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Modulated phases in BCCD and water molecule vibrations

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Polarized Raman spectra of BCCD were studied in the broad spectral range 5–3600 cm^{-1} and in the wide temperature interval 12–292 K with the aim to outline in detail the peculiar dynamics of the water molecules. The analysis of the experimental results revealed that the water molecules have to be considered as active partners in the whole process that determines the wealth of structural phase transitions in BCCD.

I. INTRODUCTION

Betaine calcium chloride dihydrate $(\mathrm{CH}_3)_3\mathrm{NCH}_2\mathrm{COO}\cdot\mathrm{CaCl}_2\cdot 2\mathrm{H}_2\mathrm{O}$, BCCD for short, is a solid hydrate. We report a relationship between its interesting properties and the peculiarities of hydrogen bonds. As Raman scattering revealed itself as a powerful technique in solid hydrate research, we have performed a detailed study of Raman spectra in order to bring to light the role played by hydrogen bonds at the successive phase transitions in BCCD.

At room temperature BCCD crystallizes in its normal (N) phase (space group $Pnma$) with four formula units in the unit cell. It is a one-dimensionally modulated system $[\mathbf{q}=\delta(T)\mathbf{c}^*]$ and exhibits an especially rich variety of modulated phases, being one of the best examples of an incomplete devil's staircase.[1–10] The translational symmetry of BCCD in the low-temperature ferroelectric (FE) phase below 46 K and in the N phase above 164 K is the same. The temperature ranges of stability of the principal phases at normal pressure are presented in Table I. An extensive review of the information available up to 1998, concerning BCCD, was published recently by Schaack and Le Maire.[11]

Previous Raman investigations of BCCD (Refs. 12 and 13) were performed in a restrict spectral region and focused on the study of low-lying excitations with the aim to detect amplitudon and phason modes in the incommensurate (INC) phases and folded optical and acoustical modes in the different commensurate (C) phases. Recently, pseudophason gap in the fourfold phase of fully deuterated BCCD crystal was successfully determined by means of a careful analysis of polarized Raman spectra.[14] Very recently, the temperature dependence of the bare amplitudon mode frequency was proposed by Gregora *et al.*[15]

At room temperature the Ca^{2+} ions and the betaine molecules occupy positions in the m mirror plane. The Ca^{2+} ions are coordinated by two Cl^- ions, two water molecules and two oxygen atoms O1 and O2 (here we use the labels introduced in Ref. 4) of the carboxyl group of the betaines. The structure is characterized by zigzagged chains along a, forming layers normal to the b direction, and lying in the m planes at $y=1/4b$ and $y=3/4b$. These layers are interconnected by H bonds $(\mathrm{Cl}\cdots\mathrm{H{-}O3})$ between the inorganic "Ca" octahedra. This system of H bonds is completely different from that observed in betaine arsenate or in betaine phosphate.

As was shown by Brill *et al.*[4] the betaine and Ca octahedra exhibit large-amplitude librational motion in the ac plane around hypothetical axes lying in the m planes, being the amplitudes of the betaine librations much larger than those of the Ca octahedra. Dvořák[18] has suggested that these large-amplitude librations could be associated with the lowest-frequency Raman and IR active modes and proposed to consider these librations as very relevant critical degrees of freedom in the phase transitions. The corresponding four lowest lying modes at 27 cm^{-1} (B_{1g}), 23 cm^{-1} (B_{3g}), 16 cm^{-1} (B_{2u}), and 20 cm^{-1} (A_u) were previously observed in Raman[12] and IR (Ref. 19) spectra. Afterwards[20], the formula unit of BCCD was considered as a rigid entity and the corresponding 12 translations and 12 librations were searched in the low-frequency region (below 100 cm^{-1}) by means of a submillimeter and far IR spectroscopy technique and the corresponding results were compared with the previously reported Raman data.[12]

Recently Hlinka *et al.*[21] treated the betaine molecules and

TABLE I. Domains of stability of the principal phases in BCCD at normal pressure (Refs. 8 and 10).

$\delta=m/n$	Temperature range (K)	(Super)space group
Normal	above 164	$Pnma$
INC	128-164	$P(Pnma){:}1s\bar{1}$
2/7	125-127	
INC	115-125	$P(Pnma){:}1s\bar{1}$
1/4	76-115	$P2_1ca$
1/5	53-75	$P2_12_12_1$
1/6	47-53	$P2_1ca$
0/1	below 46	$Pn2_1a$

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also the Ca complexes as rigid units. In (Ref. 21) the designation ''octahedra'' was fairly replaced by ''complex'' and it will be used in the following. The lowest phonon branches, which represent essentially librations and translations of each entity as a whole, were calculated from a semimicroscopic model and compared with neutron-scattering data.[21] The corresponding lowest lying optical branches as well as the acoustical ones were found below 2 THz (<70 cm^{-1}). It was shown that the soft-mode branch is related with what was called 'easy rotations' of both entities (Ca complex and betaine molecule) around their respective axes lying in the mirror plane.

So, all the previous spectroscopic investigations were focused on the very low-frequency region and were related to the rigid-body degrees of freedom. Although it was a good assumption to consider the betaines as rigid units when analyzing external vibrations of the crystal, it is obviously rather questionable to assume the rigid behavior of the Ca complex.

When coming back to the coordination of Ca^{2+} ions, it is important to outline that O1 and O2 oxygens from the carboxyl group are not symmetrically equivalent. In fact, Ca–O1 and Ca–O2 distances are different and their values are 0.2281 and 0.2249 nm, respectively.[4] Besides, the O1 oxygen is involved into a carbonyl bond with the C4 atom of betaine (C4=O1), while O2 is not (C4–O2). The two Cl^- ions and the two H_2O molecules form symmetrical coordination with the cation Ca^{2+}, and the water molecules form hydrogen bonds with Cl^- ions in the neighboring Ca complex and link layers which are parallel to the m plane at $y = 1/4b$ and $y = 3/4b$. According to x-ray-diffraction (XRD) data[4] obtained in the N phase, the water molecules occupy eightfold positions with C_1 site symmetry. The O3 oxygen atoms of the water molecules are coordinated to Ca^+ ions and both the protons (H7 and H8) of the water molecule are oriented toward the Cl^- ions, so the two water molecules and the two Cl^- ions form a slightly distorted parallelogram with hydrogen bonds O–H$\cdots$Cl along each side. In fact, it is important to emphasize that corresponding interatomic distances of O3–H7$\cdots$Cl and O3–H8$\cdots$Cl bonds are different in the N phase: 0.3239 and 0.3195 nm, respectively. As a result of such a coordination, the internal angle of the water molecule is smaller (103°) than in the free molecule (104°). Moreover, O3–H7 and O3–H8 interatomic distances have been found significantly different: 0.082 and 0.089 nm, respectively. Therefore, as follows from the topology of the hydrogen bonded network, the water molecules in BCCD are involved in unequally H bonds. These peculiarities have never been taken into account when analyzing the results concerning the lattice dynamics of BCCD, although[22] the phase transitions in hydrates would often be strongly associated with the dynamics of the water molecules.

It is clear that the two rigid-bodies approach[21] can be applied in the high-temperature range (INC and N phases) where the amplitudes of thermal vibrations are sufficiently large to neglect the differences of the interatomic distances as well as the asymmetry of the Ca complex. As a consequence of these considerations a question is addressed: why and when do easy rotations become hard? With this motivation we have carried out a detailed Raman study in the region of external and internal vibrations, that clearly shows the importance of the water molecules dynamics in the overall range of the phase transition sequence in BCCD.

II. EXPERIMENTAL DETAILS

Polarized Raman spectra have been measured on samples in the form of carefully oriented and optically polished rectangular parallelepipeds $5\times3\times2$ mm^3 with the axes X, Y, Z parallel to [100], [010], and [001], respectively. The crystallographic axes were determined with an accuracy of $\pm1°$ by x-ray diffraction.

Raman spectra were excited using the polarized light of an Ar^+ laser Coherent INNOVA 90 ($\lambda = 514$, 5 nm) in a right-scattering geometry. The scattered light was analyzed using a Jobin Yvon T64000 spectrometer equipped with a charge-coupled device (CCD) and a photon counting detector. The spectral slit width was about 1.5 cm^{-1}.

The samples were placed in a closed-cycle helium cryostat with temperature stability of about ±0.2 K. The temperature was measured with a silicon diode attached to the sample holder and the actual sample temperatures were estimated to differ by less than 1 K from the temperature readings. The temperature homogeneity in the sample was achieved with a copper mask setup.

III. EXPERIMENTAL RESULTS

A. External vibrations

The lattice dynamics of BCCD in the N phase is described in terms of 333 optical and 3 acoustical vibrational modes. There are 204 internal vibrations of the betaine molecules, 24 internal vibrations of the water molecules, and 105 external optical vibrations. Standard factor-group analysis for external vibrations in the N phase yields

$$\Gamma_{ext} = 14A_g + 13B_{1g} + 14B_{2g} + 13B_{3g} + 13A_u + 13B_{1u} + 12B_{2u} + 13B_{3u}. \tag{1}$$

External vibrations of the water molecules and $CaCl_2$ may be considered as internal modes of the Ca complex. Raman active external vibrations of the water molecules, localized in general positions, can be easily obtained:

$$\Gamma_{transl}(H_2O) = \Gamma_{libr}(H_2O) = 3A_g + 3B_{1g} + 3B_{2g} + 3B_{3g}. \tag{2}$$

As it is known,[22] the librations of the water molecules in solid hydrates are normally observed in the relatively broad spectral range from 350 to 900 cm^{-1}, and translations in between 100 and 350 cm^{-1}. Raman spectra of BCCD were compared with the corresponding spectra of a partially deuterated sample where only protons in the water molecules and partially in the CH_2 and CH_3 groups are replaced by deuterons. This comparison allows the identification of water translations, using the isotopic shift ratio $\omega_H/\omega_D = 1.05$ (see Table II). The water librations were safely detected in xx and zz geometry at 570 and 584 cm^{-1}, respectively. These peaks exhibit typical broad line shapes and a perfect shift in deuterated sample with the ratio $\omega_H/\omega_D = 1.37$. Similar fingerprints were found in other geometries.

As the internal vibrations of the betaines appear above 300 cm^{-1}, only $11A_g + 10B_{1g} + 11B_{2g} + 10B_{3g}$ Raman ac-

TABLE II. Frequencies (in cm^{-1}) of Raman peaks observed in BCCD at 172 K. All peaks below 100 cm^{-1} were also reported by Ao and Schaack (Ref. 12). The star stands for modes shifted in deuterated sample with the ratio $\omega_H/\omega_D = 1.05$.

$A_g(xx,yy,zz)$	$B_{1g}(xy)$	$B_{2g}(xz)$	$B_{3g}(yz)$
	23		21
35			
49	46	46	45
	60	58	
69			71
	78	74	
			86
93	95		
105		104	103
119*	119	116	122
~130	135	139	
155*	160		161*
166*	170	172*	167*
204	~190		
224			

tive modes due to the external vibrations of betaines, CaCl_2 and water translations are expected below this frequency. Experimental Raman spectra in the corresponding scattering geometries were fitted with a sum of damped harmonic oscillators (DHO). At low temperatures Raman peaks are better resolved, so we have analized spectra recorded at 172 K in order to compare experimental data with factor-group calculations. The low-frequency spectra of BCCD are very rich (see Table II) and below 240 cm^{-1} we observed most of the lines expected from factor-group analysis: $11A_g$, $10B_{1g}$, $7B_{2g}$, and $8B_{3g}$. Raman spectra in *zx* geometry (B_{2g}) are very weak, so the agreement between experimental data and factor-group analysis is not as good.

The water translations do not exhibit any significant temperature dependence on cooling down to 12 K. A weak hardening and activation of IR polar modes were observed in the low-temperature Raman spectra due to changes of selection rules, as expected. Raman spectra were examined for different scattering geometries and details will be published elsewhere.[23]

The temperature evolution of Raman spectra of BCCD in the region of the water librations in *zz* geometry is shown in Fig. 1 and the temperature dependence of their frequencies is presented in Fig. 2. Below $T_i = 164$ K the hardening of some modes is clearly visible and at about 125–130 K (this is not related to the existence of the 2/7 phase) we found precursor effects of the lock-in transition disclosed by a second component. A new line emerges near 600 cm^{-1} and becomes clearly resolved inside the 1/4 phase, due to a rather fast decreasing of the linewidth of the low-frequency component centered at 595 cm^{-1}. The low-frequency component of the doublet disappears abruptly at the transition to the nonmodulated FE phase that implies a zone-edge origin of this band.

The high-frequency component exhibits hardening and a further splitting which is poorly resolved in 1/4 phase but becomes perfectly resolved below the temperature range of stability of this phase and in the FE one. We conclude that the second component of the doublet (612 and 620 cm^{-1}) appears from IR spectra. Apparently due to rather flat dispersion of this branch all modes at $\mathbf{q} = n\mathbf{q}_0$ ($\mathbf{q}_0 = \delta\mathbf{c}^*$, $n = 1,2,\ldots$) have identical frequency (or separation is small compared with the finite linewidth) in all the *C* phases and only the zone-edge value of this branch has a lower frequency (595 cm^{-1}).

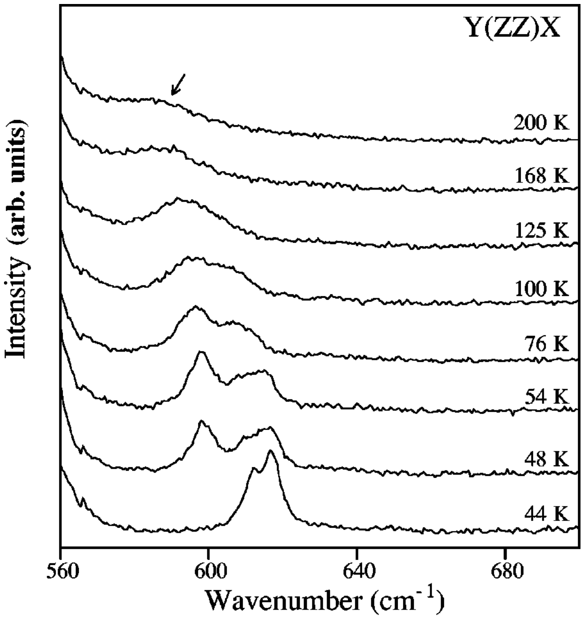

FIG. 1. Temperature evolution of Raman spectra of BCCD in the region of the water librations.

B. Internal vibrations of the water molecules

As the factor-group analysis for the internal vibrations of the water molecules in *N* phase yields:

$$\Gamma(\nu_1^{\omega}) = \Gamma(\nu_2^{\omega}) = \Gamma(\nu_3^{\omega}) = A_g + B_{1g} + B_{2g} + B_{3g} + A_u + B_{1u} + B_{2u} + B_{3u}, \tag{3}$$

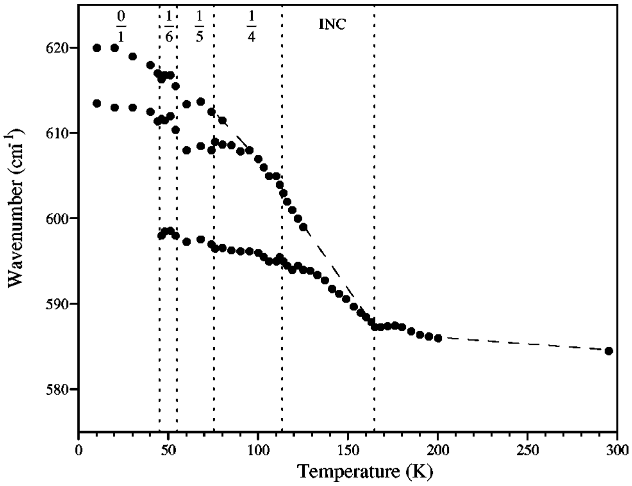

FIG. 2. Temperature dependences of the frequencies of the water librations shown in Fig. 1. Vertical dotted lines mark the phase transition temperatures. Dashed lines show the trend of the modes which are unresolved.

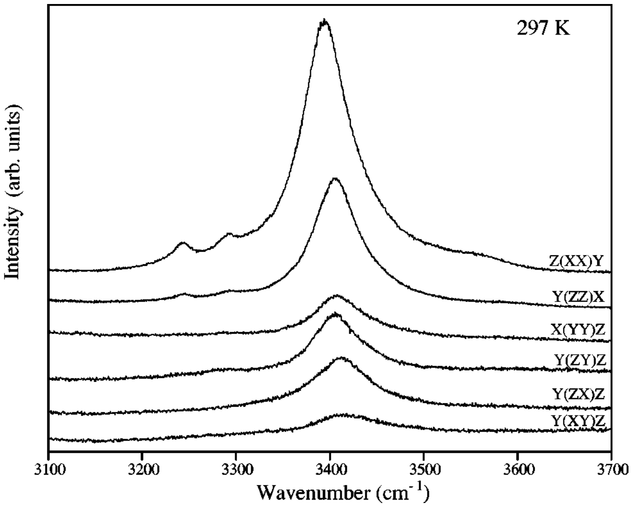

FIG. 3. Raman spectra of BCCD at room temperature in the region of the stretching vibrations of the water molecules for six scattering geometries.

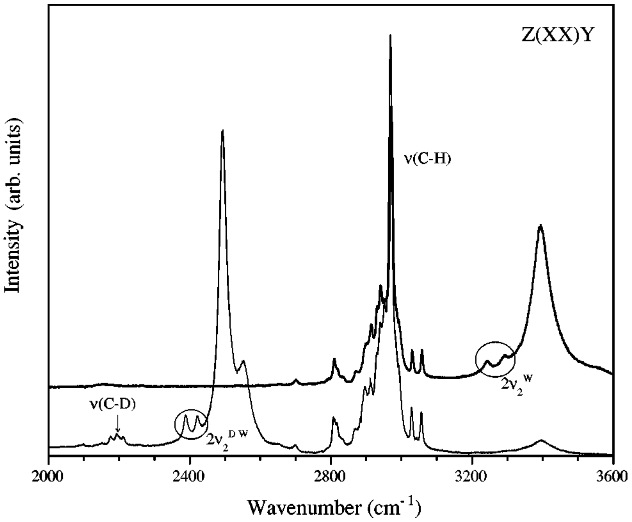

FIG. 4. Raman spectra of protonated (the upper spectrum) and partially deuterated (the lower one) BCCD in the region of C–H(D) and O–H(D) stretching vibrations.

each of three fundamental modes has only one component allowed in a particular scattering geometry. Room-temperature Raman spectra of BCCD in the region of internal vibrations of the water molecules are shown in Fig. 3. The O–H stretching modes of the water molecules in BCCD have been found to shift to lower wave numbers (compared to free water molecule values $\nu_1^\omega = 3657$ and $\nu_3^\omega = 3756\ \mathrm{cm}^{-1}$) as is usually observed in solid hydrates.[22] The intensity of the symmetrical stretching mode is usually much higher than the intensity of the asymmetrical one, so we attribute the broad band at 3400 cm^{-1} to ν_1^ω. The asymmetrical stretching mode ν_3^ω becomes detectable at lower temperatures at about 3450 cm^{-1}. The bending ν_2^ω (free molecule value 1595 cm^{-1}) was found in the range 1630–1660 cm^{-1}, where the $\nu(C=O)$ vibration of the betaine was also observed. Two weak bands centered at 3240 and 3290 cm^{-1} can be attributed to $2\nu_2^\omega$ overtones. It is clear that the internal vibrations of the water molecules are more or less affected by the structural environment in the unit cell. A downward shift of the stretching frequencies and an upward shift of the bending one are direct evidences of hydrogen bonding in the crystal. A remarkable variation of the intensity of the band at 3400 cm^{-1} in distinct scattering geometries points out to a predominant orientation of O–H bonds in the *ac* plane of the unit cell.

In the partially deuterated sample stretching bands are shifted and fulfill the usual isotopic ratio $\nu^H/\nu^D = 1.35$. As can be seen in Fig. 4, due to isotopic effects the intensities are increased while half-widths are decreased in the spectra of the deuterated sample. Consequently, the broad band at 3400 cm^{-1} in the protonated sample transforms into a well defined doublet (2494 and 2550 cm^{-1}) in the deuterated one. The separation between ν_1^ω and ν_3^ω modes is usually about 100 cm^{-1}, but this separation may be considerably reduced due to a large anharmonicity of the O–H modes in the presence of hydrogen bonding.[22]

As in the low-temperature FE (space group $Pn2_1a$, $Z = 4$) phase there are two kinds of water molecules. If eight molecules occupy two sets of fourfold general positions in the unit cell and have C_{2v} symmetry, the factor-group analysis yields

$$\Gamma(\nu_1^\omega) = \Gamma(\nu_2^\omega) = \Gamma(\nu_3^\omega) = 2A_1 + 2B_1 + 2A_2 + 2B_2. \quad (4)$$

Therefore in the FE phase all modes become both IR and Raman active and one would expect two ν_1^ω and two ν_3^ω components in each species. The number of ν_1^ω and ν_3^ω components in the modulated phases is determined by the corresponding multiplication of the unit cell with respect to the FE phase since the site symmetry of the water molecules is the same.

The temperature evolution of Raman spectra of BCCD in the region of stretching vibrations of the water molecules is shown in Figs. 5 and 6. The intense ν_1^ω band at $\sim 3400\ \mathrm{cm}^{-1}$ acquires an asymmetrical line shape just below $T_i = 164$ K and splits into several components with a decreasing temperature. Applying the fitting procedure over the entire temperature interval, we have found a temperature dependence of their frequencies which is presented in Figs. 7 and 8.

IV. DISCUSSION

A. Structural aspect of hydrogen bonding and modulation

A recent neutron-scattering study[10] revealed that the structural atomic distortions, from *N* to the low-temperature FE phase, are well described by rigid-body librations and translations of betaine molecules, while *worse* results were obtained for the same fitting with the Ca complex. These results justify the approach that considers the betaine as a rigid unit, but the same procedure is doubtful when considering the Ca complex. At phase transitions some deformations of the betaines molecules occur and they were revealed directly from XRD and neutron-scattering studies.[10,16,17] In fact, the carboxyl group behaves like a hinge which deforms as the temperature decreases.[17] However, internal deformations of the betaines are much smaller with respect to those exhibited by the water molecules. The analysis of our Raman

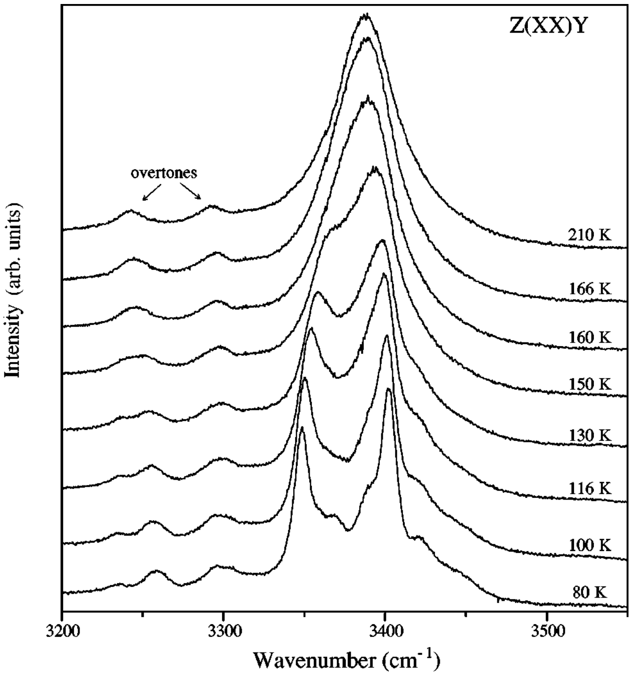

FIG. 5. Temperature evolution of Raman spectra of BCCD in the region of stretching vibrations of the water molecules in $Z(XX)Y$ geometry.

data brings to light the microscopic mechanisms involving the water molecules and that contribute to the lattice distortions at phase transitions.

Below T_i Raman spectra in the range 3350–3450 cm^{-1} were well fitted with a sum of two DHO. Both components exhibit a significant temperature dependence on further cooling and the separation between them increases. As can be seen from Figs. 5–8 the two main peaks (in all geometries) exhibit different temperature evolutions ($d\nu/dT<0$ for the higher-frequency component and $d\nu/dT>0$ for the lower-frequency one). In the 1/4 phase and in the low-temperature phases, the water molecules as well as the Cl$^-$ ions from the same Ca complex become symmetrically nonequivalent, as they occupy now fourfold general positions. Since the two main peaks correspond to symmetrical stretching vibrations of two symmetrically nonequivalent water molecules, one can conclude, from the temperature dependence of the mode

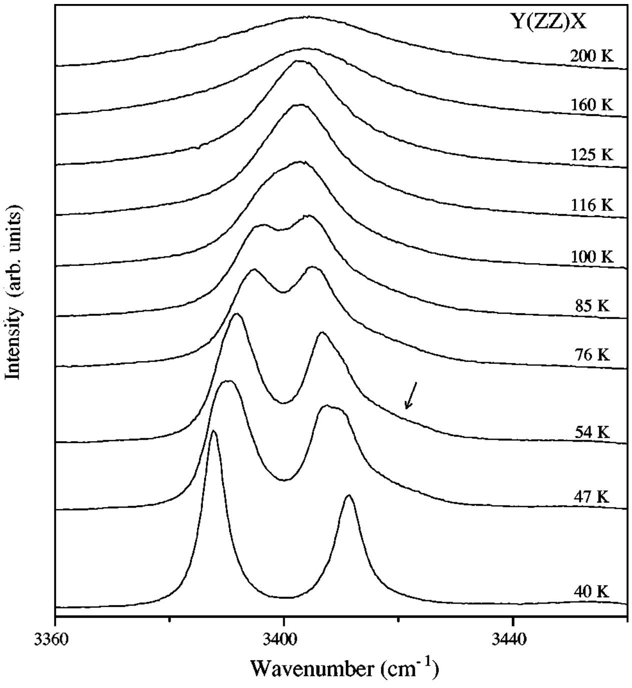

FIG. 6. Temperature evolution of Raman spectra of BCCD in the region of stretching vibrations of the water molecules in $Y(ZZ)X$ geometry. The arrow marks one of the $\mathbf{q}\neq 0$ folded modes.

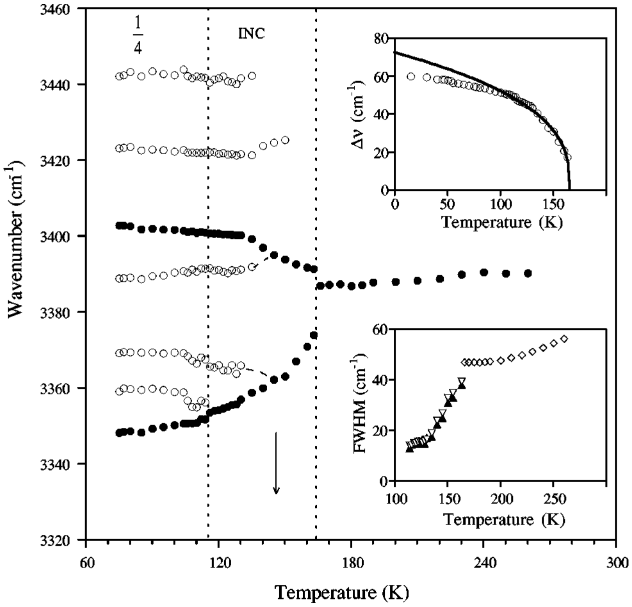

FIG. 7. Temperature dependence of the frequencies of the fitted Raman peaks shown in Fig. 5. Vertical dotted lines mark the phase transition temperatures and the arrow marks the onset of the third-order satellites. Two main peaks shown in Fig. 5 are represented in full symbols. The upper inset shows temperature dependence of the splitting between the two main peaks, and the lower one shows temperature dependence of their full width at half maximum (FWHM).

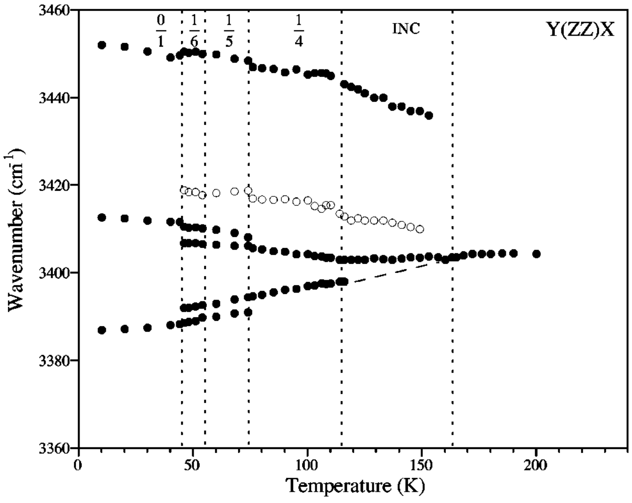

FIG. 8. Temperature dependencies of the frequencies of the fitted Raman peaks shown in Fig. 6. Vertical dashed lines mark the phase transition temperatures. Open symbols are used for the folded mode which is indicated by an arrow in Fig. 6.

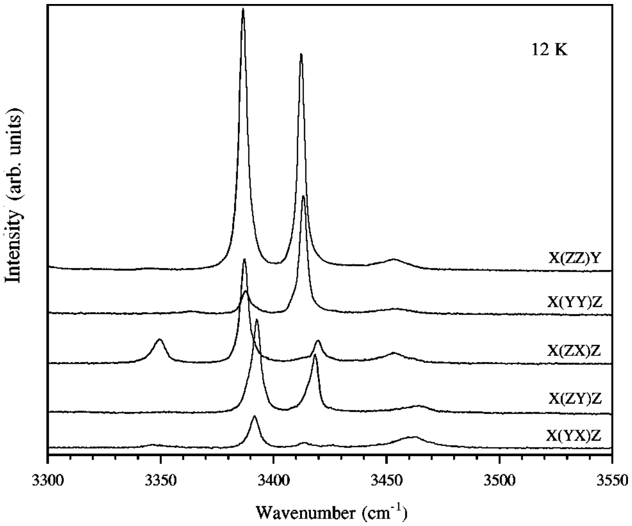

FIG. 9. Raman spectra of BCCD at 12 K in the region of the stretching O–H vibrations for different scattering geometries.

frequencies, that one of them forms a stronger H bond, while the other one forms a weaker bond, with two symmetrically nonequivalent Cl^- ions in the neighboring layer. In fact these effects start to appear in the INC phase and are obviously related to the distortion of the Ca complex which cannot be therefore considered as a rigid unit. Deformations of the Ca complex entailed by rearrangement in the H bonding were found also significant from XRD measurements (see Table 4 in Ref. 16). The observed hardening of the water librations in the INC phase is also a direct evidence that at least one of the O3–H···Cl bonds between neighboring Ca complexes is strengthened, and prevent their easy rotations as rigid units at lower temperatures.

As expected,[24] there is no detectable difference between Raman spectra in the region of stretching vibrations of the water molecules examined in six scattering geometries, just below and above the transition to the 1/4 phase, due to a continuous evolution of the modulation wave vector $\mathbf{q} = \delta(T)\mathbf{c}^*$. In contrast, at the phase transitions between the principal commensurate phases, we observed abrupt transformations of Raman spectra in the region of stretching water vibrations. Changes in Raman selection rules related to point-group symmetry as well as additional folding at the transitions $(1/4)\rightarrow(1/5)$; $(1/5)\rightarrow(1/6)$ cause significant rearrangement in Raman spectra as can be seen in Figs. 6 and 8. Most of the modes expected in modulated phases due to Brillouin-zone folding cannot be resolved, since splitting is smaller than the linewidth. At the transition to the uniform $(\delta=0)$ FE phase, at 46 K, all folded modes disappear and the spectra become simpler. Note that at each transition between the principal phases, the separation between two main peaks increases (see Figs. 6 and 8). This fact is an indication of a sequential distortion of water molecules, and is consistent with the results of a structural analysis.[10,16,17] In fact, the structures of the different commensurate phases appearing below 75 K were found similar to that of the first INC phase, except for the change of wave-vector values and greater amplitude of the distortion. One more structural feature deserves to be discussed in this context. In Fig. 9, Raman spectra at 12 K in the frequency range 3300–3550 cm^{-1} reflect the complicated set of the water molecules in the unit cell. In the FE phase there are four well separated peaks in each scattering geometry. Their intensities and wave numbers strongly deviate from the typical ν_1^ω and ν_3^ω values. Apparently, in the FE phase the water molecules are involved in hydrogen bonds of different lengths with the nearest Cl^- ions. Due to this strong asymmetry, the O-H stretching vibrations are localized. The discrimination between symmetrical and asymmetrical stretching vibrations is no longer valid and assignment to ν_1^ω and ν_3^ω modes of the free molecule actually has no meaning. In this case for the two kinds of symmetrically nonequivalent water molecules in the FE phase of BCCD, one can expect four well separated bands in the region of stretching vibrations as can be seen in Fig. 9.

B. Harmonic and square-wave modulation in BCCD

It is clear from the results displayed in Fig. 7 that new components corresponding to the symmetrical stretching vibration appear just below T_i on decreasing the temperature; i.e., the ν_1^ω mode bears strong witness of the modulated structure of BCCD. The Raman-scattering study of thiourea[25] has also clearly shown that both symmetrical and asymmetrical stretching modes of NH_2 are very sensitive to the incommensurate modulation in this compound. It is possible that the origin of this behavior is very similar to the mechanism proposed by Blinc *et al.*[26] to explain the results obtained in the Rb_2ZnCl_4 by means of NMR. The internal stretching modes of the water molecules in BCCD have very weak intermolecular mechanical coupling since the frequency difference between the modes of different types of symmetry presented in Fig. 3 is very small (less than 20 cm^{-1}). As was shown above, the O–H stretching modes are very sensitive to the local environment, which is disturbed by the incommensurate distortion. In the INC phase the translational periodicity is lost and each water molecule has different environment. In the sinusoidal regime (just below T_i) Raman spectra reflect the density of sates. The corresponding frequency distribution function can be obtained in the local approximation for the case of a one-dimensional INC modulation along the z axis.[26,27] In this approximation the given vibrational frequency ν_i depends only on the incommensurate displacement $\nu_i = \nu[U_i(z_i)]$ and can be expanded in powers of the harmonic displacements:

$$\nu_i = \nu_0 + \nu_1 \cos[\varphi(z) + \varphi_0] + \frac{1}{2}\nu_2^2 \cos^2[\varphi(z) + \varphi_0] + \dots . \tag{5}$$

Here $\nu_1 \propto \eta \propto (T_i - T)^\beta$, $\varphi(z)$ represents the phase and η the amplitude of the frozen-in modulation wave of the INC phase. φ_0 is an initial phase. In the linear case $(\nu_1 \neq 0,\ \nu_2 = 0)$, the frequency distribution function is given by[26,27]

$$g(\nu) = \mathrm{const}\left[1 - \left(\frac{\nu - \nu_0}{\nu_1}\right)^2\right]^{-1/2} \tag{6}$$

with two edge singularities at $\nu_\pm = \nu_0 \pm \nu_1$. The splitting $\Delta\nu$ between the two edge singularities increases below T_i with the critical exponet β: $\Delta\nu = 2\nu_1 \propto \eta \propto (T_i - T)^\beta$.

The splitting between the two edges, obtained in *xx* geometry, as a function of the temperature can be seen in the upper inset of Fig. 7 and obeys a power law: $\Delta\nu=\alpha(T_i-T)^\beta$, where $\alpha=12\pm1$ cm^{-1} and $\beta=0.35\pm0.02$ in the whole interval of the INC phase down to 115 K. This value of the critical exponent is almost equal to that one predicted by the three-dimensional *xy* model[28,29] and coincides with other experimental determinations of the critical exponent of the order parameter in the INC phase of BCCD, obtained from dielectric[13] and NMR (Ref. 30) measurements. It is important to outline that the frequency shifts of the ^{35}Cl edge singularities in the NMR spectra are quite symmetric (see Fig. 36 in Ref. 11) over the whole temperature interval below T_i, implying the validity of the linear approximation for BCCD. In our case, the two-edge line shape related to the O–H$\cdots$Cl stretching vibrations is not symmetrical and the intensities of the two peaks are different (Fig. 5). When one more term is included ($\nu_1\neq0$, $\nu_2\neq0$) in the expansion (5), the density of states exhibits an asymmetrical splitting with different intensities for the edge peaks.[26] Furthermore, in a nonlocal approximation, additional lines between the two edge singularities can appear. We assume that the asymmetrical line shape of the Raman response may be originated not only due to the quadratic term, but also due to the asymmetry of the O–H$\cdots$Cl hydrogen bonds. A final decision is yet to be given and further theoretical considerations are required.

On approaching the lock-in transition from above the two edges exhibit substantial narrowing (see the lower inset in Fig. 7), and additional rather weak components at ~3365 and ~3390 cm^{-1} between the two main edges start to appear below 140 K. Apparently they originate from the Brillouin-zone interior and their intensity is proportional to higher powers of the order parameter. It is known that the *N*-INC transition in BCCD is accompanied by the appearance of first-order satellite reflections and their intensity I_1 increases remarkably below $T_i{}^3$. The *n*th order satellites start to appear below 146.5 K,[17] and their intensity I_n increases smoothly when decreasing the temperature. In a sinusoidal regime, the intensity of the second-order satellites would be always larger than the third order ones and I_n/I_1^n ratio would be temperature independent. A nonsinusoidal charater of the modulation in BCCD is established below 146.5 K where I_3/I_1^3 is higher than I_2/I_1^2 and, moreover, the former term is temperature dependent.[17] When the static distortion becomes not purely sinusoidal, the phonons at $\mathbf{q}=\pm n\mathbf{q}_0$, $n=2,3,\ldots$ should be expected in Raman spectra.[12] As shown in Fig. 7 additional new lines in our Raman spectra become detectable in the same temperature interval where transformations of the shape and of the amplitude of the modulation occur. Note that separation between the two main peaks in *zz* spectra (see Figs. 6 and 8) is much smaller than in the *xx* ones. This fact reflects the anisotropy of distortions which are small along the direction of modulation (*z* axis) and large in other directions.

Thus the peculiar temperature behavior of the symmetrical stretching mode of the water molecules provides a clear evidence for the existence of two regimes in the modulation. At 164 K a two-edge behavior is observed and below 146 K an additional splitting reveals a different type of distortion that may be related to the anomalous behavior of the higher-order satellites intensities in neutron scattering.

A very weak band starts to appear in *xx* geometry below the lock-in transition to the 1/4 phase, which means that an additional distortion occurs in the temperature range close to the T_S anomaly observed in BCCD.[11] The localization of the onset of this band has a limited accuracy and can be simply due to an artifact of the data evaluation process. However, it is rather tempting, although speculative, to associate this behavior to the T_S anomaly which marks a true structural phase transition from a state with an arbitrary phase to a state with a fixed phase in the modulation.[31]

V. CONCLUSIONS

The study of Raman spectra presented in this work represents complementary information to the results previously obtained with this technique in BCCD. The agreement between experimental spectra and factor-group analysis in the region of external vibrations is very good, providing that only the betaine may be considered as a rigid unit. In the previous published results the betaine and the Ca complex have both been considered as rigid units which is a poor approximation and justifies the disagreement between theoretical models and some of the experimental results at low temperatures.[10]

A very effective hardening of libration water modes and additional splittings on further cooling clearly show that the Ca complex behaves as a nonrigid unit below the *N*-INC phase transition. Stretching vibrations of the water molecules also exhibit a significant temperature evolution. Their behavior shows that water molecules are very sensitive to the distortions of the unit cell since they form H bonds between layers. By accompanying the distortions of the unit cell, the water molecules form a stronger H bond while the other H bond becomes weaker. Water molecules in BCCD have very weak intermolecular mechanical coupling, disclosing the onset of a sinusoidal and a nonsinusoidal regime in the INC phase. Consequently, water molecules cannot be treated just as mere probes of the phase transition sequence in BCCD but have to be considered as active partners in the whole process that determines the wealth of structural phase transitions in this compound.

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