Elastic-neutron-scattering study of the devil's-staircase behavior in deuterated betaine calcium chloride dihydrate

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An elastic-neutron-scattering study of partially deuterated dihydrate betaine calcium chloride (D-BCCD) is reported. We obtain direct diffraction evidence for the occurrence of a commensurate phase with wave vector $\mathbf{q}=\delta\mathbf{c}^*=(2/9)\mathbf{c}^*$ and for the absence of modulation of the lowest-temperature phase. The existence of another incommensurate phase adjacent to the $\delta=\frac{2}{9}$ commensurate phase is pointed out and some indications of the existence of the $\delta=\frac{2}{7}$ commensurate phase are described. Diffraction data relative to the temperature dependence of the modulation wavelength and to its amplitude are discussed in the light of the present controversy relative to the theoretical scheme relevant to BCCD.

INTRODUCTION

Research on betaine calcium chloride dihydrate $[(CH_3)_3NCH_2COO\cdot CaCl_2\cdot 2H_2O$ (BCCD)] has taken a prominent place among studies of insulating materials with incommensurate phases. The reasons lie in the unusually large number of phases this substance exhibits and in the controversy about the characteristics of these phases.

BCCD is orthorhombic at ambient temperature with space group *Pnma* ($a=10.97$ Å, $b=10.15$ Å, $c=10.82$ Å, $Z=4$). The structure is based on two elementary units, sharing a pair of oxygen atoms. 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. The juxtaposition of these units forms chains along the **c** direction.

The structure is modulated in the **c** direction.[1] It exhibits several incommensurate (INC) and commensurate (C) phases occurring in the temperature range between 164 and 46 K, whose nature has not yet been unambiguously determined. X-ray-diffraction measurements[1] have shown the existence of two incommensurate phases with wave vector $\mathbf{q}=\delta(T)\mathbf{c}^*$ and four commensurate phases with $\delta=\frac{2}{7}, \frac{1}{4}, \frac{1}{5}$, and $\frac{1}{6}$.

Dielectric and pyroelectric measurements[2–6] have revealed a large number of anomalies which have been assigned to the occurrence of over 16 INC and C phases. Some of the latter have been tentatively assigned to higher orders of commensurabilities (e.g., $\delta=\frac{2}{9}, \frac{4}{15}$, and $\frac{2}{11}$) (see Table I). However, these assignments do not result directly from the measurement of δ, but rather from a symmetry analysis establishing a relationship between the order of commensurability and the dielectric polar properties of the commensurate phases.[7]

On the other hand, there is some uncertainty on the nature of the lowest-temperature phase, below 46 K. X-ray-diffraction experiments[1] have disclosed a modulated phase ($\delta=\frac{1}{6}$), while Raman[8] and electronic-paramagnetic-resonance[9] (EPR) results are consistent with a nonmodulated phase ($\delta=0$).

Attempting to interpretate the phase-transition sequence in BCCD, within the framework of a phenomenological Landau-type theory, one encounters two difficulties. First, it is not clear whether one should use a single set of irreducible order parameters[7] or two such sets.[10] A recent x-ray study[11] and some optical data[12] favor the first hypothesis, but other optical studies support the latter.[13] Recent inelastic-neutron-scattering experiments[14] leave the possibility of either interpretations.

Another difficulty of interpretation arises about the shape of the modulation in the incommensurate phases. EPR (Ref. 9) and dielectric data[5] are consistent with the occurrence of a "multisoliton" regime (i.e., a periodic array of discommensuration walls), while diffraction data are rather in agreement with the existence of a sinusoidal regime.[1,14]

In order to clarify some of these points, we have performed an elastic-neutron-scattering study as a function of temperature in partially deuterated BCCD (D-BCCD). As compared to x-ray diffraction, this technique has the advantage of avoiding the creation of irradiation defects which could stabilize commensurate phases of high order, as is known to occur in thiourea[15] and in other organic compounds.[16]

Previous studies of D-BCCD have shown that deuteration does not give rise to the large isotopic effects observed in other betaine compounds,[17,18] probably because of the fact that there are no H bonds with multiple orientations in BCCD. Hence we do not expect the results for D-BCCD to be qualitatively different from those of the standard hydrogenated compound. This expectation is supported by the fact that the temperature dependences of the dielectric constant and pyroelectric coefficient in D-BCCD reveal the same sequence of anomalies, assigned to transitions between different modulated phases, as in BCCD. The corresponding critical temperatures are only slightly shifted toward higher temperatures by 2°–5° (cf. Table I). It is worth noting, however, that the magnitude of the dielectric anomalies is strongly reduced in the deuterated compound, in particular for the INC-C phase transitions.[18,19]

EXPERIMENTAL RESULTS

The sample used in the present study was a large ($\sim$4–5 cm^3) single crystal with natural faces. It was grown from D_2O solution by controlled solvent evaporation, resulting in a partially deuterated compound.[2,18] The deuteration in the CH_3 and CH_2 groups is very low, probably 20%. The deuteration in the H_2O group is of the order of 95%.[18]

The experiments were performed on a conventional triple-axis spectrometer located at a cold-neutron guide position in the Laboratoire Léon Brillouin in Saclay, France.

Pyrolytic graphite crystals were used as 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 sample was wrapped in aluminum foil and fixed on the cold finger of a closed-cycle cryostat. The sample chamber of the cryostat was flooded with helium gas in order to guarantee a homogeneous temperature distribu-

TABLE I. Enumeration of the commensurate phases conjectured to exist in BCCD and D-BCCD, on the basis of available experimental data. Column 1: wave vector of the modulation as fraction $\delta=m/n$ of the reciprocal-lattice vector $\mathbf{c}^*$. Column 2: temperature range of stability of the corresponding commensurate (C) phase according to the dielectric data in Ref. 4. Column 3: crystallographic direction of the dielectric spontaneous polarization P_S, whenever relevant; [(0) means that $P_S=0$ in the considered phase]. Columns 4 and 5: Temperature range of stability of C phases according to, respectively, x-ray data in Ref. 1 and dielectric data in Ref. 20.

$\delta=\frac{m}{n}$	T_1-T_2 (K) BCCD	Direction of P_S	T_1-T_2 BCCD	T_1-T_2 D-BCCD
$\frac{2}{7}$	127.8–124.5	**b**	127–125	130–127
$\frac{3}{11}$	118.4–117.4	(0)		
$\frac{4}{15}$	116.0–115.7	**b**		
$\frac{6}{23}$	115.4	**b**		
$\frac{1}{4}$	115.3–75.8	**a**	116–73	116.9–79.2
$\frac{2}{9}$	75.8–75.2	**b**		
$\frac{1}{5}$	75.2–53.3	(0)	73–53	79.2–56.5
$\frac{2}{11}$	53.3–53.0	**b**		
$\frac{1}{6}$	53.0–47.1	**a**	53–47 and <43	56.5–49.8
$\frac{2}{13}$	47.1–46.9	**b**		
$\frac{1}{7}$	46.9–46.2	(0)		
$\frac{1}{8}$	46.2–46.0	**a**		
$\frac{1}{1}$	46.0 and below	**b**	47–43	49.8 and below

tion within the sample. The temperature could be set with an accuracy of 0.1 K and kept constant within ±0.03 K.

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 **q** scans along the $\mathbf{c}^*$ axis, around the "main" Bragg reflections (0,6,0), (0,3,1), (0,4,6), and (0.7,1). The fits were based on Gaussian line shapes for the satellites. In all the 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. In the region of the transitions between distinct phases, the fits provided us with data relative to the coexistence of different modulation wave vectors.

We have plotted, in Fig. 1, the temperature dependence of the modulation wave number $[\delta(T)]$ [Fig. 1(a)] and of the integrated intensity of the satellites $[I(T)]$ [Fig. 1(b)]. These plots correspond to the data obtained during cooling of the sample. In the same figure, we have superimposed [Fig. 1(c)] the variations of the dielectric

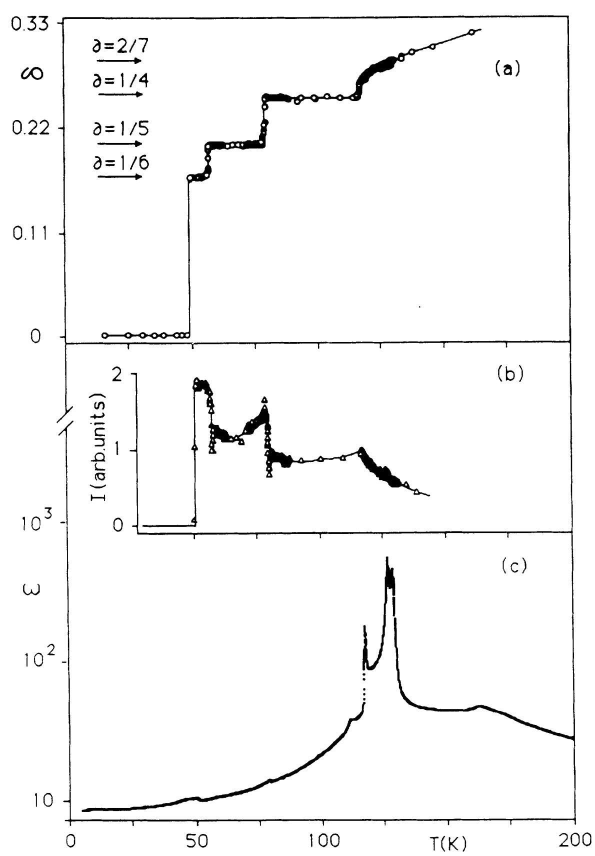

FIG. 1. Temperature dependence, on cooling, in D-BCCD (a) of the modulation wave number $\delta(T)$, (b) of the satellites intensity $I(T)$, and (c) of the dielectric constant $\epsilon(T)$.

constant of the deuterated compound, as deduced from a recent study.[20] One can note an excellent coincidence of the anomalies detected in the neutron scattering and of those obtained in the dielectric measurements.

Let us first discuss the most apparent features of the variations of $\delta(T)$. Between 164 and ~130 K, we are in the expected range of the upper incommensurate phase (INC 1). This is in agreement with the observation that δ varies almost linearly with temperature.

A variation in δ is also observed in the range 130–115 K, where the second incommensurate phase (INC 2) is expected to exist. In this range the observed variation of δ is not linear and terminates by a steep decrease, at the lower limit of stability of this phase.

At lower temperatures we can observe clearly three plateaus corresponding, respectively, to the three commensurate phases with $\delta=\frac{1}{4}$, $\frac{1}{5}$, and $\frac{1}{6}$. Their range of existence is found, respectively, at $80<T<117$ K, $57<T<79$ K, and $50<T<56$ K. These "simple" commensurate phases were already observed in the hydrogenated compound by x-ray diffraction.

The first result directly established by the present diffraction data is the fact that the stable phase below 50 K has $\delta=0$ and is therefore unmodulated. Indeed, one can note in Fig. 1 the abrupt vanishing of the satellites intensities below ~50 K, i.e., below the range of the commensurate $(\frac{1}{6})$ phase. The persistence of this vanishing has been checked down to 15 K. Such a result confirms inferences based on Raman-scattering[8] data and EPR measurements.[9] It infirms assertions based on x-ray data which assigned part of the low-temperature range to a reentrant phase with $\delta=\frac{1}{6}$.[1]

Let us now discuss the detailed behavior of D-BCCD in the narrow regions separating the phases of large temperature extension described above.

Around 80 K we clearly observe, in a range of 2 K, the coexistence of two satellites [Fig. 2(a)] between the plateaus $\delta=\frac{1}{4}$ and $\frac{1}{5}$. In order to investigate this behavior, we have performed diffraction experiments in this temperature range at intervals of 0.1 K.

A direct transition from the $\delta=\frac{1}{4}$ phase to the $\delta=\frac{1}{5}$ phase would necessarily be of first order since the corresponding wave vectors are distinct and since the satellites intensity does not vanish. Accordingly, the coexistence of two satellites is not unexpected, since, for a first-order transition, the transition region is a region of phase coexistence. However, a careful analysis of the diffraction spectrum in this region reveals a more complex situation in which two subranges must be distinguished within the considered 2-K interval [Fig. 2(b)]. Between 80 and 79.4 K, the fit of the spectra reveals the coexistence of a satellite with $\delta=\frac{1}{4}$ and a satellite with $\delta=\frac{2}{9}$. Between 79.4 and 78.5 K, this second satellite is no longer locked at $\frac{2}{9}$, but is found to vary continuously between this value and $\delta=\frac{1}{5}$. In this temperature range, the satellite at $\delta=\frac{1}{4}$ is still observed, with weaker intensity.

Hence two results derive from the former analysis. On the one hand, a commensurate phase with $\delta=\frac{2}{9}$ is detected in a diffraction experiment. Such a result substantiates previous claims of the existence of such a phase made on the basis of pyroelectric and dielectric measurements.

On the other hand, a second result consists in the existence of an incommensurate phase sandwiched between the $\delta=\frac{2}{9}$ and $\delta=\frac{1}{5}$ phases.

The transition scheme in this temperature range is more complex than described previously. Instead of a single transition ($\frac{1}{4}\rightarrow\frac{1}{5}$), one has a sequence of three transitions: $\frac{1}{4}\rightarrow\frac{2}{9}$, $\frac{2}{9}\rightarrow$INC, INC$\rightarrow\frac{1}{5}$.

It can be inferred from the variations of δ and observed coexistence of satellites that the transition from $\frac{1}{4}$ to $\frac{2}{9}$ is first order, while the other two transitions surrounding the additional incommensurate phase are continuous. The latter assumption is, in particular, consistent with the absence of a satellite with $\delta=\frac{1}{5}$ in the coexistence range. The continuous character of the transitions bordering the additional incommensurate phase implies that this phase, which has been detected on cooling, should also be observable on heating: Its existence is not hidden by a metastability of the surrounding phases.

The same type of careful scanning has been performed for the boundary region between the $\frac{1}{5}$ and $\frac{1}{6}$ phases at about 56 K, in order to obtain evidence for a phase with $\delta=\frac{2}{11}$. Again, the coexistence of two satellites was observed. The analysis of the data shows unambiguously that a satellite with $\delta=\frac{1}{5}$ exists in the higher-temperature zone of the boundary region and that a satellite with $\delta=\frac{1}{6}$ exists in the lower-temperature zone of this region. However, the identification of the nature of the second satellite accompanying either of these lines was not conclusive. The analysis yields an acceptable fit for a variety of δ values, such as $\frac{2}{11}$; the analysis would also be consistent with the mere coexistence of the $\frac{1}{5}$ and $\frac{1}{6}$ phases. It is worth pointing out that very recent dielectric results[20] seem to indicate that, possibly, in D-BCCD the $\frac{2}{11}$ phase may only be stable under application of an electric field. This contrasts with the situation of the hydrogenated BCCD, where this phase seems to exist even in the absence of an electric field.

A third boundary range of interest lies in the vicinity of 130 K. Previous experiments had asserted that the frontier between the two incommensurate phases at ~ 130 K corresponds to the range of stability of a ~ 2-K-wide commensurate phase with $\delta=\frac{2}{7}$. We have given careful attention to this range by performing repeated diffraction experiments in it. The obtained satellite positions and shapes were analyzed. Figure 3 displays an enlarged plot of $\delta(T)$ as well as the plot of the dielectric constant near 130 K.

In a temperature range around 1.5 K, it seems that the variations of δ display a very small slope around δ values close to $\frac{2}{7}$. However, the dispersion of the data does not allow the unambiguous identification of a plateau. Nevertheless, this behavior contrasts with the steeper linear decrease of δ in the upper incommensurate phase and with the nonlinear variation of δ in the lower one. Hence the corresponding dip in the $\delta(T)$ curve is consistent with the presence of an intermediate phase with $\delta=\frac{2}{7}$. Such an intermediate phase is clearly shown by the dielectric

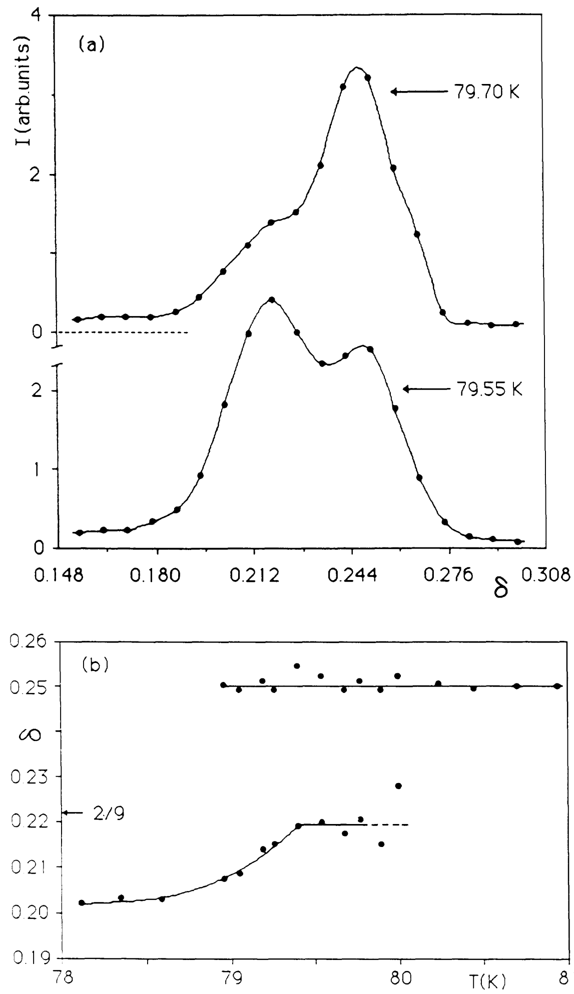

FIG. 2. (a) Satellite line shape at two different temperatures in the range of the transition $\frac{1}{4}\rightarrow\frac{1}{5}$. (b) Fitted temperature dependence, on cooling, of the modulation wave number of coexisting satellites in the borderline between the $\frac{1}{4}$ and $\frac{1}{5}$ C phases.

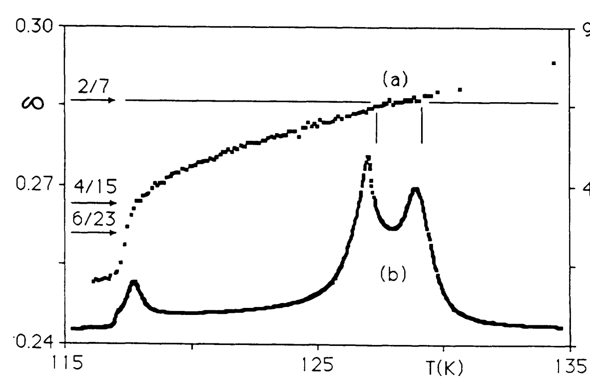

FIG. 3. (a) Variations in D-BCCD, as a function of temperature, of the modulation wave number $\delta(T)$ in the vicinity of 115 K. (b) Temperature dependence in the same range, on cooling, of the dielectric constant $\epsilon(T)$.

data. The absence of a well-defined plateau in the neutron data could indicate a more complex situation, the nature of which can be clarified by the recent observation that the dielectric constant has a large value in the range between the two incommensurate phases and is affected by thermal hysteresis.[21] These effects are usually found within an incommensurate phase near the lock-in transition. Possibly, we have to deal, in the deuterated compound, with a "quasicommensurate $\delta=\frac{2}{7}$ phase" with some remaining discommensurations of the kind observed in barium sodium niobate.[22]

Let us now consider the overall variations of the intensity of the diffraction satellites (Fig. 1). Between 165 and 15 K, these variations display several interesting features. The intensity does not show the monotonously increasing variation on cooling, which is often observed in incommensurate systems.[23] Instead, we observe a succession of increases, plateaus, and steep discontinuities. It is also remarkable that a significant and unusual decrease of the intensity occurs, on cooling, in part of the range of existence of the $\delta=\frac{1}{5}$ phase. This nonstandard behavior of the intensity contrasts with the standard montonically decreasing "devil's-staircase-like" behavior of the modulation wave number $\delta(T)$. As will be pointed out in the forecoming discussion, such an anomalous variation of the intensity may be an important clue to the nature of the order parameter in the considered system.

DISCUSSION

We now discuss the consistency of these contrasting behaviors of $\delta(T)$ and $I(T)$ within the framework of the various Landau-type phenomenological interpretations which have been considered recently.

Let us first assume that the sequence of phases can be described by a single irreducible set of order parameters (i.e., a single degree of freedom) having the Γ_3 symmetry described in Ref. 7. As mentioned in the Introduction, the validity of this assumption has been tested by means of careful x-ray measurements at ~ 140 K, i.e., in the incommensurate phase, close to the suspected range of the $\frac{2}{7}$ phase.[11] In this framework two categories of possible schemes can be considered, corresponding either to a sinusoidal regime or to a multisoliton regime, for the modulation.

The sinusoidal scheme has been previously worked out in detail.[24] It relies on a free-energy density of the form

$$f(\xi)=t\xi^2+\frac{1}{4}\xi^4-\frac{1}{4}\left[\frac{\delta\xi}{\delta Z}\right]^2+\frac{1}{4}\left[\frac{\delta^2\xi}{\delta Z^2}\right]^2+\mu\xi^2\left[\frac{\delta\xi}{\delta Z}\right]^2+\text{lock-in terms}\ , \qquad (1)$$

where ξ is an adimensional order parameter, where t, proportional to $(T-T_0)$, and μ are coefficients. In this model the temperature dependence of $\delta(T)$ results from the term $\mu\xi^2(\delta\xi/\delta Z)^2$, which represents the coupling between the modulation amplitude (proportional to ξ) and its wave number (proportional to $\delta\xi/\delta Z$). The fit within this model, of the overall variations of $\delta(T)$ for hydrogenated BCCD, has been previously performed with satisfactory qualitative results.[24] In particular, the model yields the correct initial slope for $\delta(T)$ and a consistent width for the major plateaus at $\delta=\frac{1}{4}$, $\frac{1}{5}$, and $\frac{1}{6}$. It also accounts for the occurrence of a reentrant incommensurate phase between 115 and 130 K. In the same scheme, based on the free-energy density (1), the variations of the neutron-scattering intensity (proportional to the square of the modulation amplitude ξ^2) are related to the existence of the coupling term with coefficient μ. These variations were not considered previously.[24] We have derived them, as well as the detailed temperature dependence of $\delta(T)$ near 115 K, by using the free-energy coefficients previously determined in Ref. 24. Figure 4 shows the calculated variations of $\delta(T)$ and $I(T)\propto\xi^2(T)$.[23] It appears clearly that, in the vicinity of 115 K, these functions are in poor agreement with the experimental data. Neither the magnitude of the variations of the intensity nor the apparent continuity of the 115-K transition are correctly accounted for.

In the view of accounting more satisfactorily for these variations, we now abandon the sinusoidal picture and consider the occurrence of a multisoliton regime in the system. We place ourselves in the framework of the standard "imposed amplitude approximation" $[\xi\propto(T-T_1)^{1/2}]$.[23] In this framework one expects a continuous lock-in transition at 115 K and a logarithmic variation of $\delta(T)$ near the lock-in transition:

$$\delta(T)=\delta_c+\text{const}\Big/\ln\left[\frac{16}{1-[(T_0-T)/(T_0-T_l)]^{p-1}}\right]. \qquad (2)$$

$2p$ is the degree of the "lock-in" term $[\xi^{2p}(\cos(2p\varphi))]$ in the relevant free energy,[23,25] and T_l is the lock-in temperature.

Figure 5 shows the excellent fit obtained for the wave number $\delta(T)$ derived from the neutron data near 115 K with $T_0=134.5$ K, $T_l=117.0$ K, $p=4$, and $\delta_c=\frac{1}{4}$.

This agreement shows the relevance of such a scheme for interpretating experimental data in the vicinity of the

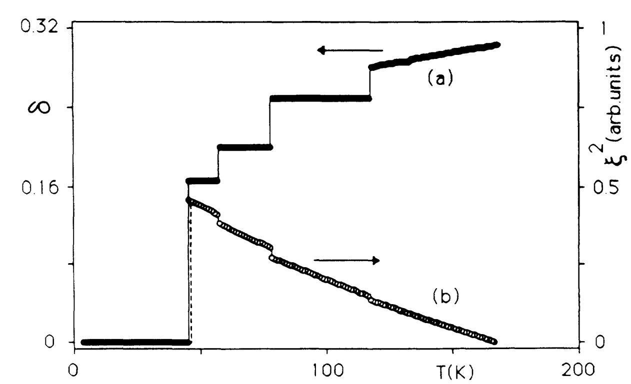

FIG. 4. Calculated variations in the framework of the theoretical model in Ref. 24 of (a) the modulation wave number $\delta(T)$ and (b) the squared amplitude of the order parameter $\xi^2(T)$.

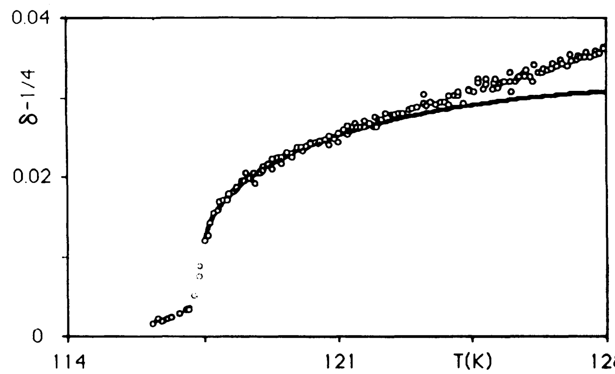

FIG. 5. Comparison between the experimental temperature dependence of the modulation wave number $\delta(T)$ (open circles) and the dependence calculated from Eq. (2) relative to the multisoliton model (solid line).

incommensurate-commensurate transition at about 115 K, as previously established for the dielectric measurements.[5] It also leads to the inference that this transition is of second order, in accordance with the absence of the coexistence of satellites pointed out above. The same transition was reported as first order in hydrogenated BCCD.[26] Possibly, this change of order may be an effect of the deuteration. Note that, in this framework, the temperature dependence of the scattering intensity $I(T)$ is postulated to obey a linear law. The observed shape departs from this description by a small convexity above 115 K.

There are two main difficulties in extending the preceding theory to the interpretation of $I(T)$ in other regions of the phase diagram. On the one hand, the large jumps noticed at ~78 and ~56 K clearly depart from the imposed amplitude approximation.[23] These jumps rather denote a strong coupling between the value of the modulation amplitude and its wave number. On the other hand, the observed decrease of intensity below 80 K contrasts with an expected increase of the intensity on cooling.[27] The experimental observation would also be incompatible with the sinusoidal scheme. In any of the models based on a single set of order parameters, the amplitude of the modulation and hence the scattering intensity are expected to increase monotonically on cooling, in contrast with the observed behavior.

A possible way of accounting for the anomalous behavior of the intensity is to recur to a theoretical framework previously invoked[10] for different experimental reasons.[28] In this framework two irreducible sets of order parameters, coupled to each other, were considered. As mentioned in Ref. 11, such an assumption contradicts the x-ray data in the range of temperatures above ~140 K. However, its validity cannot be ruled out at lower temperatures. This hypothesis would be adequate to interpret the observed nonmonotonic behavior of the intensity. Indeed, its basic idea consists in assuming that the onset of a secondary order parameter with symmetry Γ_2 (Refs. 7 and 10) will be "triggered" below the ~80-K transition by the primary order parameter (symmetry Γ_3), which is, alone, active at higher temperatures. The possibility of such a triggering is known to require two conditions: (i) A sufficiently low value of the soft normal mode associated with the secondary order parameter. Recent inelastic-neutron-scattering measurements[14] have shown that this condition is fulfilled. (ii) A sufficiently large value of the static amplitude of the primary order parameter. The fact that the triggering is inactive at ~140 K implies that the latter condition is not fulfilled above 140 K.

However, as apparent in Fig. 1, the amplitude experiences a steep upward variation on cooling at ~80 K. We can therefore make the assumption that this upward jump has the consequence that the amplitude acquires large enough values to allow a triggering of the secondary order parameter. Relying on previous theoretical investigations of coupled systems of this type,[29] we can infer that, as a consequence of this triggering, the secondary parameter will "borrow" amplitude from the primary order parameter. Thus, in a certain interval of temperatures, the amplitude of the primary order parameter, which is reflected in the intensity of the measured satellite, will decrease. A departure from the usual monotonic variations of $I(T)$ can therefore be accounted for. In principle, the "lost" intensity will be transferred to certain "main Bragg peaks," in relation with the lowering of the point-group symmetry of the system, which is another standard consequence of the triggering.[29]

Note that an electric polarization, with a large component along **b** and a small component along **a**, was observed below 47 K in BCCD.[2,30] This behavior suggests that an additional breaking of point-group symmetry possibly occurs at low temperatures, in agreement with the triggering mechanism. However, owing to the smallness of the polarization along **a**, this result has still to be confirmed.

CONCLUSIONS

In summary, the present neutron-scattering study of D-BCCD has provided the following results: (i) Direct diffraction evidence has been found for the existence of the $\frac{2}{9}$ phase. (ii) An additional incommensurate phase with narrow range of stability has been found sandwiched between the $\frac{2}{9}$ and $\frac{1}{5}$ phases. (iii) Some indications of the presence of the $\frac{2}{7}$ phase have been detected in the temperature dependence of the wave vector of the modulation. (iv) The thermodynamic order of several of the transitions in the phase diagram has been clarified: The transitions between commensurate phases are of first order, while the transitions between commensurate and incommensurate phases seem to be of second order. (v) It has been established that the lowest-temperature phase is not modulated: It is a distorted form of the high-temperature phase involving the same number of atoms per unit cell. (vi) Through fits of the neutron data, we have tested several phenomenological models of the phase diagram. The simplest multisoliton approximation with "imposed amplitude" seems to be acceptable for interpreting the behavior in the vicinity of the incommensurate-commensurate transitions. This approximation is, however, inadequate to account for the overall features of the phase diagram in which there is, clearly, a strong coupling between the amplitude and wave number of the modulation. On the other hand, though the assumption of a single irreducible order parameter is valid above ~ 100 K (in agreement with the x-ray data in that temperature range), a coupled-order-parameter scheme may be relevant to interpret the neutron intensity data below 80 K.

Further work should use a more accurate temperature setting in order to investigate the existence of narrower commensurate phases. It should aim at finding evidence for a coupled-order-parameter scheme at low temperatures. It should also attempt to solve the apparent contradiction between the absence of higher-order satellites and the relevance of the multisoliton (i.e., nonsinusoidal) scheme for interpreting the observed behavior close to certain transitions.

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