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Effect of hydrostatic pressure on the modulated structure of deuterated betaine calcium chloride dihydrate

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In this work we present a study of elastic neutron scattering in deuterated betaine calcium chloride dihydrate under hydrostatic pressure. This study provides clear evidence for the existence of a large number of high-order commensurate phases induced by pressure. Structural branching processes as predicted by the analysis of axial next-nearest-neighbor Ising models have been observed.

INTRODUCTION

Betaine calcium chloride dihydrate, $(CH_3)_3NCH_2COOCaCl_2\cdot 2H_2O$ (BCCD) exhibits a large number of commensurate (C) and incommensurate (INC) phases, some of them of high commensurate order and of very narrow temperature ranges of stability.[1-3]

The research on BCCD has taken a relevant place among the studies of insulating materials with modulated phases. The reasons lie in the unusually large number of phases this substance exhibits and in the controversy about the characteristics of these phases.

Above 164 K BCCD is orthorhombic with space group *Pnma* ($a=10.97$ Å, $b=10.15$ Å, $c=10.82$ Å, $Z=4$). The unit cell has two elementary units, sharing a pair of oxygen atoms.[4] One is the betaine radical $(CH_3)_3NCH_2COO$, and the other is a distorted octahedron, containing the Ca^{2+} ions and constituted by two Cl^- ions, two water molecules, and two oxygen atoms which also belong to the carboxyl group of the betaine radical. These units form chains along the **c** direction.

Below 50 K it becomes ferroelectric, and in this phase there are also four molecules per unit cell.[4,5] Between these two temperatures, the structure is modulated along the **c** axis [$\mathbf{k}=\delta(T)\mathbf{c}^*$], and a study of x rays provided evidence for $\delta=\frac{2}{7}, \frac{1}{4}, \frac{1}{5}$, and $\frac{1}{6}$ *C* phases.[6] Pyroelectric and dielectric measurements revealed a large number of anomalies in the temperature range 50–164 K, which were related, on the basis of a symmetry analysis, to high-order commensurate phases with $\delta=\frac{4}{15}, \frac{6}{23}, \frac{2}{9}, \frac{2}{11}, \frac{2}{13}, \frac{1}{7}$, and $\frac{1}{8}$.[2,3] The space groups of all these phases are unknown with the exception of the space group of the $\delta=\frac{1}{4}$ C phase, which is $P2_1ca$.[7] The study done in BCCD under pressure up to 5.5 kbar clearly revealed the splitting of certain anomalies in the dielectric constant $\varepsilon(T)$,[8,9] which were related to the onset of new C and INC phases induced by pressure.

As is well known the appearance of structural branching processes was predicted by the analysis of ANNNI models (axial next-nearest-neighbor Ising) which are the prototype of many spinlike constituent models.[10,11] The (p,T) phase diagram of BCCD was described in the frame of an ANNNI model which 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. $\chi=J_2/J_1$ is the single essential parameter of the model. The (p,T) phase diagram of BCCD is interpreted with the interaction J_0, J_1, and J_2 depending on pressure and temperature.[11] In particular, when two C phases with patterns $\langle S_1\rangle$ and $\langle S_2\rangle$

become unstable they vanish and can yield stable phases of patterns $\langle S_1^n S_2^m \rangle$ with n,m integers.[10] BCCD is a striking illustration of this situation, and its phase diagram, conjectured from the experimental study of $\varepsilon(T)$ under pressure, shows branching processes with similar topology, between $\delta=\frac{1}{5}$ and $\frac{1}{6}$ C phases, $\delta=\frac{1}{4}$ and $\frac{1}{5}$ C phases, and between the normal and $\frac{1}{4}$ C phases.[8] The values assigned tentatively to the modulation wave numbers of the new phases are $\delta=\frac{4}{17}, \frac{4}{13}, \frac{2}{9}, \frac{3}{14}, \frac{4}{19}$ (between $\delta=\frac{1}{4}$ and $\frac{1}{5}$); $\delta=\frac{3}{17}, \frac{4}{23}, \frac{2}{11}, \frac{4}{21}, \frac{3}{16}$ (between $\delta=\frac{1}{5}$ and $\frac{1}{6}$), and $\delta=\frac{6}{23}, \frac{5}{19}, \frac{4}{15}, \frac{3}{11}, \frac{2}{7}, \frac{3}{10}$ (between $\delta=\frac{1}{4}$ and the normal phase).[8]

In this work we report the results obtained in an experimental study of elastic neutron scattering in D-BCCD, under hydrostatic pressure, performed to check assumptions relative to the modulation wave numbers of the new high-order C phases and to share some light on the complex behavior of BCCD. A (p,T) phase diagram is presented, on the basis of neutron-scattering results, and compared to the one obtained from macroscopic measurements.[8,9] Finally, the (p,T) phase diagram is discussed in the light of ordinary Landau theory, and of microscopic models.

EXPERIMENTAL SETUP

A neutron-scattering study was performed in partially deuterated BCCD (D-BCCD) which presents the same phase transition sequence as BCCD,[12] at the Laboratoire Leon Brillouin in VALSE, a three-axis spectrometer, on a cold source.

Pyrolithic graphite crystals were used as a monochromator and analyzer. A graphite filter was put into the incident beam in order to eliminate second-order contaminations. The measurements were done with a constant incident neutron energy of 14.7 meV with collimations of about 30′. Elastic scans were performed in a (1,0,0) scattering plane allowing one to examine $(0,k,l)$ reflections.

The high-pressure cell is an aluminum alloy (7049-AT6) vessel with helium gas as a pressure medium. This cell is cylinder-shaped with a diameter of 16 mm and a height up to 55 mm can be used. The pressure value is determined by the (T,p) evolution of Manganin gauges located on the pressure cell itself.

The pressure is measured with a precision of ±80 bars and the temperature is controlled with an accuracy of ±0.01 K.[13,14] In our case a trapezoidal-shaped plate with a volume ~0.9 cm^3 (area ~1 cm^2 and thickness ~0.9 cm) was used.

The modulation wave vector $\delta(T)\mathbf{c}^*$ and its amplitude were deduced, at each temperature, from fits of the calculated spectra to the experimental position, intensity, and width of the satellite diffraction peaks. These were obtained by performing essentially omega scans. The typical separation between the main Bragg and satellite reflections was 0.14 Å^{-1}, whereas both types of the reflections were resolution limited with a typical width (FWHM) of 0.01 Å^{-1}. Inside the incommensurate phase the intensity of the satellite peaks strongly increases when cooling, at 2.9 kbar they have a typical relative value of 33% of the corresponding Bragg intensity at $T=177$ K and 50% at $T=150$ K (within the $\delta=\frac{1}{6}$ C phase). The fits were based on Gaussian line shapes for the satellites. In all cases, it was checked that the width of the satellite reflections was determined by the instrumental resolution which is available for the considered instrumental configuration at each point of reciprocal space. Only first satellites were observed, although, in some cases, higher-order satellites were carefully searched for.

EFFECT OF HYDROSTATIC PRESSURE

In Figs. 1(a) and 1(b), the temperature dependence of the modulation wave number $\delta(T)$ and the integrated intensity of the satellites $I(T)$, at ambient pressure, 2.5, 2.9, and 4 kbar are displayed. As was reported previously, the study of elastic neutron scattering at ambient pressure provided direct evidence for the $\delta=\frac{1}{4}, \frac{2}{9}, \frac{1}{5}$, and $\frac{1}{6}$ C phases, and for a nonmodulated structure at low temperatures.[12] Some indications of the presence of the $\delta=\frac{2}{7}$ C phase have been detected. Three INC phases were found in the 116–164 K range of temperatures and an additional narrow INC phase was disclosed, sandwiched between the $\frac{2}{9}$ and $\frac{1}{5}$ C phases.[12,15] Some of these features are very explicit in Fig. 1(a).

Before analyzing in detail the plots depicted in Fig. 1, we compare the more apparent results obtained for certain values of pressure, with those obtained at atmospher-

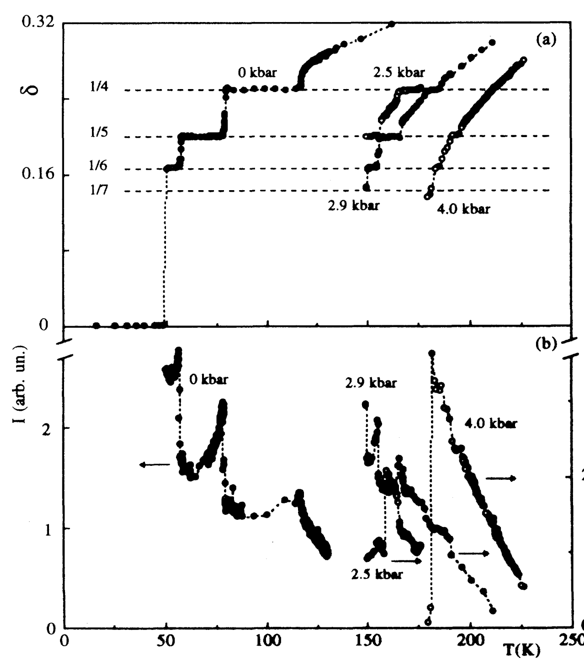

FIG. 1. (a) Modulation wave number as a function of the temperature at various hydrostatic pressures (atmospheric, 2.5, 2.9, and 4 kbar). (b) Temperature dependence of the integrated intensity of the satellites $(0,6,\pm\delta)$ at various hydrostatic pressures (atmospheric, 2.5, 2.9, and 4 kbar). The intensities at atmospheric pressure and at other pressures were obtained in different sized samples.

ic pressure. For all the values studied, the temperature range of stability of $\delta=\frac{1}{4}$, $\frac{1}{5}$, and $\frac{1}{6}$ C phases decreases with increasing pressure. This effect is more explicit for the $\delta=\frac{1}{4}$ C phase and less important for the $\delta=\frac{1}{6}$ C phase, i.e., when the pressure varies from the atmospheric pressure to 4 kbar, the temperature ranges of stability of the $\delta=\frac{1}{4}$, $\frac{1}{5}$, and $\frac{1}{6}$ C phases decrease by 9.3, 20, and 50 %, respectively.

The whole temperature range of stability, for the modulated structure sequence, decreases with increasing pressure. The critical temperatures for the different phase transitions increase with increasing pressure, and dT_c/dp varies between +14 and +30 K/kbar, which are rather high values.[16]

Incommensurate phases, with temperature ranges of stability of several degrees, are very visible at 2.5, 2.9, and 4 kbar, between the $\frac{1}{4}$ and $\frac{1}{5}$ C phase and between $\frac{1}{5}$ and $\frac{1}{6}$ C phases, while at atmospheric pressure they are stable in very narrow temperature ranges, smaller than 1 K.[3,12] In the temperature ranges associated with these incommensurate phase branching processes are expected to occur.

Let us now analyze in more detail the behavior of $\delta(T)$ and $I(T)$, in the range where the structural combination of branching and bifurcation sequences are predicted. In Fig. 2, for 4 kbar in the temperature range bordered by the $\delta=\frac{2}{7}$ and $\frac{1}{4}$ C phases, between 202 and 230 K, we can see very small plateaus corresponding to $\delta=\frac{4}{15}$, $\frac{5}{19}$, and δ close to $\frac{6}{23}$. For 2.9 kbar, in the temperature range 174–202 K, two small plateaus at $\delta=\frac{4}{15}$ and $\frac{6}{23}$, can be seen in Fig. 3. These results clearly confirm the existence of a branching structure between the $\delta=\frac{2}{7}$ and $\frac{1}{4}$ C phases, in very good agreement with the predictions stated by Ao et al.[8]

For 2.5 and 2.9 kbar, Fig. 4 shows $\delta(T)$ and $I(T)$ for the temperature range bordered by the $\delta=\frac{1}{4}$ and $\frac{1}{5}$ C phases, where the occurrence of another branching structural process was assumed. Plateaus at $\delta=\frac{4}{17}$, $\frac{3}{13}$, and $\frac{2}{9}$, and the hint of a plateau at $\delta=\frac{3}{14}$, suggested by a change of slope in $\delta(T)$ for 2.9 kbar, provide good evidence for the existence of high-order C phases bordered by INC phases. In Fig. 2 we can see that 4 kbar pressure also induces the $\delta=\frac{3}{13}$ C phase. The scarce data available around 167 K did not allow us to check the existence of the $\delta=\frac{4}{19}$ C phase, but, except for this C phase, we have found all the high-order C phases reported previously[8] in the branching process zone bounded by the $\delta=\frac{1}{4}$ and $\frac{1}{5}$ C phases. In this zone we have found some evidence for the existence of the $\delta=\frac{5}{21}$ C phase at 4 kbar (Fig. 2). The branching process between the $\frac{1}{5}$ and $\frac{1}{6}$ C phases was not

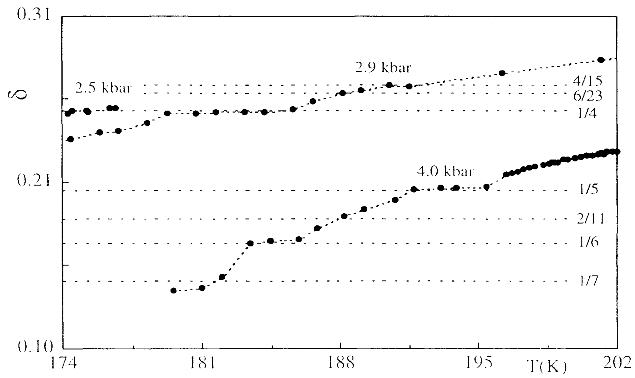

FIG. 3. Enlarged section of Fig. 1(a), showing the modulation wave number vs temperature, between 174 and 202 K.

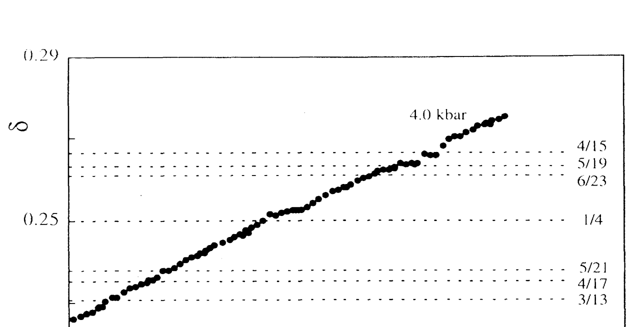

FIG. 2. Enlarged section of Fig. 1(a), showing the modulation wave number vs temperature, between 202 and 230 K.

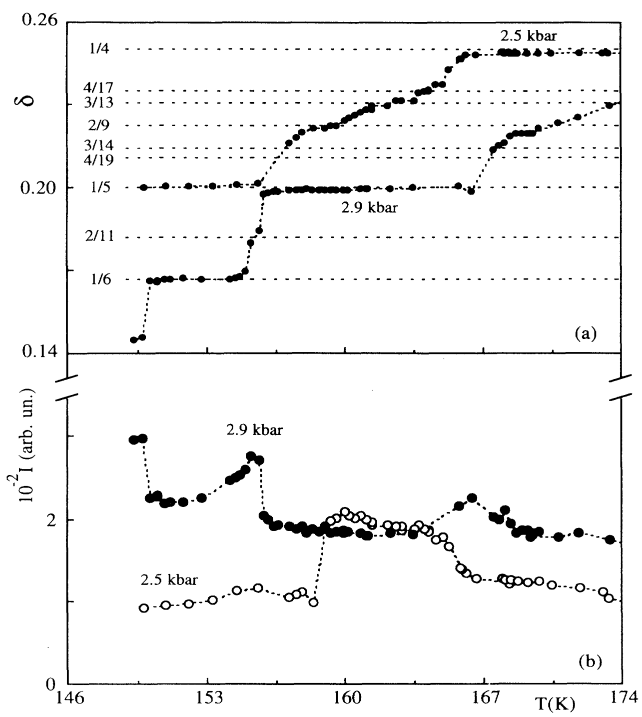

FIG. 4. Enlarged section of Figs. 1(a) and 1(b), between 146 and 174 K. (a) Modulation wave numbers vs the temperature; (b) integrated intensity of the satellites $(0,6,\pm\delta)$ as a function of the temperature.

studied in detail, but we have obtained evidence for the $\frac{2}{11}$ C phase as shown in Fig. 4, for 2.9 kbar.

In contrast with the behavior of the integrated intensity of satellites at atmospheric pressure, where very explicit anomalies reveal the onset and the disappearance of high-order commensurate phases, the variation of $I(T)$ at other pressures is smoother with the erasure of some discontinuities, steps, and plateaus, as can be seen in Fig. 1(b). In particular, for 4 kbar, $I(T)$ behaves like a quasimonotonous function, with very small anomalies in the upper and lower bordering zones of C phases. At atmospheric pressure, the large jumps of $I(T)$, at ~ 56 and ~ 78 K, denote a strong coupling between the underlying lattice and the modulated lattice. The anisotropic character of this coupling, which is more prominent in the **c** direction, was revealed by a study of the temperature dependence of the intensity of Bragg peaks, obtained by reflexion on planes perpendicular to the **b** and **c** axes.[17]

For 2.9 kbar [Fig. 1(b)], $I(T)$ exhibits very explicit anomalies near the $\delta = \frac{2}{9}$ and $\frac{2}{11}$ C phases, whereas the variation of $I(T)$ is rather smooth for $T \geq 160$ K, like the behavior of $I(T)$ for 4 kbar. The scarce data available for 2.5 kbar does not allow us to draw full conclusions about $I(T)$, but we have to point out the visible anomalies of $I(T)$ found in the range of temperatures, where narrow high-order C phases occur.

It is a quite general result in our experiments that clear anomalies in $I(T)$ occur at the temperatures bordering the narrow high-order C phases as we can see in Fig. 1(b). A similar behavior was found in the intensity of satellites associated to the $\delta = \frac{6}{29}$ C phase, observed for the 2 kV/cm dc electric field biased D-BCCD.[18] The experimental results displayed in Fig. 3 also provide some evidence for the $\delta = \frac{1}{7}$ C phase, stable in a very narrow temperature range.

In Fig. 5, the (p,T) phase diagram is displayed. It summarizes the main results obtained. The general features are similar to those obtained from the study of the temperature dependence of $\varepsilon(T)$,[8] but in our study the modulation wave numbers result from direct measurements for either C or INC phases. On approaching the Lifshitz point, the C phases should be completely suppressed by INC phases and the Lifshitz point is expected to occur at $T_L \leq 346$ K and $P_L = 11.6$ kbar for BCCD.[8] Extrapolation from data displayed in Fig. 5 leads to $T_L \sim 350$ K and $P_L \sim 10$ kbar for D-BCCD.

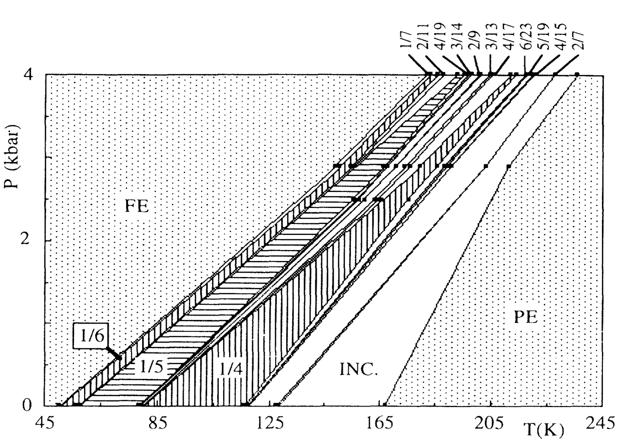

FIG. 5. Pressure-temperature phase diagram in D-BCCD. PE, paraelectric region; FE, ferroelectric region; hatched areas, commensurate phases; open areas, incommensurate phases.

CONCLUDING REMARKS

On basis of an ANNNI model, the phase diagram of BCCD was obtained by Siems and Tentrup.[11] High-order commensurate phases, with the predicted modulation wave numbers mentioned before, between the $\frac{2}{7}$ and $\frac{1}{5}$ C phases, were found in the present work with exception of the $\delta = \frac{4}{19}$ and $\frac{3}{11}$ C phases. These phases are localized in temperature ranges not studied with enough detail. However, in the ANNNI models it is difficult to go beyond a qualitative agreement and identify the structural elements to spinlike constituents having ferro- or antiferroelectric interactions. Chen and Walker developed a symmetry-based, competing-interaction model for BCCD where the physical meaning of the different terms in the energy are more apparent.[19] A large number of high-order commensurate phases were also predicted by this model.

The stability of modulated structures can also be discussed in terms of a Landau free-energy expansion in which the modulation amplitude is taken as the primary order parameter.[20] This approach was used to describe successfully the phase transition sequence in BCCD by taking a one-dimensional order parameter and an effective fourth degree term in umklapp expressions.[21] However, the model considered in this way does not describe correctly the temperature dependence of the integrated intensity of the satellites.[12] The complex behavior of the temperature dependence of the intensity of satellites is not well understood for the time being and deserves further attention.

As we have seen, the pressure dependence of T_c was determined up to 4 kbar for the different phase transitions, and its derivative dT_c/dp is always positive. The long period distortion in BCCD is related to the partial softening of an optic branch near the Brillouin-zone center,[22] and the softening of this phonon is caused by the cancellation of the short-range forces by the long-range dipolar forces. As the pressure derivative of T_c is positive, this means the overcancellation of electrostatic interaction, relatively pressure insensitive, by the negative (i.e., attractive) short-range interactions.[16]

In conclusion, we have obtained experimental results in good agreement with the predictions of theoretical models and direct diffraction evidence for the occurrence of a large number of high-order commensurate phases, stable in narrow ranges of temperature. Novel features concerning the temperature dependence of the modulation numbers of the incommensurate phases induced by pressure have been revealed. This neutron study has disclosed a C phase with $\mathbf{k} = \frac{5}{21}\,\mathbf{c}^*$.

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