PHYSICAL REVIEW B VOLUME 39, NUMBER 16 1 JUNE 1989

Pyroelectric detection of high-order commensurate phases with a narrow range of stability in betaine calcium chloride dihydrate

J. L. Ribeiro, M. R. Chaves, and A. Almeida
Centro de Física da Universidade do Porto, Instituto Nacional de Investigação Científica, Universidade do Porto, 4000 Porto, Portugal

J. Albers, A. Klöpperpieper, and H. E. Müser
Fachbereich Physik, Universität des Saarlandes, 6600 Saarbrücken, West Germany

(Received 19 December 1988)

Betaine calcium chloride dihydrate exhibits a sequence of structural transitions from a *Pnma* phase to different commensurate or incommensurate phases modulated along the **c** axis. By measurements of the pyroelectric effect we have obtained the first experimental evidence of the existence of three new intermediate high-order commensurate phases, in agreement with recent theoretical predictions. The effect of a dc-bias electric field in the temperature range of stability of these phases is also reported.

Microscopic models developed for incommensurate systems[1] have emphasized the possible existence of commensurate phases having a high order of commensurability [i.e., corresponding to a ratio $\delta(T)=m/n$ between their wave vector and the period of the reciprocal basic lattice, having a large denominator] and a narrow temperature range of stability. In regard of these theoretical predictions, experimental evidence for the existence of these phases is scarce and its intrinsic origin is sometimes questionable.[2] The detection of these phases by the most adapted experimental techniques (x rays or neutron diffraction) is usually hampered by the narrow temperature width of these phases and, sometimes, by the effect of irradiation which perturbs the system considered.[3,4]

In the present work, we have taken advantage of the favorable situation prevailing in betaine calcium chloride dihydrate-$(CH_3)_3NCH_2COO{*}CaCl_2{*}2H_2O$ (BCCD), where commensurate phases have a definite polar character, in order to achieve their successful detection by means of measurements of the pyroelectric effect. The recently discovered incommensurate system BCCD is, among insulating materials, the one which is the best illustration of an "incomplete devil's staircase" behavior.[5,6] Up to now, at least six distinct modulated phases have been identified in it, besides the highest-temperature crystalline phase of reference. Two of these phases are incommensurate and four are commensurate, all having a single modulation direction along the **c** axis of this orthorhombic crystal.[6,7] The values of $\delta(T)$ $[\mathbf{q}=\delta(T)\mathbf{c}^*]$ characterizing the commensurate phases are $\frac{2}{7}$ (127 K $>T>$ 125 K), $\frac{1}{4}$ (116 K $>T>$ 75 K), $\frac{1}{5}$ (75 K $>T>$ 51 K), and $\frac{1}{6}$ (51 K $>T>$ 47 K).[5-7] The two incommensurate phases occur between 164 and 127 K and between 125 and 116 K. There is reasonable agreement of the results of the various techniques used to investigate this material [dielectric,[5] x rays,[6] pyroelectric,[8] Raman scattering,[9] EPR (Ref. 10)] in regard to the essential features of its phase diagram, for $T>T_6=51$ K.

A recent theoretical model[11] has shown that the six modulated phases mentioned above can be described consistently by a single set of irreducible order parameters having in common the same "small" representation. An interesting consequence of this model is that in this system, the commensurate phases have polar properties of three possible types, depending on the nature of their commensurate wave vector $\mathbf{q}=\delta(T)\mathbf{c}^*$ $[\delta(T)=m/n]$. Namely, if m is even and n odd the phase is polar with its spontaneous polarization (**P**) directed along the b axis. Likewise if m is odd and n even, **P** is directed along the **a** axis. Finally, if both m and n are odd the commensurate phase should not be polar. In a previous work,[8] we have brought a clear confirmation by means of pyroelectric measurements to the validity of this model by showing that the phases $\delta(T)=\frac{1}{4}$ and $\delta(T)=\frac{1}{6}$ are polar along **a** while the phase $\delta(T)=\frac{2}{7}$ is polar along **b** and the phase $\delta(T)=\frac{1}{5}$ is nonpolar.

At present, two important features of the phase diagram of BCCD remain unclear. One concerns the nature of the stable phases below $T_7=47$ K. This problem will not be dealt with here. The other concerns the dielectric behavior on approaching from above the phase transitions at $T_4=116$ K, $T_5=75$ K, and $T_6=51$ K, which are, respectively, associated with the transitions between the phases *INC*2 and $\delta(T)=\frac{1}{4}$, the phases $\delta(T)=\frac{1}{4}$ and $\delta(T)=\frac{1}{5}$, and the phases $\delta(T)=\frac{1}{5}$ and $\delta(T)=\frac{1}{6}$. It has been noted by Perez-Mato[11] that the divergence of the

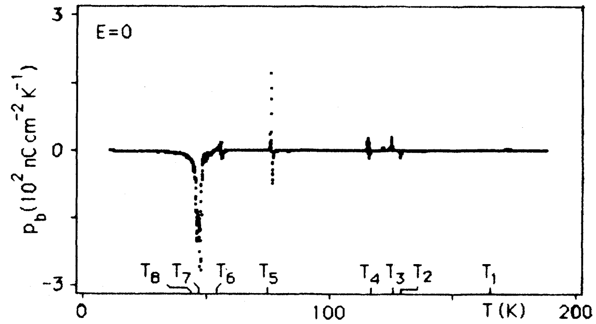

FIG. 1. Pyroelectric coefficient along the **b** axis vs temperature.

dielectric constant observed experimentally at $T_4=116$ K, as well as the anomalies observed at $T_5=75$ K and $T_6=51$ K, are not consistent with the sequence of transitions reported in literature. The observed divergences would rather reveal transitions toward polar phases whose directions of polarization are along the **b** axis. On this basis and relying on the correspondence between polarization direction and commensurate wave vector stressed above, it has been conjectured[11] that three narrow commensurate phases could exist between the phases: *INC*2 and $\delta(T)=\frac{1}{4}$, $\delta(T)=\frac{1}{4}$ and $\delta(T)=\frac{1}{5}$ and $\delta(T)=\frac{1}{5}$ and $\delta(T)=\frac{1}{6}$ with $\delta(T)=m/n$ (m, even; n, odd). The values $\delta(T)=\frac{4}{15}$, $\delta(T)=\frac{2}{9}$ and $\delta(T)=\frac{2}{11}$ were tentatively assigned to these phases. The existing x-ray data[6] show an increase of satellite width in the incriminated ranges of temperature. This behavior can be consistent with the preceding conjecture since the onset of a higher-order commensurate phase could produce the rise of additional unresolved satellites. Besides, when applying a strong electric field along **b** additional quasiplateaus of the **q** vector in the adequate range of q values are found. These plateaus have been assigned to the partial conversion of the C phases into *INC* phases. Such a circumstance appears very unlikely since one usually expects an electric field to favor the stabilization of commensurate polar phases rather than incommensurate ones with zero macroscopic polarization.

In the present work we show that in agreement with the preceding conjecture, pyroelectric measurements reveal the existence of narrow intermediate phases of definite polar character (**P**‖**b**) in the vicinity of T_4, T_5, and T_6. The study of pyroelectric coefficient under a dc bias electric field applied along the **b** axis confirms the polar character of these phases by showing an increase of their temperature ranges of stability.

The pryoelectric coefficient at zero-bias field was mea-

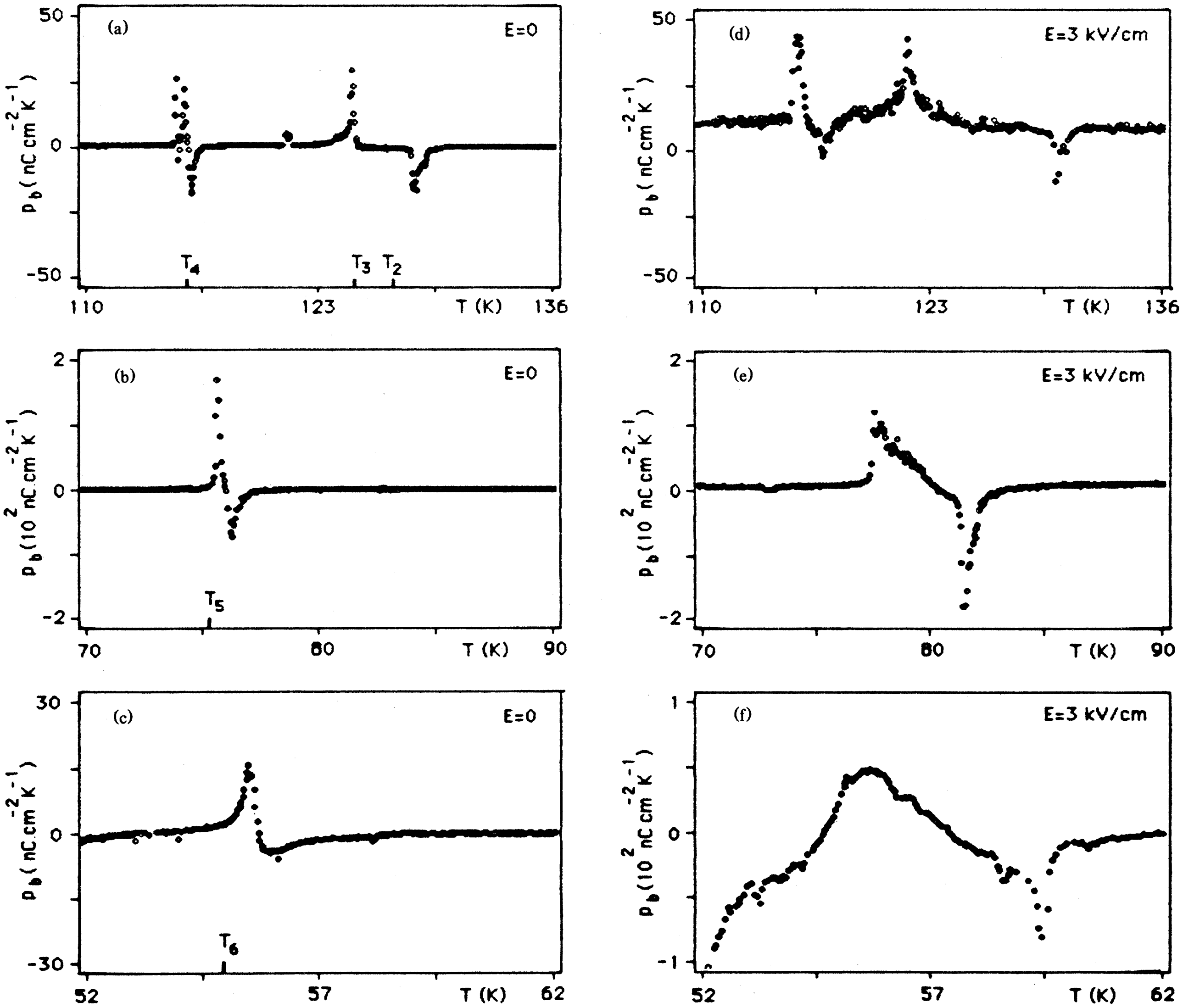

FIG. 2. Temperature dependence of pyroelectric coefficient: 2(a), 2(b), and 2(c) show in detail results depicted in Fig. 1; 2(d), 2(e), and 2(f) show the effect of a dc electric field on the high-order commensurate phase.

sured in the **b** direction using a short-circuit technique described in Ref. 12. The measurements of the pyroelectric current with an applied dc field were done by monitoring the voltage across a resistance in series with the sample. In the whole temperature range studied, the high value of the dc electric resistivity of BCCD ($\rho > 10^{13}$ Ω cm) guarantees that the ohmic electric current can be neglected in regard to the pyroelectric one. The temperature was measured using a chromel-iron–doped gold thermocouple with a minimum sensitivity of 18 μV/K. The voltage was measured by a microvoltmeter with a resolution of 0.1 μV. The resolution expected in the measurement of the temperature is about 0.005 K. The typical dimensions of the samples were $5\times5\times1$ mm^3 with gold electrodes provided by sputtering. The samples were cooled down at low rates ($|dT/dt| < 0.5$ K/min) under a dc bias field of the order of 1 kV/cm, in order to minimize domain formation. The measurements reported here were done by increasing the temperature at rates from 0.5 to 1 K/min.

Figure 1 shows the pyroelectric coefficient along **b** at zero-bias field $[p_b(T)]$ as a function of temperature in the range from 10 to 200 K. Anomalies of $p_b(T)$ occur at $T_2=127$ K, $T_3=125$ K, $T_4=116$ K, $T_4'=115$ K, $T_5'=77$ K, $T_5=75.5$ K, $T_6'=56$ K, $T_6=55$ K, $T_7=48$ K, and $T_8=45$ K. The limits of the commensurate phase $\delta(T)=\frac{2}{7}$ are marked by small pulses of opposite sign of the pyroelectric current at $T_2=127$ K and $T_3=125$ K, revealing the polar nature of that phase. Below this phase, the integration on temperature of the pyroelectric coefficient shows that the phase *INC*2, $\delta(T)=\frac{1}{4}$, $\delta(T)=\frac{1}{5}$, and $\delta(T)=\frac{1}{6}$ are nonpolar along **b**. At $T_7=48$ K, $p_b(T)$ shows an intense peak reaching values of the order of 0.3 μC/(cm^{2}K), followed by a secondary peak at $T_8=45$ K. The anomaly at T_7 marks the onset of a ferroelectric phase, also observed by hysteresis loop measurements.

In spite of the fact that no spontaneous polarization along **b** is ascribed to the three commensurate phases occurring between T_4 and T_7, the pyroelectric coefficient exhibits clear anomalies in the vicinity of the transition points (Fig. 1). As can be seen in more detail in Fig. 2(a), on approaching from above the lock-in transition to the phase $\delta(T)=\frac{1}{4}$, we observe a structured anomaly in which a sharp minimum and a sharp maximum in $p_b(T)$ occur, respectively, at $T_4=116$ K and $T_4'=115$ K. As can be seen in Fig. 3(a), this behavior corresponds to the rise and disappearance of a polarization of the order of 5 nC/cm^2 within the temperature range of 1 K, showing that a narrow intermediate phase must occur between the *INC*2 phase and the $\delta(T)=\frac{1}{4}$ phase. Quite similarly, the double peaks observed in $p_b(T)$ at $T_5'=77$ K and $T_5=75.5$ K [Fig. 2(b)] as well as at $T_6'=56$ K and $T_6=55$ K [Fig. 2(c)] can be assigned to the onset and disappearance of intermediate phases limited by the $\delta(T)=\frac{1}{4}$ and the $\delta(T)=\frac{1}{5}$ phases and by the $\delta(T)=\frac{1}{5}$ and the $\delta(T)=\frac{1}{6}$ phases, respectively. The polar character of these intermediate phases can be clearly seen in Figs. 3(b) and 3(c) where the corresponding polarizations are shown. A dc electric field along **b** is expected to increase the temperature range of stability of the phases which are polar along this direction, in particular, the phase $\delta(T)=\frac{2}{7}$ and the three intermediate phases referred to above. The pyroelectric coefficient measured under a bias field of $E=3$ kV/cm shows slightly shifted critical temperatures: $T_2(E)=131$ K, $T_3(E)=122$ K, $T_4'(E)=118$ K, $T_4(E)=115$ K, $T_5'(E)=81$ K, $T_5(E)=78$ K, $T_6(E)=55$ K, and $T_7(E)=50$ K. The secondary peak observed at zero field at T_8 cannot be resolved. As can be seen in detail in Figs. 2(d), 2(e), and 2(f) the anomalies associated with the onset and disappearance of the phase $\delta(T)=\frac{2}{7}$ and of the intermediate phases occurring in a vicinity of T_4, T_5, and T_6 show that these phases have their temperature ranges increased to 9, 3, 3, and 4 K, respectively.

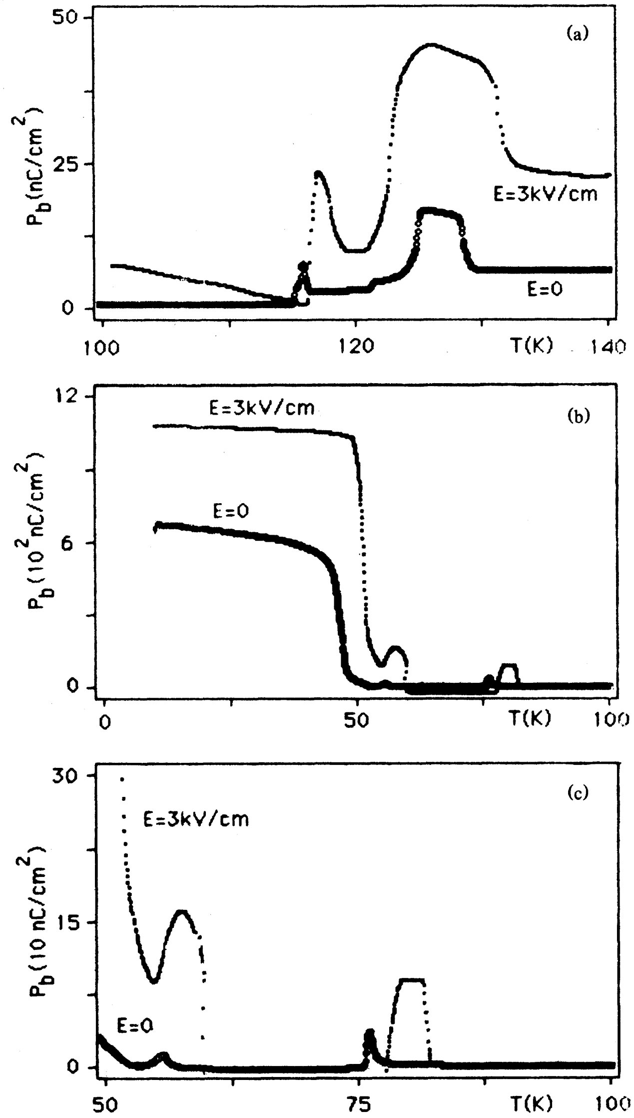

FIG. 3. Polarization vs temperature along the **b** axis in different ranges of temperature, for $E=0$ and $E=3$ kV/cm.

These experimental results are clear evidence of the existence of three commensurate polar phases sandwiched between lower-order commensurate phases or between *INC*2 phase and a low-order commensurate phase. From the fact that these phases are polar along **b** we can conclude that their modulation wave vectors are of the type $\delta(T)=m/n(m$, even; n, odd). The results are also in agreement with the predictions of the symmetry analysis reported by Perez-Mato in what concerns the effect of a dc-bias field along **b** in the temperature range of stability of the different modulated phases.[11] In particular these results are the first to show experimental evidence of the increase of the temperature range of stability of the phase $\delta(T)=\frac{2}{7}$ under a dc bias field.

The analysis of the behavior of the dielectric constants in this material, the details of which will be reported elsewhere, gives additional support to the present conclusions by showing that the anomalies observed in the vicinity of T_4, T_5, and T_6 can be consistently explained by assuming the existence of the intermediate phases and by confirming the widening of their temperature range of stability under a dc bias field.

Note. After preparing this manuscript the authors received knowledge of dielectric measurements of H. G. Unruh, presented in an internal report (Sonderforschungsbereich 130, Bericht 1986–1988, Saarbrücken (Oct. 1988). There, too, the existence of the above mentioned three intermediate phases is documented and further new phases are reported.

The authors are deeply indebted to Professor J. C. Tolédano from Centre National d'Etudes des Télecommunications, Paris, for stimulating discussions and for valuable help during the preparation of this manuscript. They also thank Dr. Perez-Mato (University of Bilbao) for helpful discussions and J. C. Azevedo (Centro de Física da Universidade do Porto) for computing assistance. This work was partially supported by Gesellschaft für Technische Zusammenarbeit (Federal Republic of Germany), Service Cultural Scientifique et de Coopération Technique de l'Ambassade de France au Portugal and CI-14/87 (Universidade do Porto).

---

[1] P. Bak, Rep. Prog. Phys. **45**, 587 (1982); T. Janssen, in *Incommensurate Phases in Dielectrics*, edited by R. Blinc and A. P. Levanyuk (North-Holland, Amsterdam, 1986), p. 67, and references therein.

[2] A. H. Moudden, D. E. Moncton, and J. D. Axe, Phys. Rev. Lett. **51**, 2390 (1983).

[3] E. Fjaer, R. A. Cowley, and T. W. Ryan, J. Phys. C **18**, L41 (1985).

[4] D. Durand, F. Dénoyer, R. Currat, and C. Vettier, Phys. Rev. B **30**, 1112 (1984).

[5] H. J. Rother, J. Albers, and A. Klöpperpieper, Ferroelectrics **54**, 107 (1984); A. Klöpperpieper, H. J. Rother, J. Albers, and H. E. Müser, Jpn. J. Appl. Phys. **24**, 24-2, 829 (1985).

[6] W. Brill and K. H. Ehses, Jpn. J. Appl. Phys. **24**, Suppl. 24-2 826 (1985).

[7] W. Brill, W. Schildkamp, and J. Spilker, Z. Kristallogr. **172**, 281 (1985).

[8] J. L. Ribeiro, M. R. Chaves, A. Almeida, J. Albers, A. Klöpperpieper, and H. E. Müser, Ferroelectrics Lett. **8**, 135 (1988).

[9] R. Ao and G. Schaack, Indian J. Pure Appl. Phys. **26**, 124 (1988).

[10] J. L. Ribeiro, J. C. Fayet, J. Emery, M. Pézeril, J. Albers, A. Klöpperpieper, A. Almeida, and M. R. Chaves, J. Phys. (Paris) **49**, 813 (1988).

[11] J. M. Perez-Mato, Solid State Commun. **C7**, 1145 (1988).

[12] M. R. Chaves, M. H. Amaral, and S. Ziolkiewicz, J. Phys. (Paris) **41**, 259 (1980).