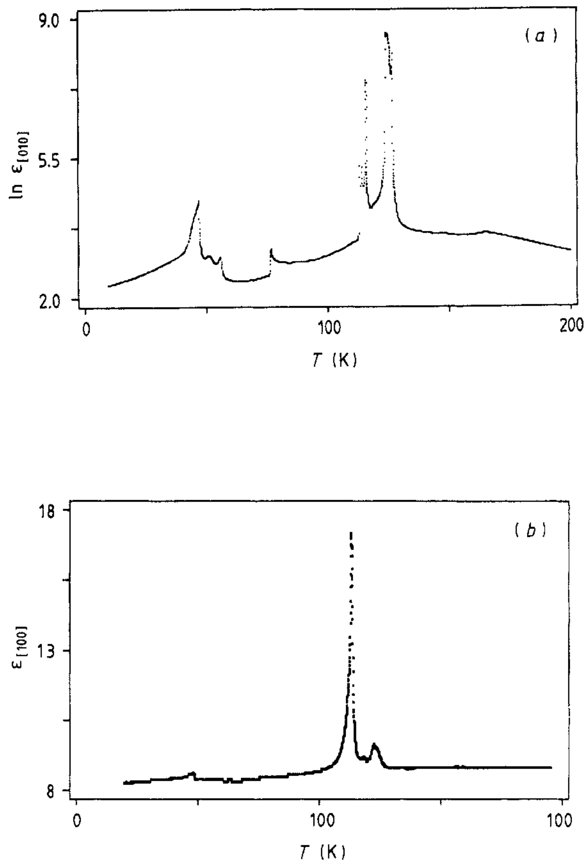

Figure 1. (*a*) Logarithm of the dielectric constant along the crystallographic direction [010] as a function of temperature. (*b*) Dielectric constant along the crystallographic direction [100] as a function of temperature.

sidering the average free energy density over a period of the modulation wave ($F = (1/x_0)\int_0^{x_0} f(x)\,\mathrm{d}x$), we can obtain this temperature dependence by imposing that, in thermal equilibrium, $(\partial F/\partial m) = 0$. This condition leads to

$$m^{1/2}/E(m) = [\sqrt{\kappa(\bar{\chi}_0\xi^2 - \gamma)}\,4/\pi\delta]\,\rho_0^{n-1}. \tag{4}$$

Equations (3) and (4) can be used for the analysis of the experimental temperature dependence of the dielectric constant in the vicinity of a lock-in transition to a polar phase (δ = even/odd or δ = odd/even). It should be noted that (3) can be fitted to the experimental data by adjusting a single constant $A = \bar{\chi}_0^2\xi^2/(\bar{\chi}_0\xi^2 - \gamma)$ if the weak temperature dependence of χ_0 is neglected.

3. Results and discussion

The dielectric constants $\varepsilon_{[010]}$ and $\varepsilon_{[100]}$ were measured as functions of temperature at a constant frequency of 10 kHz using an AC voltage of 1.5 V. The temperature was monitored with a chromel-iron-doped gold thermocouple with a minimal sensitivity of 18 μV K^{-1}, using a microvoltmeter with a resolution of 0.1 μV.

The temperature dependence of $\varepsilon_{[010]}$ and $\varepsilon_{[100]}$ is shown respectively in figures 1(*a*) and 1(*b*) for increasing temperature measurements. As can be seen $\varepsilon_{[010]}(T)$ shows anomalies at $T_1 = 164$ K, $T_2 = 126$ K, $T_3 = 124$ K, $T_4 = 116$ K, $T_{4'} = 115$ K, $T_5 = 77$ K, $T_6 = 56$ K, $T_7 = 51$ K and $T_8 = 47$ K, while $\varepsilon_{[100]}(T)$ shows a single clear anomaly at $T_{4''} = 114$ K. The small shoulder centred at about 123 K in figure 1(*b*) is considered to be due to a small misorientation of the sample and will not be taken into account.

The higher-temperature anomalies ($T > 114$ K), shown in more detail in figure 2, reflect the sequence of phase transitions from the reference phase down to the commensurate $\delta = 1/4$ phase. These anomalies can be described using (3) and (4).

The transition from the P*nma* phase to the first incommensurate phase at $T_1 = 164$ K is marked by the small anomaly in $\varepsilon_{[010]}$ displayed in figure 2(*a*). For $T > 170$ K we found that $\varepsilon_{[010]}(T)$ follows a Curie–Weiss law ($\varepsilon = C/(T - T_0)$) with a Curie constant $C = 2635$ K and a Curie temperature $T_0 = 95.5$ K. Just below T_1 down to 158 K a linear dependence can be ascribed to $\varepsilon_{[010]}{}^{-1}(T)$, in agreement with the behaviour expected from (3). In fact, as T approaches $T_1 = 164$ K from below, $m \to 0$ (4) and therefore, $\varepsilon \to \bar{\chi}_0$ (see (3)). The temperature dependence of the dielectric constant $\varepsilon_{[010]}$ just below T_1 can therefore be expressed as

$$\varepsilon = \chi_0/[1 + 2\Omega(\alpha_0/\beta)\chi_0(T_I - T)]. \qquad (5)$$

The fit of this equation to the experimental data in the temperature range $158\ \mathrm{K} < T < 164\ \mathrm{K}$ gives $\Omega\alpha_0/\beta = 1.625 \times 10^{-4}\ \mathrm{K}^{-1}$.

The anomalies in $\varepsilon_{[010]}$ at $T_2 = 126$ K and $T_3 = 124$ K reflect the lock-in of the modulation wavevector at the value $\delta = 2/7$. For this commensurate phase, the coupling between the primary order parameter and P_y is allowed by symmetry and therefore $\varepsilon_{[010]}$ is expected to be sensitive to the corresponding lock-in transition. In figure 2(*b*) the experimental curve $\varepsilon_{[010]}(T)$ observed in the temperature range between $T = 142$ K and $T = 122$ K is compared with a theoretical curve calculated from (3) with $n = 7$ and $A = 0.45$. As can be seen, the critical behaviour observed for $T \geqslant 127$ K can be well described by the fitting. The agreement between the experimental and theoretical curves is good up to values of m of the order of 0.998 to which correspond values of the dielectric constant of the order of 10^4. This transition can therefore be considered as one of the best examples, among insulating materials, of a continuous lock-in transition. However, even for the purest samples measured, a high value of the dielectric constant is observed between T_2 and T_3, which suggests, on the grounds of the model described in [9], that the soliton density remains non-zero in all the small temperature range of stability of the phase $\delta = 2/7$.

Below $T_3 = 124$ K down to the onset of the commensurate phase $\delta = 1/4$, the modulation wavevector changes from $2/7 = 0.285$ to $1/4 = 0.25$. Figures 2(*c*) and 2(*d*) show respectively the behaviour of $\varepsilon_{[010]}(T)$ and $\varepsilon_{[100]}(T)$ in the corresponding temperature region. As mentioned above, $\varepsilon_{[010]}(T)$ displays two distinct anomalies at $T_4 = 116$ K and $T_{4'} = 115$ K. These two anomalies are well resolved and are separated by a sharp decrease of the value of $\varepsilon_{[010]}(T)$ at about $T = 115.6$ K. In contrast, $\varepsilon_{[100]}(T)$ shows a relative maximum at $T_{4''} = 114$ K and displays only a small shoulder at $T_4 = 116$ K. This situation clearly suggests a more complex phase sequence than a single transition between the phases INC2 and $\delta = 1/4$.

Relying on the previous analysis it can be assumed that the anomalies observed in $\varepsilon_{[010]}(T)$ at $T_4 = 116$ K and $T_{4'} = 115$ K mark the onset and disappearance of a commensurate phase of the type δ = even/odd. This assumption is supported by recent pyroelectric measurements which show the rise of a small polarisation along [010] in the corresponding temperature region [8].

The simplest rational value of δ = even/odd in the range between $\delta = 2/7$ and $\delta = 1/4$ is $\delta = 4/15$. The existence of a lock-in transition from INC2 to this narrow

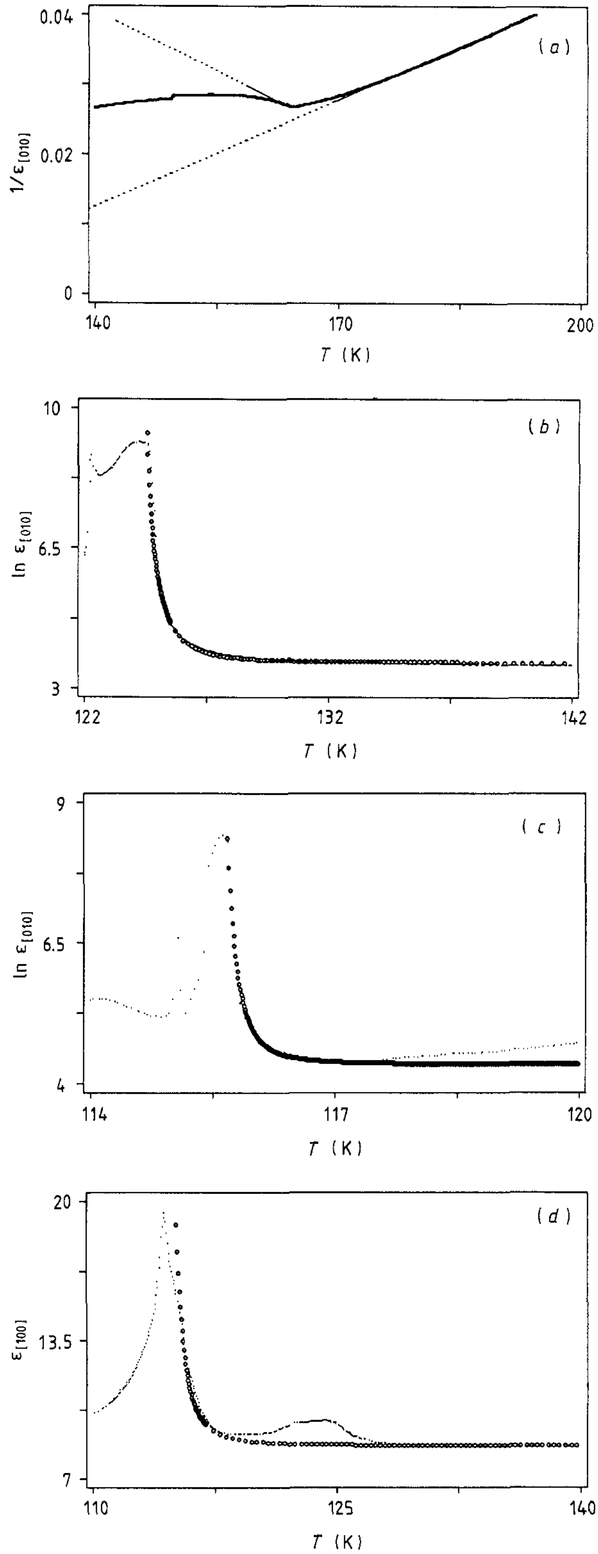

Figure 2. (*a*) Plot of the inverse of the dielectric constant along [010] as a function of temperature in the vicinity of the transition from the P*nma* phase to INC1 at $T_1 = 164$ K. The dotted lines show the fit to a Curie–Weiss law ($T > 170$ K) and to equation (5) ($164\ \mathrm{K} > T > 158$ K). (*b*) Logarithm of $\varepsilon_{[010]}$ as function of temperature in the vicinity of the transition from the INC1 phase to the $\delta = 2/7$ phase. The experimental data (dots) are compared with a fitted curve (circles) obtained from (3) with $A = 0.45$ and $n = 7$. (*c*) Logarithm of $\varepsilon_{[010]}$ as function of temperature in the vicinity of the transition from the INC2 phase to the $\delta = 4/15$ phase. The experimental data (dots) are compared with a fitted curve (circles) obtained from (3) with $A = 0.165$, $\chi_0 = 77$ and $n = 15$. (*d*) $\varepsilon_{[100]}$ as a function of temperature in the vicinity of the transition to the phase $\delta = 1/4$. The experimental data (dots) are compared with a fitted curve (circles) obtained from (3) with $A = 0.007$.

commensurate phase can be checked by the study of the critical behaviour of the dielectric constant using (3). Figure 2(*c*) shows the curve calculated from this equation in the range between 116 K and 120 K, assuming a lock-in transition to a phae $\delta = 4/15$ and considering A and χ_0 as adjustable parameters. The constant value fitted for χ_0 corresponds to an average of all the other contributions for the value of the dielectric constant. The fitted values of the two parameters are $A = 0.165$ and $\chi_0 = 77$. The theoretical curve can describe the experimental data in the region between 116 K and 118 K, i.e. in the vicinity of the lock-in temperature. The deviations observed for $T \geq 118$ K reflect the rise of other contributions to the dielectric constant which were not considered in the fitting and are associated with the onset of the phase $\delta = 2/7$ at $T_3 = 124$ K.

The anomaly in $\varepsilon_{[100]}(T)$ at $T_{4''} = 114$ K marks the onset of the commensurate phase $\delta = 1/4$. The existence of an anomaly in the dielectric constant along [100] at the transition to this phase can be expected from the symmetry considerations mentioned above since, for $\delta = 1/4$, P_x is a possible secondary order parameter. From the difference in temperature between $T_{4''}$ and $T_{4'}$ it can be conjectured that an additional phase may exist sandwiched between the phase $\delta = 4/15$ and $\delta = 1/4$ (see table 1).

Figure 2(*d*) shows a detail of $\varepsilon_{[100]}(T)$ in the temperature region between 110 K and 140 K. In the same figure is plotted a curve calculated from (3) with $n = 4$ and using the experimental values of $T_c = 114$ K, $T_I = 164$ K and $\chi_0 = 8.56$. The only adjustable constant considered in the fit was $A = 0.007$. Neglecting the rounded shoulder centred at 123 K observed in $\varepsilon_{[100]}(T)$, we observe a qualitative agreement between the two curves for $T \geq 116$ K. The deviations observed for $T < 116$ K can be understood as due to the onset of the phase $\delta = 4/15$ and may be considered as an additional evidence of the existence of this phase.

Below $T_{4''} = 114$ K, $\varepsilon_{[010]}(T)$ displays four anomalies at $T_5 = 77$ K, $T_6 = 56$ K, $T_7 = 51$ K and $T_8 = 47$ K, as can be seen in more detail in figure 3(*a*). In this temperature region both calorimetric [13] and x-ray [2] data suggest that the phase transitions are of first order and therefore a quantitative analysis of the critical regimes observed in the dielectric constant cannot be obtained from the local phenomenological description considered here. Some qualitative remarks can, however, be made on the basis of the symmetry considerations referred to above.

According to the phase transition sequence described in references [2–4] the temperatures T_5 and T_6 are associated with the transitions from $\delta = 1/4$ to $\delta = 1/5$ and from $\delta = 1/5$ to $\delta = 1/6$, respectively. For these transitions, P_y cannot be coupled to the primary order parameter and, therefore, no anomalies in $\varepsilon_{[010]}(T)$ should be expected at these transition points.

Considering the correspondence between the polarisation direction and commensurate wavevector parity stressed in the introduction it was conjectured in [7] that these two anomalies could be associated with the existence of two narrow commensurate phases existing between the phases $\delta = 1/4$ and $\delta = 1/5$ and between the phases $\delta = 1/5$ and $\delta = 1/6$, both having a δ = even/odd commensurate wavevector. The simplest rational values of δ corresponding to these phases are $\delta = 2/9$ and $\delta = 2/11$, respectively.

The existence of these two polar phases has been recently detected by pyroelectric measurements [8]. According to our results the position and the widths of the anomalies observed in the dielectric constant at $T_5 = 77$ K and $T_6 = 56$ K, which can be calculated from the difference in temperature between the maximum and the minimum in $(\mathrm{d}\varepsilon_{[010]}/\mathrm{d}T)$ (see figures 3(*b*) and 3(*c*)), corresponding exactly to the widths and positions of the polarisation pulses along [010] observed by pyroelectric measurements.

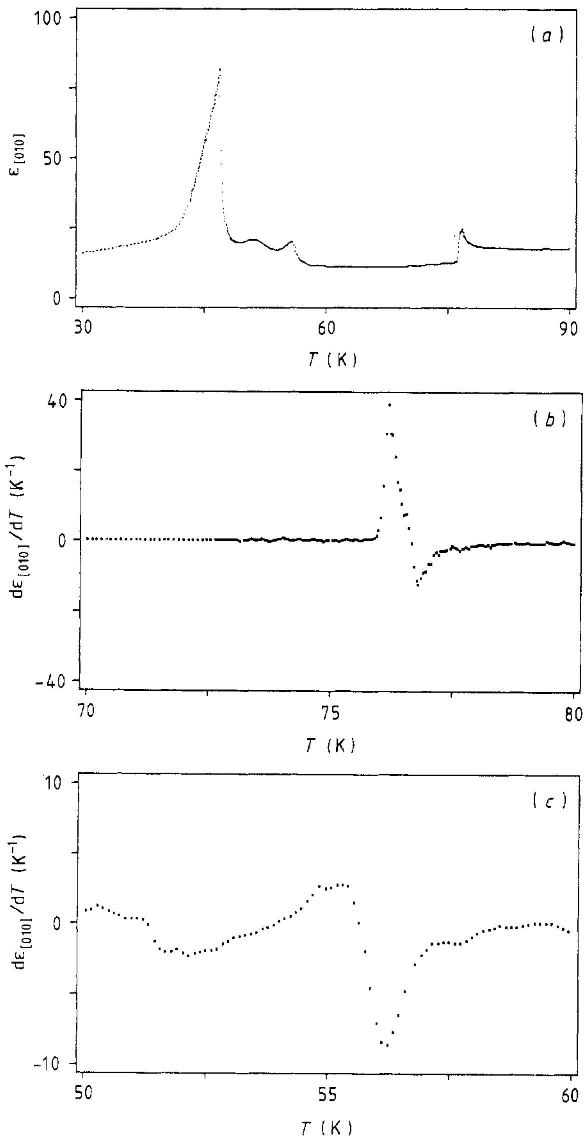

Figure 3. (*a*) Details of the lower temperature anomalies observed at $T_5 = 77$ K, $T_6 = 56$ K, $T_7 = 51$ K and $T_8 = 47$ K. (*b*) Temperature derivative of the dielectric constant along [010] as a function of temperature in the vicinity of $T_5 = 77$ K. The separation in temperature between the opposite peaks is 1 K. (*c*) Temperature derivative of the dielectric constant along [010] as a function of temperature in the vicinity of $T_6 = 56$ K. The separation in temperature between the opposite peaks is 1.5 K.

From these results the two phases are located between 76.5 K and 77.5 K and between 55 K and 56.5 K, respectively.

In what concerns the two anomalies observed in $\varepsilon_{[010]}(T)$ at $T_7 = 51$ K and $T_8 = 47$ K we can assume, using the same symmetry considerations as before, that they must correspond to the onset of two different phases, both polar along [010]. As mentioned in § 1, the nature of these phases is still a matter of some controversy (see also table 1) and can only be decided by using more adapted microscopic techniques. We point out, however, that the re-entrance of the $\delta = 1/6$ phase, reported by x-ray measurements, is not compatible, on the grounds of the model described, with the existence of a spontaneous polarisation along [010] in all the temperature range below T_7. For the phase sequence suggested by Raman studies, according to which T_7 and T_8 correspond respectively to the critical temperatures of the transitions from the phase $\delta = 1/6$ to a higher-order modulated phase and from this phase to a non-modulated phase ($\delta = 0$), we can expect a spontaneous polarisation along [010] below T_7 only if the higher-order commensurate phase reported is of the type δ = even/odd. We stress, however, that in this temperature region, the different phases are separated by first-order transitions and, therefore, a metastable coexistence of phases, which can be separated by rather low free energy differences, may be expected. In this case, and by analogy with the situation found in $SC(NH_2)_2$ [15], the observed phase diagram can depend on the experimental technique used for its detection. For example, a small AC electric field applied in a particular direction in a dielectric constant measurement can be enough to stabilise phases which are polar along that direction.

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Note added. After preparing this manuscript the authors became aware of dielectric measurements of H G Unruh, presented in an internal report (SFB 130, Bericht 1986–1988, Saarbruecken (October 1988)). This report also documents the existence of the above-mentioned three intermediate phases and reports new phases.

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