Accumulation of Structure Combination Branching Processes in Betaine Calcium Chloride Dihydrate

S. Kruip, G. Schaack, and M. Schmitt-Lewen
Physikalisches Institut der Universität, D-8700 Würzburg, Germany
(Received 10 July 1991)

The dielectric constants of betaine calcium chloride dihydrate have been measured under hydrostatic pressure ($190 \leq p \leq 320$ MPa) and at varying temperatures ($140 \leq T \leq 210$ K) in the region of structure branching processes between the $\langle 22 \rangle$ and $\langle 23 \rangle$ commensurate phases. Along the various phase boundaries the dielectric permittivity exhibits maxima, which have been attributed to an accumulation of structure branching processes, as predicted by statistical spin models. The accumulation points are quasitricritical points, which have not been observed before. Our results compare favorably with recent calculations based on the axial next-nearest-neighbor Ising model.

PACS numbers: 64.60.Kw, 64.70.Rh, 77.80.Bh

In a spatially modulated phase of a crystalline lattice the positions of (some of) the atoms depart in a periodic way from the positions of the regular unmodulated lattice structure. In the most simple case the modulation is one dimensional (wave vector $\mathbf{q}$) and occurs, e.g., along the c^* axis in reciprocal space: $\mathbf{q}(T) = \delta(T)\mathbf{c}^*$; $|\delta| < 1$. The periodicity of this modulation is either incommensurate (IC) or commensurate (C) with the underlying lattice, if δ is either irrational or rational. In the last decade numerous crystals have been found [1] demonstrating structural phase transitions into various sequences of IC or C phases, depending on temperature T or some other external parameter, e.g., hydrostatic pressure p. These materials exhibit several unusual features not encountered in ordinary phase transitions [1]. Of relevance for the following are structural branching processes (bifurcations), i.e., transitions into phases with increasing complexity of modulation, and their accumulation in certain T or p intervals.

The theoretical interpretation of such modulation structures has developed in parallel. Essentially two approaches have been followed: the phenomenological description in powers of the order parameter [2], and the various microscopic spin models with competing interactions [3]. Especially these rather simple spin models predict a fascinating abundance of different C or IC phases, depending only on slight variations of a few interaction parameters. The ANNNI model (axial next-nearest-neighbor Ising) is the prototype of many spin models and its phase diagram has been studied in greater detail [3–7] than for any other model [8,9]. Here we compare our results with the predictions of this model.

The ANNNI model treats the different spin structures in a primitive tetragonal lattice of Ising pseudospins, which are coupled ferroelectrically (J_0) in the basal plane and between neighboring planes (J_1), but antiferroelectrically between next-nearest-neighbor planes (J_2), thus introducing frustration. $\kappa = -J_2/J_1$ is the single essential parameter of the model.

A C spin structure is characterized by the sequence of the numbers of neighboring planes with identical spin directions, and is denoted by symbols containing, within brackets, the smallest period in the sequence. For example, $\langle 2223 \rangle = \langle 2^3 3 \rangle$ ($\delta = \frac{2}{9}$) represents a periodic arrangement of two neighboring planes with spins up, two with spins down and up, and finally three down. The wave vector $\delta\mathbf{q}$ corresponding to a structure $\langle n_1 n_2 \cdots n_j \rangle$ is [7] $\delta = 0.5j/\sum_{i=1}^{j} n_i$. Taking temperature in a mean-field approximation into account, sequences of C and IC phases will be encountered ("incomplete devil's staircase"). Structure branching processes occur if two adjacent C phases with modulation patterns $\langle S_1 \rangle$ and $\langle S_2 \rangle$ become unstable and combine to form new phases, $\langle S_1 S_2 \rangle$, $\langle S_1 S_2 S_2 \rangle$, ..., $\langle S_1 S_2{}^{(n)} \rangle$, intercalating the former [4], as observed in betaine calcium chloride dihydrate (BCCD) recently [10].

For $n \to \infty$ these structure branching processes accumulate towards specific quasitricritical points in the phase diagram [accumulation points (AP)] [4–8], where a sequence of distinct (n finite) first-order C transitions changes to a continuous variation of δ (IC phase, C-IC transition of second order). In the frame of the ANNNI model the APs are of central importance in the analysis of the C-IC transition. They are characteristic of modulated systems, as is, e.g., the Lifshitz point. The existence of such APs has not yet been demonstrated experimentally. Their theoretical prediction, on the other hand, in close agreement with experimental results in specific systems, as presented in this Letter, should be a challenging test for every new model for modulated systems, either phenomenological or microscopic.

Typical Landau models for long-wavelength modulations will not easily account for these processes. Displacement models have been developed which combine both the phenomenological approach of low-order Landau-type expansions with the presence of competing interactions between neighboring pseudospins responsible for the modulation [8,9], at the expense of introducing more than one adjustable parameter.

BCCD [$(CH_3)_3N^+CH_2COO^- \cdot CaCl_2 \cdot 2H_2O$, *Pnma* ($D_{2h}^{16}$), $Z = 4$ at $T = 300$ K] is an addition compound of the α amino acid betaine and an inorganic component. BCCD has become prominent for its surprisingly rich phase diagram [11] displaying an incomplete devil's staircase with a first transition to an IC phase at $T_I = 164$ K and finally a transition to a low-temperature ferroelectric

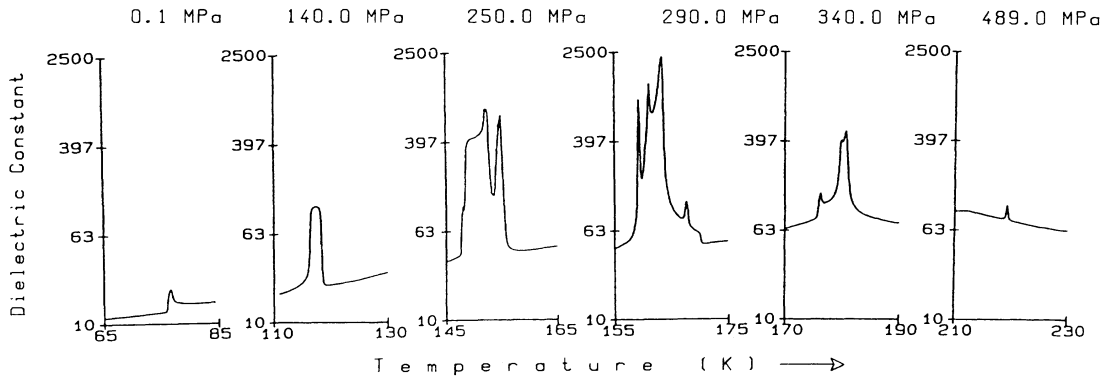

FIG. 1. Dielectric anomalies in BCCD at various hydrostatic pressures in the region of structure branching processes between the $\delta=\frac{1}{4}$ and $\delta=\frac{1}{5}$ phases. The anomaly at 489 MPa is due to the narrow $\frac{2}{9}$ (⟨2223⟩) phase.

($\delta=0$) phase at $T_C=46$ K [12,13]. $\delta(T)$ has been determined at ambient pressure by x-ray diffractometry [14]. $\delta(T_I)=0.32$, and δ decreases continuously with T in the IC phases, but locks in at discrete rational values ($\delta=\frac{2}{7},\frac{1}{4},\frac{1}{5},\ldots,0$) at various temperatures $164<T<46$ K [13]. At hydrostatic pressure two regions of structural branching processes occur [10], and a Lifshitz point probably exists in BCCD at higher pressures. The modulation occurs along $\mathbf{c}^*$. For $p>0$ an empirical relation $\delta(T,p)$ has been derived for BCCD [see Ref. [10], formula (1)].

We have measured $\varepsilon(p,T)$ of BCCD ($\nu=10$ kHz) under quasi-isobaric conditions in Δp intervals of 10 MPa in the branching region between the $\delta=\frac{1}{4}$ and $\frac{1}{5}$ C phases: (⟨22⟩↔⟨2223⟩↔⟨23⟩). Structural branching processes into the phases ⟨22232323⟩ (i.e., $\delta=\frac{4}{19}$), ⟨222323⟩ ($\frac{3}{14}$), ⟨$2^5$3⟩ ($\frac{3}{13}$), and ⟨$2^7$3⟩ ($\frac{4}{17}$) have been observed here as reported previously [10]. In Fig. 1 the dielectric anomalies $\varepsilon(p\approx\text{const},T)$ along the b axis have been plotted on a logarithmic scale. The splitting (branching) of the anomalies and very prominent extrema of their size (near $T=160$ K and $p=260$ MPa) are apparent. Such extrema of ε were found on every phase line or phase boundary in this region. We identify these extrema of $\varepsilon(T,p)$ with the APs for reasons discussed below. Similar effects have been detected in the narrow branching region between the ⟨23⟩ and the ⟨3⟩ phases but have not been evaluated quantitatively because of ambiguities in the fits due to strong overlap of the various anomalies. Such effects appear to be present also between the ⟨2⟩ and the ⟨12^3⟩ phases, indicating a virtual AP at negative pressure. In both these regions the ε anomalies demonstrate a similar behavior and size as shown in Fig. 1.

We have fitted [1] a Curie law to the observed ε anomalies, sparing the C region of the $\delta=\frac{2}{9}$ phase:

$$\varepsilon(p,T)=\varepsilon_{bg}+\sum_i C_i(p)/(T-T_i)\,, \qquad (1)$$

where ε_{bg} and $C_i(p)$ are the fit parameters. ε_{bg} is the dielectric background; C_i is the observed Curie constant for anomaly i at phase boundary i peaking at T_i and is evaluated by measuring $\varepsilon(p\approx\text{const},T)$ and fitting the data with (1) to get all C_i values. For the quality of the fits see Ref. [15]. In Fig. 2 we have plotted $C_i(p,T)$ for two different boundaries or narrow phases i representing a strong and the weakest anomaly as examples. As p decreases, C_i slowly increases, passes a broad maximum near the AP [$C_i(T_{AP},p_{AP})$], and decays rapidly. Fits in the latter region have low precision because of strong overlap of anomalies.

The occurrence of structural branching processes and APs is usually interpreted by considering the interaction energy of (almost) planar defects [domain walls, discommensurations (DCs)], which decreases with increasing distance between them [5–7]. Along the lower boundary of the ⟨$2^3$3⟩ phase, e.g., adjacent to ⟨22⟩, branchings of

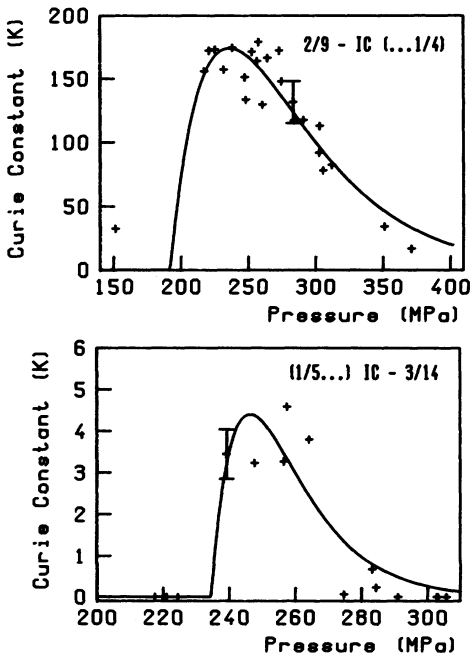

FIG. 2. Two examples of the pressure dependences of the Curie constants C_i in Eq. (1) along the phase boundaries (i) indicated (cf. Table I).

the type $\langle(2^3 3)^j 22\rangle$ will occur; in the limit $j \to \infty$ an accumulation of such processes will be found with the 22 sequence as a DC. With j increasing, the stability of phases (j) will decrease, until an AP is reached. At the upper boundary, towards the $\langle 23\rangle$ phase, an AP $\langle(2^3 3)^j 23\rangle$ will be encountered with 23 as DC.

The theory of the dielectric behavior of a modulated system near an AP has not been evaluated so far; studies of this and other means to observe APs in experiments are urgently needed. Thus we have to use heuristic arguments for a qualitative interpretation of our results: A phase with a long-wavelength modulation, i.e., with large j, will not be permanently stable due to entropic effects; however, for polar phases it may contribute to polarization fluctuations and thus to the dielectric susceptibility because of low ΔF [16]. We expect a maximum of C_i in a region where the density of phases with large j is highest, i.e., close to an AP. The course of $C_i(p)$ will thus depend on the density of C phases in a certain pressure or temperature interval and on the probability of the occurrence of a phase with a modulation $\delta_n = m/n$; $m,n \in \mathbb{N}$. This probability $W(n)$ will increase [3] with the stability of phase δ_n: $W(n) \sim \exp\{-n/n_0\}$. We have deliberately chosen $n_0 = 25$. In the range of interest here, this function can be approximated linearly by $A(p - p_0)$ for the ease of numerical fits. The density dN/dp of phases beyond the AP has been determined using the derivatives $\partial N/\partial p|_T$ and $\partial N/\partial T|_p$, which have been taken for the $\langle 2^j 3\rangle$ phases from the $\delta(p,T)$ relation [10]. The numerical results can be approximated by an exponential: $dN/dp \sim \exp\{-(p - p_0)/B\}$. Altogether, the observed Curie constants $C_i(p)$ were fitted by the relation

$$C_i(p) = A_i(p - p_{0,i}) \exp\{-(p - p_{0,i})/B_i\}, \qquad (2)$$

where A_i, B_i, and $p_{0,i}$ are fit parameters. $p_{0,i}$ is the pressure where the branching process into phase i is first discernible, $p_{AP,i} = p_{0,i} + B_i$; $C_i(p_{AP}) = A_i B_i / e$. While expression (2) is entirely *ad hoc* for the reasons given above, the exponentials are suggested by pertinent expressions occurring in the theoretical investigations [5–7].

TABLE I. Locations of accumulation points (AP) in the (p,T) phase diagram of BCCD between the $\delta = \frac{1}{4}$ ($\langle 22\rangle$) and $\delta = \frac{1}{5}$ ($\langle 23\rangle$) C phases, and maxima of fitted Curie constants $C_i(T_{AP})$.

Phase transition (δ)	T_{AP} (K)	p_{AP} (MPa)	C_i (K)
$(\frac{1}{5}\ldots)$IC-$\frac{2}{9}$	151.8	246.5	158
$\frac{2}{9}$-IC$(\ldots\frac{1}{4})$	151.3	236.3	170
IC-$\frac{3}{14}$-IC	151.5	246.5	4.4
IC-$\frac{4}{19}$-IC	158.1	274.4	11.4
$\frac{1}{5}$-IC	160.0	281.0	14
IC-$\frac{3}{13}$-IC	149.8	230.4	6.8
IC-$\frac{4}{17}$-IC	150.6	227.3	13.5
IC-$\frac{1}{4}$	150.6	225.3	8

The solid lines in Fig. 2 present the best fits (see Table I). For more details see Ref. [17]. The contributions to dielectric fluctuations due to the roughening of DCs are not considered.

In Fig. 3, a section of the (p,T) phase diagram of BCCD is plotted, where eight observed APs are located. The numerical values taken from the extrema of Eq. (2) are compiled in Table I. The theoretical predictions from the ANNNI model [4,6,7] locate the APs at $T_{AP} \approx 0.52 T_l(\langle 3\rangle)$ [7,18]. $T_l(\langle 3\rangle)$ is the transition temperature where the (extrapolated) $\langle 3\rangle$ phase meets the T_l line: $T_l(\langle 3\rangle) \approx 306$ K. Thus $T_{AP}^{ANNNI} \approx 159$ K, which compares surprisingly well with our observed values. Moreover, Fisher and Szpilka [6] have incorporated several types of many DC interactions into their analysis of domain walls in the ANNNI model and have predicted a shift of the APs on phase boundaries with increasing j to lower temperatures. This is again in qualitative agreement with our findings. On the other hand, the ANNNI model predicts a change of the phase transition at the AP from first to second order due to its quasitricriticality or, stated differently, due to the change of the DC interaction from oscillatory to monotonic behavior (with an infinite distance between DCs at the AP as a consequence) [7]. According to our observations, the transitions are always *first order*: In a real crystal there always exists a finite concentration of pinning centers for the modulation at crystal defects and thus a finite concentration of DCs.

We have observed APs at every phase boundary studied, in contrast to the ANNNI model, which does not allow APs for phases stemming from its multiphase point at $\kappa = \frac{1}{2}$. Again, defects should raise the multidegeneracy of this point in a real crystal.

Finally, the APs are found on "similar" positions of the respective phase boundaries, indicating the fractal topology (self-similarity) of the (p,T) phase diagram of

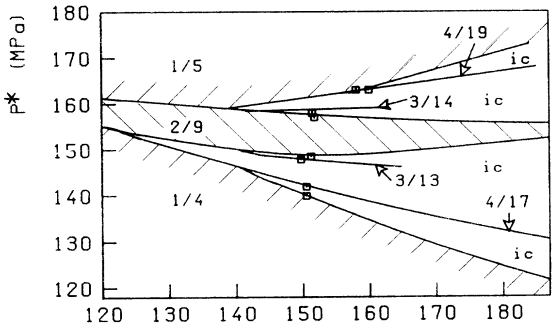

FIG. 3. Section of the (p,T) phase diagram of BCCD with the observed accumulation points indicated (squares). For clarity of data presentation the vertical axis has been rescaled by $p^* = p - m(T - T_0)$, where $m = 3.47$ MPa/K and $T_0 = 126$ K (the shear of the diagram around $T = T_0$ is to plot the $\delta = \frac{2}{9}$ phase almost horizontally).

BCCD. It appears challenging in this context to trace the formal analogy of the sequence of branching points towards an AP with the bifurcation route to deterministic chaos: Both can be interpreted as second-order pseudo phase transitions [19]. In a modulated crystal the density of DCs is the order parameter of this transition with T_C occurring at T_{AP}, the conjugated field is the energy per single DC, and the order-parameter susceptibility corresponds to the inverse energy density of DCs. The AP thus separates in an ideal defect-free crystal a region of closely lying C phases from a true IC region.

The role of defects as pinning centers in BCCD has been emphasized by experiments [20] on BCCD where a small percentage of Cl^- ions are substituted by Br^- ions with a larger ionic radius. The sizes of the ε anomalies are drastically reduced; APs are still discernible near $T=150$ K, but only on the phase boundaries with the lowest j, while phases with larger j are suppressed. With respect to the pseudo phase transition at T_{AP} this corresponds to an increasing rounding of the transition beyond the rounding already present in nominally pure material (Fig. 2).

The support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[1] The experimental situation has been reviewed by H. Z. Cummins, Phys. Rep. **185**, 211–409 (1990); see also, *Modern Problems in Condensed Matter Sciences,* edited by R. Blinc and A. P. Levanyuk (North-Holland, Amsterdam, 1986), Vol. 14.2.

[2] J. C. Tolédano and P. Tolédano, *The Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987).

[3] W. Selke, in "Phase Transitions and Critical Phenomena," edited by C. Domb and J. L. Lebowitz (Academic, New York, to be published). For previous reviews see W. Selke, Phys. Rep. **170**, 214–264 (1988); J. Yeomans, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1988), Vol. 41, pp. 151–200; T. Janssen and A. Janner, Adv. Phys. **36**, 519–624 (1987); P. Bak, Rep. Prog. Phys. **45**, 587–629 (1982).

[4] W. Selke and P. Duxbury, Z. Phys. B **57**, 49–58 (1984).

[5] A. M. Szpilka and M. E. Fisher, Phys. Rev. Lett. **57**, 1044–1047 (1986).

[6] M. E. Fisher and A. M. Szpilka, Phys. Rev. B **36**, 644–666 (1987); **36**, 5343–5362 (1987); **36**, 5363–5376 (1987).

[7] R. Siems and T. Tentrup, Ferroelectrics **98**, 303–336 (1989).

[8] T. Janssen and J. A. Tjon, J. Phys. A **16**, 673–696 (1983).

[9] Z. Y. Chen and M. B. Walker, Phys. Rev. Lett. **65**, 1223–1226 (1990); Phys. Rev. B **43**, 760–764 (1991).

[10] R. Ao, G. Schaack, M. Schmitt, and M. Zöller, Phys. Rev. Lett. **62**, 183–186 (1989).

[11] G. Schaack, Ferroelectrics **104**, 147–158 (1990).

[12] R. Ao and G. Schaack, Indian J. Pure Appl. Phys. **26**, 124–130 (1988).

[13] H. G. Unruh, F. Hero, and V. Dvorak, Solid State Commun. **70**, 403–408 (1989).

[14] W. Brill and K. H. Ehses, Jpn. J. Appl. Phys. **24**, Suppl. 24-2, 826–828 (1985).

[15] S. Kruip, Diploma thesis, University of Würzburg, 1990 (unpublished).

[16] D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions* (Benjamin, Reading, 1975).

[17] S. Kruip, G. Schaack, and M. Schmitt-Lewen, in Proceedings of the European Meeting on Ferroelectricity 7, Dijon, 1991 [Ferroelectrics (to be published)].

[18] T. Tentrup and R. Siems, Ferroelectrics **105**, 379–384 (1990); **105**, 385–390 (1990).

[19] H. G. Schuster, *Deterministic Chaos* (VCH, Weinheim, 1988), 2nd ed.

[20] G. Lingg, M. le Maire, G. Schaack, M. Schmitt-Lewen, and G. Strauss, in Ref. [17].