Multicritical Point and Structure Branching Patterns in the Modulated Phases of Betaine Calcium Chloride Dihydrate (BCCD)

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The low-frequency ($\nu = 10$ kHz) dielectric constants and hysteresis loops of BCCD have been measured under hydrostatic pressure ($p < 550$ MPa) and at varying temperatures (115 K $< T <$ 260 K). Several new pressure-induced commensurate and incommensurate phases have been detected and interpreted using the anisotropic next-nearest-neighbor Ising model. Structure branching processes with similar topology in different regions of the phase diagram have been observed. The existence of a Lifshitz point in BCCD is suggested.

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The present situation in the field of spatially modulated periodic crystal structures is characterized, on the one hand, by the high degree of sophistication of the different theoretical models that have been evaluated over the last few years,[1] and the high level of qualitative understanding achieved by them. On the other hand, only a few systems have been found and analyzed experimentally[2] that demonstrate to some extent all the peculiarities of the calculated results and that may incite and guide new theoretical research. Quantitative agreement between theory and experiment is still widely lacking. This Letter is intended to direct attention to a material which presents may of the theoretical predictions in a hitherto unknown copiousness, giving more details than the K_2SeO_4, $SC(NH_2)_2$ or TMA systems (tetramethylammonium compounds).[2] BCCD $[(CH_3)_3{}^+NCH_2\text{-}COO^-\cdot CaCl_2\cdot 2H_20]$ is a recently discovered[3] ferroelectric (FE) material, an addition compound of α-amino acids and an inorganic component, such as triglycine sulfate (TGS), trisarcosine calcium chloride (TSCC), etc. A sequence of several phase transitions has been reported[3]: $T_I = 164$ K, $T_1 = 127$ K, $T_2 = 125$ K, $T_3 = 116$ K, $T_4 = 75$ K, $T_5 = 74.4$ K, $T_6 = 52.5$ K, $T_7 = 46.4$ K, $T_c = 45.4$ K. It has been shown[4] by x-ray diffractometry that below T_I the structure is modulated in the z direction, while the FE axis is along the y axis. Between 164 and 127 K the modulation vector $q_z^* = \delta(T)c^*$ changes continuously with temperature from $\delta_I(p=0) = 0.32$ to $\frac{2}{7}$. A commensurate (C) region ($\delta = \frac{2}{7}$) follows at 127 K $> T >$ 125 K; then an incommensurate (IC) phase ($\frac{2}{7} > \delta > \frac{1}{4}$) is encountered again. Below 116 K a sequence of C transitions has been observed ($\delta = \frac{1}{4}, \frac{2}{9}, \frac{1}{5}, \frac{1}{6}, \frac{1}{7}$), separated by first-order transitions. At 45.4 K the FE phase is entered ($\delta = 0$).[5] Additional commensurate phases have been observed at ambient pressure by Unruh[6] and also in the course of this work.

The structure $[D_{2h}^{16}$ $(Pnma)$, $Z = 4$ at $T = 300$ K$]$[7] consists of planar sheets of betaine molecules and $Ca\text{-}O_2\text{-}Cl_2\text{-}(H_2O)_2$ octahedrons; both groups share the carboxyle oxygens. The sheets are oriented parallel to the (010) plane; the octahedrons are interconnected in the y direction by hydrogen bonds only. Hence the (010) plane is a clevage plane of the crystal.

We have observed the dependence of the dielectric constants $\epsilon_x, \epsilon_y, \epsilon_z$ on hydrostatic pressure p and on temperature T. The measurements have been performed by our slowly increasing or decreasing the temperature at constant pressure ($|dT/dt| < 10$ K/h). The thermal hysteresis of the various phase transitions observed by us is generally smaller than 1 K. Crystals of different origin behave almost identically; crystals of apparently higher optical quality demonstrate a more detailed phase diagram.

No dielectric anomalies (DA) have been observed for ϵ_z. With increasing hydrostatic pressure all DA's shift to higher temperatures with slightly different slopes. Except at T_I, the strengths and widths of the DA's also change with pressure. They generally increase, but beyond a certain pressure they decrease and may finally completely disappear.

In Fig. 1 the phase diagram of BCCD is shown as derived from our measurements of ϵ_y and ϵ_x in the p-T range considered. In certain pressure and temperature regions new anomalies arise, indicating the appearance of new, pressure-induced C or IC phases. The widths of C phases with a broad temperature interval of stability and labeled by $\delta = 1/n$ will decrease with increasing p. The phases with $\delta = 2/n$ increase with p, but finally their widths decrease, forming cusps protruding deeply into an IC region. The two borderlines of these phases start and finally meet again as tangents. Phases with $\delta = 3/n$ and higher modulation display no observable width but are only indicated by a line of DA's with increasing and finally decreasing strength. Most of these phases have also been traced by the observation of hysteresis loops[8] ($E < 900$ V cm^{-1}). The ranges of existence in the (p,T) plane of a C phase decrease with increasing numerator of δ. Different from the predictions of most models, none of the C phases appears to extend toward the disorder line $T_I(p)$.

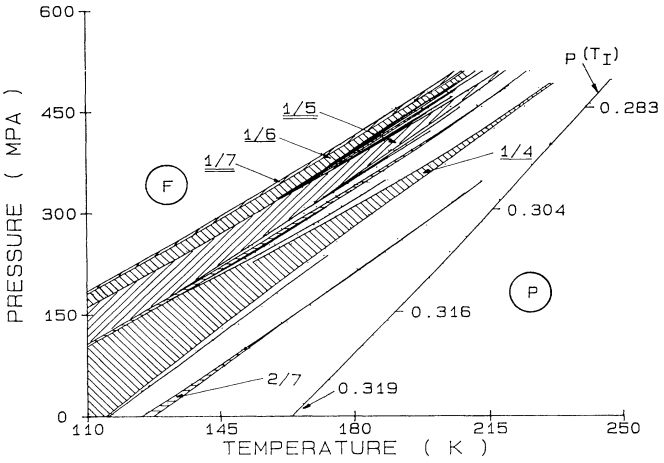

FIG. 1. Pressure-temperature phase diagram of BCCD. P: paraelectric region; F: ferroelectric region; hatched areas: commensurate phases (with δ values given); blank areas (except P and F): incommensurate phase. The phase boundaries cut by the pressure axis extrapolate perfectly to the temperatures T_i given in the text for ambient pressure. The numbers along the P-IC transition $T_I(p)$ are $\delta(p)$ values calculated from (1). δ values (commensurate) underlined one, weak spontaneous polarization P in x direction observed for these phases; underlined twice, $P \approx 0$; not underlined, $P \| y$.

The size of the DA's and the spontaneous polarization P observed along x is in most cases $\leq 1\%$ ($\leq 5\%$ for P) of the effect in the y direction, indicating the improper character of ferroelectricity in this direction.[9] For a few phases a DA and a hysteresis loop have only been observed in the x direction (Fig. 1).

We have assigned values of the modulation δ to the various new, pressure-induced phases using information from the already known C phases[4] at ambient pressure, from the hysteresis loops observed, and from the obvious similarities of different regions of the p-T phase diagram (Fig. 2). Most of all, we have used plots of δ vs T at constant p, where the known C phases with broad temperature intervals of existence ($\delta = \frac{1}{4}, \frac{1}{5}, \frac{1}{6}, \ldots$) are represented by the center values of these temperature intervals. Smooth quasicontinuous curves are obtained from these plots and the new pressure-induced phases fit surprisingly well. The δ values thus obtained for the C phases form a sequence of Farey numbers. The isobars of δ have been fitted by functions[10] $\delta_p(T) = A'(T - T_0')^{1/2} + \delta_0'$, with A', T_0', and δ_0' as parameters. By taking the pressure dependence of these parameters into account, an empirical function $\delta = f(p,T)$ has been derived:

$$\delta(p,T) = A \ln\{C(p+p_0)\}[T - T_0 - Bp + Dp^2]^{1/2} + \delta_0(1-\alpha p), \quad (1)$$

with the parameters $A = 3.24 \times 10^{-3}$ K$^{-1/2}$; $C = 2.30$ MPa^{-1}; $p_0 = 130.0$ MPa; $T_0 = 45.8$ K; $B = 0.35$ K MPa^{-1}; $D = 8.5 \times 10^{-5}$ K MPa^{-2}; $\delta_0 = 0.12$; $\alpha = 2.0 \times 10^{-4}$ MPa^{-1}. This "equation of state" of the modulated phase of BCCD is of course valid only in the region of IC or narrow C phases (except close to the FE phase boundary) and can be used to calculate the δ values of the disorder line $T_I(p)$, δ_I; some results obtained are given in Fig. 1. The δ_I values so determined can be fitted well by a parabola: $\delta_I(p) = \delta_I(0) + Gp + Hp^2$, where $\delta_I(0) = 0.319$, $G = 1.82 \times 10^{-5}$ MPa^{-1}, and $H = -2.19 \times 10^{-7}$ MPa^{-2}. The modulation $\delta_I(p_L) = 0$ is extrapolated at $p_L = 1.25$ GPa; the equation $\delta_I(p_L) = \delta_0'(p_L)$ results in $p_L = 1.05$ GPa.

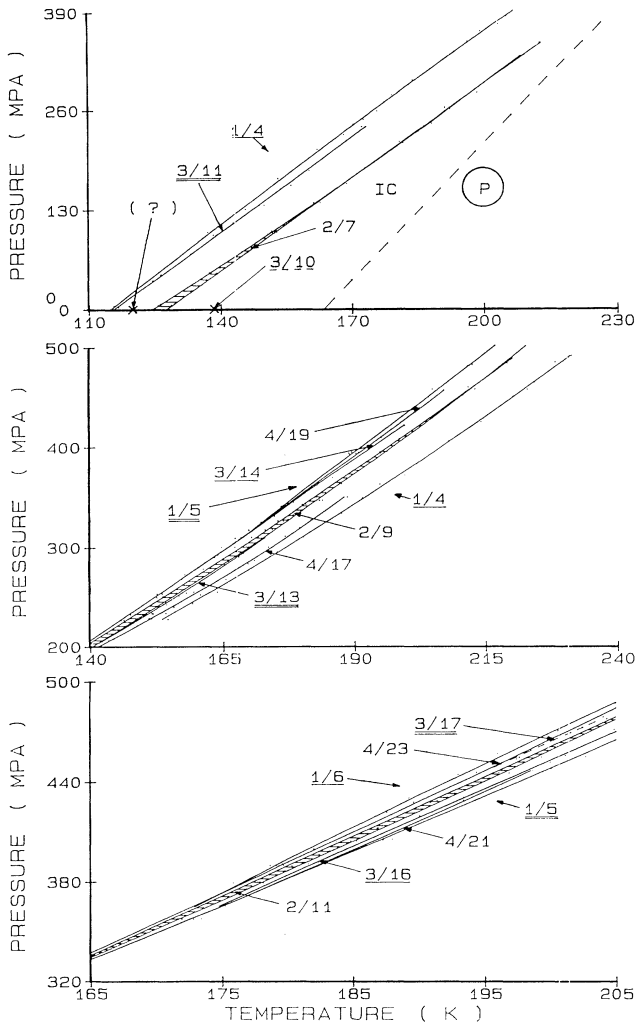

FIG. 2. Enlarged sections of the p-T phase diagram (Fig. 1), demonstrating the topological similarities in the structural branching regions. A fourth branching region is indicated between the $\frac{1}{6}$ and the $\frac{1}{7}$ phases but not resolved. δ values as in Fig. 1.

BCCD appears to be the only known ferroelectric substance where within the same crystal such a large number of IC and C phases are encountered. The material is especially attractive because the branching processes of

C phases (bifurcations), driving the system into the various high-order C phases, can be followed in detail. The branching points, however, cannot be marked exactly by our measurements. Selke and Duxbury[11] have theoretically investigated these branching processes using the anisotropic next-nearest-neighbor Ising model. As a result of these processes, the system changes at low temperatures from the case of a harmless devil's staircase[11] at $p=0$ to an incomplete staircase at $p>0$. The state of a complete devil's staircase demanded by the majority of models is not attained here, but is obviously suppressed by thermal fluctuations, which support an IC phase instead of a high-order C phase. Also in agreement with theoretical predictions[11,12] is the observation that these regions, where narrow C phases and IC phases are intercalated, have similar shapes in the various temperature regions (Fig. 2). This has to be expected because the underlying lattice dynamical problem is intimately related to a discrete symplectic (mapping) transformation.[13] It would be desirable to search for fractal, self-similar structures in these phase regions.

The occurrence of the various DA's and of spontaneous polarization in the x and y directions (Figs. 1 and 2) suggests as a general rule, as Unruh[6] has observed, that the C phases with $\delta=2n/(2m+1)$ display spontaneous ferrielectric polarization in the y direction, while the phases with $\delta=(2n-1)/(2m+1)$ are not polar, and the phases $\delta=(2n-1)/2m$ $(n,m\in N)$ show a residual (improper) polarization in the x direction.[9] It is remarkable that the polar phases ($P\parallel y$), without complete compensation of electric moments in the structure, display narrow temperature intervals of stability, while the weakly polar ($P_{\rm imp}\parallel x$) or nonpolar phases exist over large intervals. It is easily seen from an inspection of the pertinent spin structures that a complete compensation of dipolar moments is achieved for $\delta=$odd/odd, but cannot be achieved for $\delta=$even/odd; for $\delta=$odd/even (improper FE) more detailed considerations are required.[9]

The predictions of the anisotropic next-nearest-neighbor Ising model are of relevance for our results,[11,14] but other models may also work or will even fit better. The anisotropic next-nearest-neighbor Ising-phase diagram is usually displayed versus temperature as a function of the ratio $\kappa=-J_2/J_1$ of two competing interaction energies J_1,J_2 of Ising-type spins ordered ferromagnetically in planes perpendicular to the modulation axis. The region of modulated structures, the disordered region, and the ferroelectric phase meet at $\kappa=0.27$ at the multicritical Lifshitz point, where the two phase boundaries coincide as tangents.[15] BCCD fits into this diagram qualitatively for $0.27<\kappa<0.5$ (multiphase point), with decreasing κ for growing p. A Lifshitz point can be extrapolated from the crossing of our $T_I(p)$ and $T_c(p)$ lines at $T_L=346$ K, $p_L=1.16$ GPa. These values are lower bounds only.

The widths Δ_δ, i.e., the stability of the C phases along the p axis close to $T_L(p)$, has been calculated as follows[16]: $\Delta_\delta\sim[(T_{0,\delta}-T)/T_{0,\delta}]^{\xi_\delta}$, assuming $T_{0,\delta}$ to lie on $T_I(p)$, where ξ_δ has been calculated by the renormalization-group method. We tried to fit the observed widths Δ_δ with this expression and used the effective values $T_{0,\delta}$, where the C phase ends, as parameters. We have obtained for $\delta=\frac{1}{4}$, $T_{0,\delta}=228\pm7$ K (233 ± 6 K). The number in parentheses has been calculated with use of the mean-field values of ξ_δ. The $T_{0,\delta}$ value calculated is smaller than the end-point value (Fig. 1) and about 40 K smaller than the extrapolated $T_I(p)$ value. Similar discrepancies have been found for other C phases: $\delta=\frac{1}{5}$, $\frac{2}{7}$, and $\frac{2}{9}$.

Better agreement has been obtained by assuming an exponential dependence of Δ_δ on T:

$$\Delta_\delta=C_\delta\{\exp[-A(T-T_{0,\delta})/\delta]-1\}.$$

The following values for A (δ) have been obtained (K^{-1}): 0.137 $(\frac{2}{7})$; 0.094 $(\frac{1}{4})$; 0.070 $(\frac{2}{9})$; and 0.082 $(\frac{1}{5})$. Accordingly, the sum of the widths of all C phases encountered along an isobar relative to the total width of the modulated phase should also decay with increasing pressure (Fig. 1). It can be anticipated that on approaching the Lifshitz point the C phases are completely suppressed by IC structures. The strengths, ϵ_s, of the DA's decrease on approaching T_L and can be fitted with the *Ansatz* $\epsilon_{s,\delta}(p)=A\exp(-B'p/\delta)$, $B'=(6.0\pm0.3)$ GPa^{-1} for $\delta=\frac{2}{7}$ and $\frac{2}{9}$. All these exponential decays apparently indicate the role of fluctuations on approaching the disorder line or the Lifshitz point.

The spatial modulation of the BCCD structure possibly consists of a transverse ($\parallel y$) periodic warping of the (010) planes of the betaine zwitterions and the octahedrons. This is consistent with the occurrence of the spontaneous polarization in the y direction and is also in agreement with the spectroscopic results,[5] which support a librational soft mode along the x axis with relaxational character.

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