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Abstract. Polarized Raman spectra of Cs_2CdBr_4 single crystals were measured in the frequency range 0–350 cm^{-1} at 100–290 K. The spectra are analysed within the framework of the Landau theory of structural phase transitions; the analysis indicates that the transition to the triclinic phase with $P\bar{1}$ symmetry is accompanied by unit-cell volume multiplication.

1. Introduction

At room temperature and atmospheric pressure, Cs_2CdBr_4 (CCB) crystals possess a β-K_2SO_4-type structure (Plesko *et al* 1980). As in many other crystals of this structural type, a sequence of phase transitions (PTs) is observed in CCB on cooling (Maeda *et al* 1983) (see also table 1 where, for comparison, data on PTs in Cs_2HgBr_4 (CHB) are also given). Unlike zinc-containing halides, in which commensurately modulated low-temperature phases are ferroelectric as a rule, the low-temperature phases of CCB and CHB are non-polar ferroelastic (centrosymmetric).

Table 1. Phases, space groups, number (Z) of formula units in the unit cell, wavevectors k and transition temperatues for CCB and CHB crystals.

Phase	Space group	Z	k	T (K) CCB[a]	CCB[b]	CHB[b]
I	Pnma	4	0			
	Incommensurate[c]			247	252	245
II	P$_{1ss}^{Pnma}$		$0.15a^*$	230	237	232
III	$P2_1/n11$	4	0	209		
IV	$P2_1/n11$ or $P\bar{1}$	?		163	158	167
V	$P\bar{1}$	4	0	130		85
IV	$P\bar{1}$	8	$\frac{1}{2}(b^* + c^*)$			

[a] Data from Altermatt *et al* (1984).
[b] Data from Zaretskii and Depmeier (1991).
[c] Data from Speziali and Chapuis (1989).

Dielectric measurements of CCB have been reported by Maeda *et al* (1983), who also demonstrated the switching of ferroelastic domains under the action of external stress ^{81}Br

NQR experiments were done by Plesko *et al* (1980). Nakayama *et al* (1987) used their own ^{81}Br NQR data to carry out a model calculation of electric field gradients in the incommensurate phases of CCB and CHB. The elastic properties of CCB were measured at 10 MHz by Vlokh *et al* (1990) and by Rodriguez *et al* (1991), who also performed Raman spectra measurements. The birefringence and effective piezo-optical coefficients of CCB were measured by Vlokh *et al* (1988).

In this paper we report a Raman spectra study of CCB single crystals at 100–290 K, thus extending the work of Rodriguez *et al* (1991). The results are discussed within the framework of the Landau theory of structural phase transitions.

2. Experimental methods

The CCB single crystals were grown from the melt of CsBr and CdBr$_2$ in a molar ratio of 2:1. CsBr (Merck, suprapur) and CdBr$_2$. 4H$_2$O (Merck; purity, 99%) were dried at 220 °C in air, mixed carefully and then dried in a quartz ampoule at 260 °C under vacuum. The ampoule was then sealed and used for Bridgman growth at a rate of 0.5 mm h^{-1}. The resulting crystals (17 mm in diameter and 60–70 mm in length) were transparent and colourless, with some cracks. The samples were prepared from optically homogeneous parts by cutting with a diamond saw, grinding and polishing with diamond pastes.

Raman spectra were excited with polarized radiation of an ILA-120 argon ion laser ($\lambda_0 = 488$ nm; approximate power, 200 mW) and recorded with a DFS-24 spectrometer in the 90° scattering configuration. The spectral width of the slits was 2 cm^{-1}. The accuracy of line frequency determination was ± 2 cm^{-1} for sharp bands and ± 5 cm^{-1} for diffuse bands and line shoulders. The temperature measurements were carried out in an optical chamber, stabilized to within ± 0.2 K (cooled with liquid-nitrogen vapours). A Cu–constantan thermocouple yielded an absolute accuracy of ± 1 K.

3. Experimental results and analysis of the spectra

The polarized Raman spectra of CCB single crystals are shown in figure 1. The frequencies of the bands and shoulders are listed in table 2. It is seen from figure 1 that there are three well distinguished spectral ranges: 0–50 cm^{-1}, 60–90 cm^{-1} and 170–210 cm^{-1}. This type of spectrum could be expected on the basis of x-ray data analysis, which indicates that [CdBr$_4$]$^{2-}$ ions are close to tetrahedral rigid groups in the CCB lattice (Altermatt *et al* 1984). In this case the range 0–50 cm^{-1} corresponds to the lattice optical modes (translations of Cs$^+$ and [CdBr$_4$]$^{2-}$ and librations of [CdBr$_4$]$^{2-}$). The second and the third ranges correspond to the Cd ligand optical modes. The lowest-frequency lines correspond to the deformation modes of [CdBr$_4$]$^{2-}$ and high-frequency lines correspond to the stretching vibrations.

Inspection of figure 1 shows that this structure of spectra remains the same within the temperature range studied.

3.1. The phonon mode symmetry classification

Above 252 K, the high-temperature modification of CCB has an orthorhombic symmetry with *Pnma* space group ($a = 1.0228$ nm, $b = 0.7931$ nm and $c = 1.3966$ nm at 295 K (Altermatt *et al* 1984)) and four formula units in the unit cell. As in all the crystals of β-K$_2$SO$_4$ type and this symmetry, the a axis is pseudo-hexagonal ($c/b \simeq \sqrt{3}$). There are two kinds of caesium ion (Cs(I) and Cs(II)) which are positioned on the m-symmetry
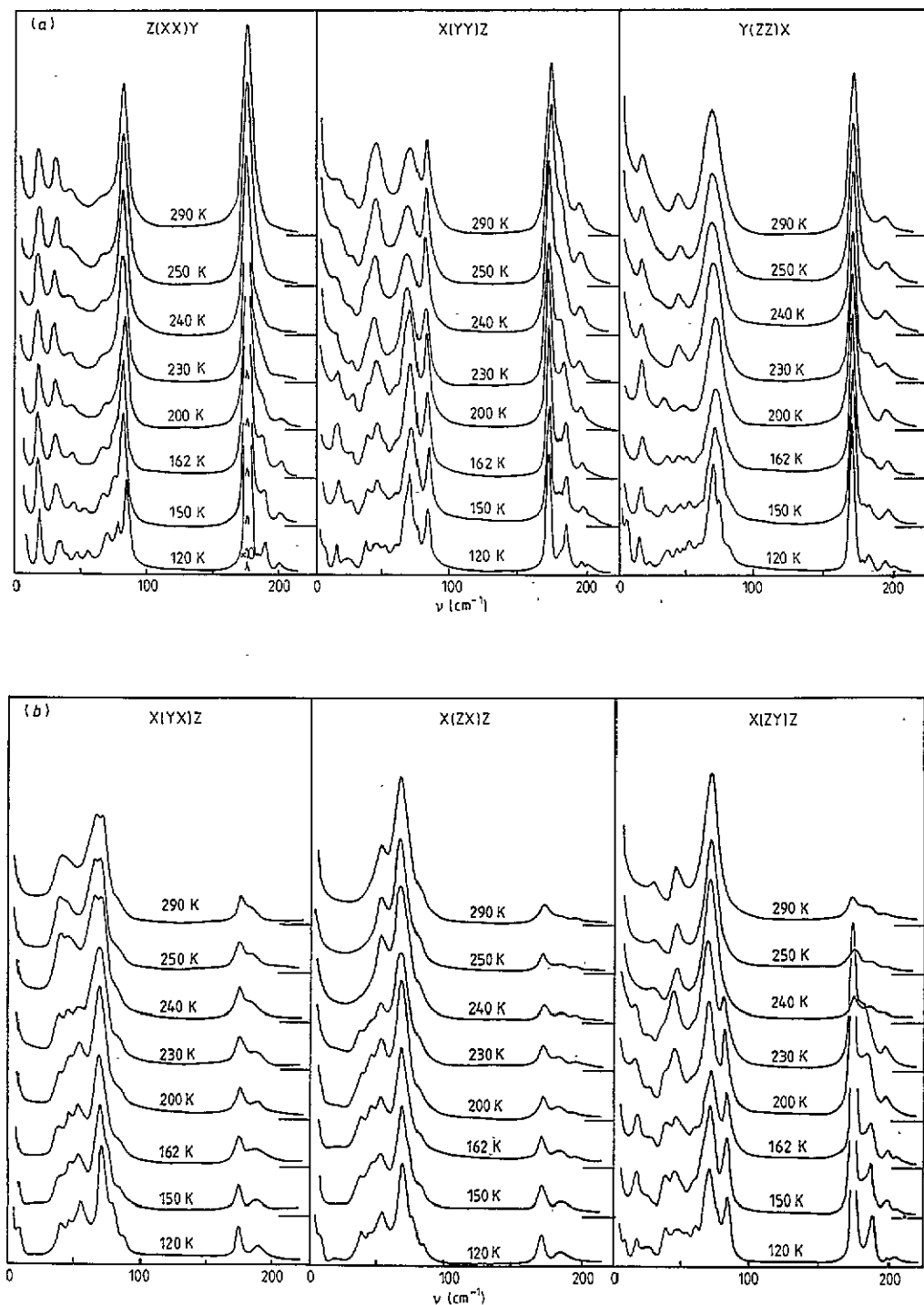
Figure 1. Raman spectra of CCB single crystals at 120–290 K: (*a*) $Z(XX)Y$, $X(YY)Z$ and $Y(ZZ)X$ orientations; (*b*) $X(YX)Z$, $X(ZX)Z$ and $X(ZY)Z$ orientations.

Table 2. Frequencies of lines in the Raman spectra of CCB single crystals at various temperatures and their assignments.

T (K)	Z(XX)Y				Z(YY)X				Y(ZZ)X				X(ZY)Z				X(ZX)Z				X(YX)Z				Assignments
	290	230	162	120	290	230	162	120	290	230	162	120	290	230	162	120	290	230	162	120	290	230	162	120	Frequency (cm^{-1})
								8				8				8				8				8	
	18	18	18	18	18	17	18	18	18	18	18	17		17	17	17				18				18	
					28	28	28	26	28	28		24	28	28	27	27									Lattice modes
		30	30	30																					
				34								34													
				39		41	40	40			37	38		37	39	40		39	39	40	39	38	38	39	
	46	43	45	46	46				45	45	46		46	44	46	45		47	47	45	43	46	47	46	
						48	48	49		48	51	50				49									
				55			55	55				54				54	54	54	55	55		54	53	55	
						59	62	62	58	59	62	62		58	60	62									
																					66				
	71	69	69	70	71	73	73	73	71	72	73	73	71	71	72	72	68	69	70	72	71	69	71	72	ν2, ν4
			77	79				79				77								78				78	
	83	84	84	85	84	84	85	86		83	85	85		83	84	85	81	81	82	85	81	82	83	85	
	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	176	176	176	176	176	176	ν1
	184	184	184	185	184	184	184	186		183	183	183	183	184	185	185	186	186			183	183	184	184	
			188	191		190	190	190		187	188	188		189	189	189			189	191			189	191	ν3
	199	201	201	201	200	201	202	202	198	200	202	202	198	198	202	202	198	198							
				206				207				207		207	207	207									

plane (c position). The Cd ions and two Br ions from $[CdBr_4]^{2-}$ occupy the same position, whereas the two remaining Br ions are in the eightfold (general) d position. For this case, the mechanical representation has the following form:

$$\Gamma_{mech}(I) = (7A_g + 5A_u + 5B_{1g} + 7B_{1u} + 7B_{2g} + 5B_{2u} + 5B_{3g} + 7B_{3u})_{ext}$$
$$+ (6A_g + 3A_u + 3B_{1g} + 6B_{1u} + 6B_{2g} + 3B_{2u} + 3B_{3g} + 6B_{3u})_{int}.$$

The genesis of the internal modes from the factor group analysis for the modes of a free tetrahedral ion is given in a correlation diagram in table 3. The comparison of the observed spectra with the factor group predictions (as seen from tables 2 and 3 and figure 1) shows quite satisfactory agreement.

Table 3. Correlation diagram for internal modes of CdBr₄ ions in phase I (space group, *Pnma*).

modes, free ion symmetry T_d	local symmetry C_s (σ^{xz})	factor-group symmetry D_{2h}	activity	ν_1	ν_2	ν'_3	ν'_3	ν_4	ν'_4
$4\nu_1$ A	A'	A_g	aa,bb,cc / xx,yy,zz	ν_1 (175)	ν_2 (68)	ν'_3 (185)	ν'_3 (198)	ν_4 (71)	ν'_4 (83)
		B_{1g}	ab / xy	–	ν_2 (65)	ν_3 (186)	–	ν_4 (71)	–
		B_{2g}	ac / xz	ν_1 (175)	ν_2 (53o+68)	ν'_3 (187)	ν'_3 (?)	ν_4 (68)	ν'_4 (?)
$4\nu_2$ E	A''	B_{3g}	bc / yz	–	ν_2 (65)	ν_3 (186)	–	ν_4 (70)	–
		A_u	– / –	–	ν_2 (?)	ν_3 (?)	–	ν_4 (?)	–
		B_{1u}	c / z	ν_1 (?)	ν_2 (?)	ν'_3 (?)	ν'_3 (?)	ν'_4 (?)	ν'_4 (?)
$4\nu_3'$		B_{2u}	b / y	–	ν_2 (?)	ν_3 (?)	–	ν_4 (?)	–
$4\nu_4$ F_2		B_{3u}	a / x	ν_1 (?)	ν_2 (?)	ν'_3 (?)	ν'_3 (?)	ν_4 (?)	ν'_4 (?)

Difficulties arise when identifying the external modes. The number of spectral lines observed is much lower than the number of lines predicted. Let us try to understand this discrepancy by considering the genesis of phase I spectra from the spectra of a latent phase. (Although the term 'latent phase' does not differ significantly from the well known terms 'prototypic phase' or 'hypothetical phase', we feel that it is more suitable for describing our case.)

The hypothetical α-K_2SO_4-type structure has a hexagonal lattice of $P6_3/mmc$ symmetry; when this is assumed for CCB, the ions will occupy the following sites:

$Cs^+(I)$, 2d, $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4}$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$, D_{3h}; $Cs^+(II)$, 2a, $(0, 0, 0$ and $0, 0, \frac{1}{2})$, D_{3d};

$CdBr_4^{2-}$, 2c, $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$ and $\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$, D_{3h}.

The unit cell contains two formula units. The necessary condition for the existence of this structure is orientational mobility of the anion sublattice (at every given moment, the $[CdBr_4]^{2-}$ ions occupy the f position of C_{3v} symmetry). The formation of the real phase I of $Pnma$ symmetry from the latent phase of $P6_3/mmc$ symmetry takes place at a PT with doubling of the unit-cell volume; this PT is induced by an order parameter transforming according to M_4 from the M point of the latent-phase Brillouin zone ($k_{12} = \frac{1}{2}b_1$) (Shiozaki *et al* 1977). (We write the wavevectors and representations according to Kovalev (1965); the zone centre representations of the phases in question are labelled in the notation of Mulliken (1933).) Thus the spectra of the phase I will be formed from the modes of the Γ and M points of the latent $P6_3/mmc$ phase. The transformation mechanism of the mechanical representation for the external modes of the $P6_3/mmc$ phase into the corresponding representation of the $Pnma$ phase is given in the correlation diagram in table 4. The external modes are subdivided into translational (t) and librational (l) modes. In square brackets, following the type of vibration, the assignment of the mode to a sublattice is given. Let us remark that, when assigning modes, the following two cases should be distinguished between:

  (i) when only one mode belongs to the symmetry species in question and
  (ii) when more than one mode belongs to the same symmetry species.

In case (ii), the corresponding coordinates are mixed together and we have in fact no pure vibrations of one sublattice but rather vibrations of one sublattice against another (or others). This remark applies to all such assignments in this paper, formally expressed in terms of pure translations or vibrations.

It is seen from table 4 that only three modes, namely two translations of the E_{2g}^h type (t(CdBr$_4$) and t(Cs(I)) and a libration of the E_{1g}^h type (l(CdBr$_4$)), are active in the latent (hexagonal) phase. In phase I, the translations split into a pair of doublets of $A_g^o + B_{3g}^o$ symmetry, and the libration yields two lines of $B_{1g}^o + B_{2g}^o$ symmetry.
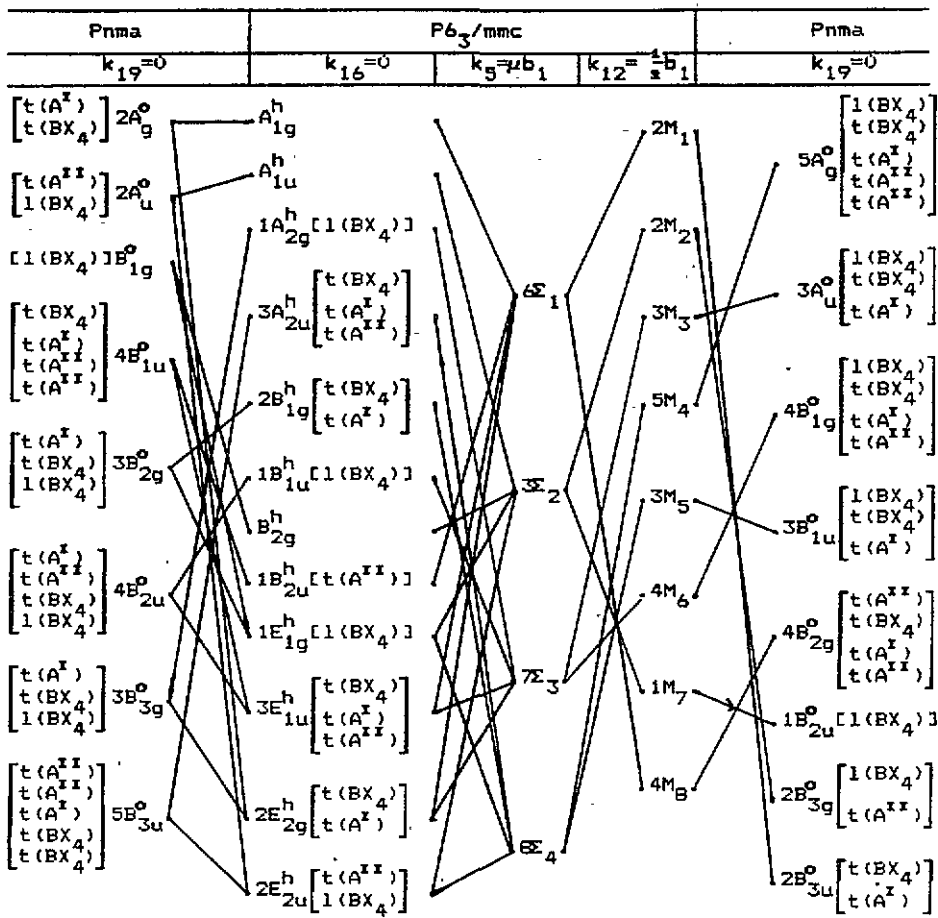
Since the Raman tensor component α_{XX} of the E_{2g}^h mode equals zero in the latent phase, the intensity of the corresponding translational modes in the XX spectrum of phase I must be low. (Let us recall that the x axis is pseudo-hexagonal in phase I of $Pnma$ symmetry and we do not change the orientation for the latent (hexagonal) phase.) For the YY, ZZ and YZ spectra, the lines of translational modes under consideration must have approximately equal intensities. This is true provided that structure deformations arising at the $P6_3/mmc \rightarrow Pnma$ PT are not large. X-ray data (Altermatt *et al* 1984, Zaretskii and Depmeier 1991) support this assumption.

On the basis of what has already been said and from the character of the spectra (see figure 1), one can conclude that the lines at 45 and 30 cm^{-1} (or 17 cm^{-1}) correspond to these translational modes. Since the mass of $[CdBr_4]^{2-}$ exceeds considerably the mass of Cs$^+$(I), the vibrations of the latter should lie at higher frequencies. Additional information on the numerical values of the frequencies of translational modes can be inferred from a plausible assumption that the low-frequency translation corresponds to the rigid-layer mode (let us recall that the structure of CCB can be taken to be quasi-layered; there are two layer packets (perpendicular to the x axis) in the unit cell). The frequency values corresponding to the modes of a rigid layer can be estimated using elastic moduli data. For CCB, the elastic properties were determined by Vlokh *et al* (1990) and by Rodriguez *et al* (1991); for CHB crystals, the elastic properties are nearly the same (Plesko *et al* 1981).

The results of the estimates that we made are shown in figure 2. We have described the methods of calculating frequencies of the rigid-layer modes elsewhere (Torgashev *et al* 1992). It follows from figure 2 that the lowest-frequency translation modes must lie in the

Table 4. Mechanical representations of external modes for crystals having a K$_2$SO$_4$-type structure in the phases $P6_3/mmc$ and $Pnma$: t, translational modes; l, librational modes.

$$\Gamma^h_{mech} = 2(A^h_{2u} + B^h_{1g} + E^h_{1u} + E^h_{2g})^t_{(c),(d)} + (A^h_{2u} + B^h_{2u} + E^h_{1u} + E^h_{2u})^t_{(a)}$$

$$+ (A^h_{2g} + B^h_{1u} + E^h_{1g} + E^h_{2u})^l_{(c)}$$

$$= 3A^{IR}_{2u} + A_{2g} + 2B_{1g} + B_{1u} + B_{2u} + E^R_{1g} + 3E^{IR}_{1u} + 2E^R_{2g} + 2E_{2u}$$

$$\Gamma^o_{mech} = 7A_g + 5A_u + 5B_{1g} + 7B_{1u} + 7B_{2g} + 5B_{2u} - 5B_{3g} + 7B_{3u}.$$

12–40 cm^{-1} range of the spectra. The frequency values of the translational modes of Cs sublattices can somewhat increase the upper limit of this range. Also, intuitively, it is clear that the large inertia moment of CdBr$_4$ tetrahedra can cause an extension of this range to lower frequencies by affecting the frequency values of the libration modes.

These estimates show that the external modes lie in the frequency range from 10 to 50 cm^{-1}. In other words, we need to cram 48 dispersion curves into a range about 40 cm^{-1} wide. This naturally dictates the continuous character of the external-mode spectra, as found in our experiments. The intense peaks of the low-frequency CCB spectrum appear to be conneced with three Raman-active modes of the latent phase. It should be noted that
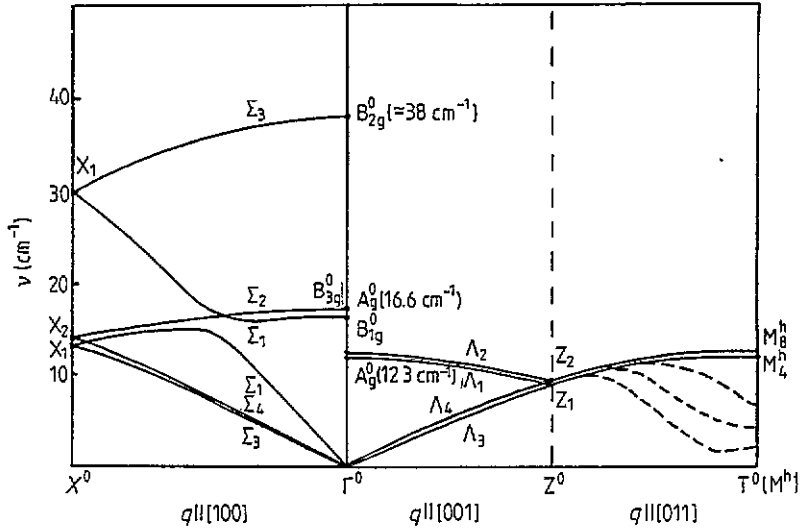
Figure 2. Dispersion branches of low-frequency translational modes of CCB for phase I (*Pnma*); elastic data for CHB (Plesko *et al* 1981) were used in the calculations.

both the enrichment of Raman spectra of phase I on account of the cell multiplication at the $P6_3/mmc \rightarrow Pnma$ PT and the removal of the prohibition of the Raman activity of the part of the lines from the latent phase zone centre lead only to 'spreading' of the spectra.

3.2. The spectral temperature evolution

Within experimental error, there is no difference between spectra of phase I and (incommensurate) phase II; not even a trace of amplitude or phase modes is seen in phase II (cf figures 1 and 3). The strong relaxational contribution to the low-frequency scattering remains in fact unchanged. This indicates that a great part of the structural disorder of phase I remains conserved in the incommensurate phase II.

The PT I→III (if it were realized directly) at $k = o$ is induced by an order parameter, which transforms according to the B_{3g}^0 representation of phase I. Since the u_{yz} component of the deformation tensor transforms according to the same representation, the transition I→III may be considered as a proper (or pseudo-proper) ferroelastic transition. A softening of the elastic constant c_{44} is to be expected at this transition. Correlations between the symmetry types of phases I and III are listed in table 5; the spectra of phase III at 230 K are shown in figure 1, and the line frequencies are listed in table 2. In accordance with the symmetry lowering to monoclinic and the orientation of the unit cell in this phase in relation to that in I (the dyad of III is parallel to x of I), just the YZ spectra transform essentially, since the totally symmetric modes are allowed by the selection rules there. Thus the intensities of $\nu_1(\alpha_{yz})$ and $\nu_4(\alpha_{yz})$ modes (lines at 175 cm^{-1} and 82 cm^{-1}, respectively), rise sharply. Also, further weaker lines emerge; however, it is necessary to note that no essential shifts in line frequencies are observed. This indicates that only slight distortions accompany this transition, in accordance with x-ray data at 230 K which show only rotations of [CdBr$_4$]$^{2-}$ by 7–8° from the average positions in phase I (Altermatt *et al* 1984).

Down to a temperature of 201 K, no significant change in the spectral form is seen; below this temperature, however, a further depolarization of spectra takes place (see figures 1 and 3, e.g. the activation of 33 and 35 cm^{-1} lines in the ZZ orientation). This may be ascribed
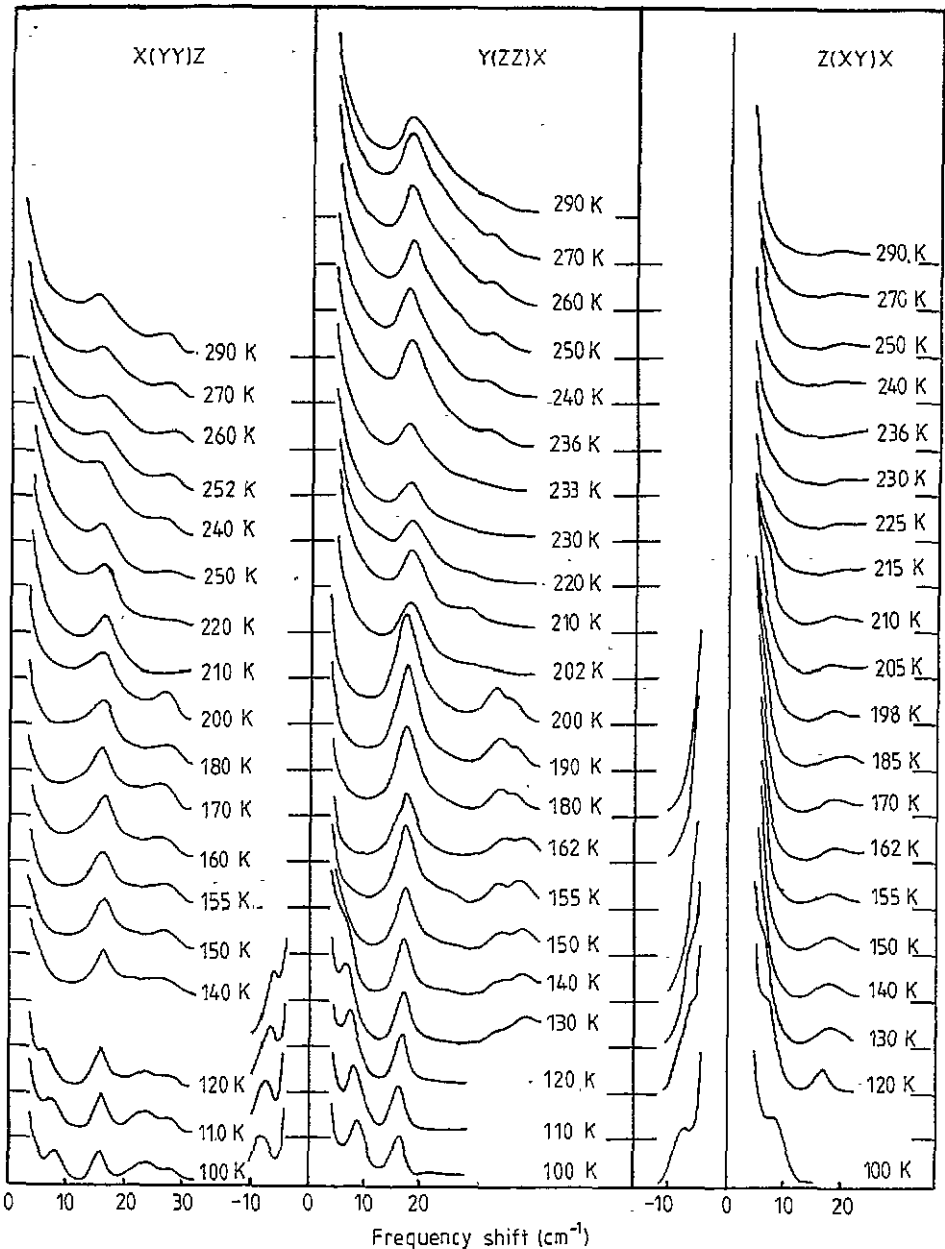
Figure 3. Low-frequency part of the Raman spectra of CCB single crystals at 100–290 K.

to a further symmetry lowering to triclinic. An x-ray study (Zaretskii and Depmeier 1991) revealed a second-order PT to phase IV, for which either the $P\bar{1}$ or the $P2_1/n$ space group was proposed. The existence of the PT at 201 K is also supported by an essential fall in the Rayleigh background intensity, undoubtedly the consequence of further lattice ordering.

Further changes in the spectra have been observed below about 160 K; Altermatt *et al* (1984) assume that an equitranslational PT to the triclinic phase of $P\bar{1}$ symmetry takes place

Table 5. Compatibility relations between irreducibile representations of phases I, III and IV of the CCB crystal.

Pnma	$P\frac{2_1}{n}11$	$P\bar{1}11$
A_g	A_g	A_g
A_u	A_u	
B_{1g}		
B_{1u}	B_g	
B_{2g}		A_u
B_{2u}	B_u	
B_{3g}		
B_{3u}		

there. The distinct appearance of a soft mode in the low-frequency spectra (see figure 3, Rayleigh line slope in ZZ orientation, at 140 K) contradicts, however, their interpretation. Since x-ray data (see table 1) indicate that the inversion centre remains conserved at this PT, the observed soft mode should be activated owing to the PT, with a multiplication of the unit-cell volume. Total depolarization of the soft mode (in other words, its manifestation in all the orientations studied) confirms the triclinic symmetry of this phase as well. We thus suggest that the PT at about 160 K leads to the triclinic phase with unit-cell volume multiplication.

Our data do not allow us to draw unambiguous conclusions concerning the PT at 130 K described by Zaretskii and Depmeier (1991). In the temperature range 100–140 K, the spectra exhibit minute changes only; we suppose that these changes may be accounted for entirely by the temperature factor, and an increase in the soft-mode frequency.

4. Discussion and conclusions

Contrary to the work of Altermatt *et al* (1984), our results show that the lowest temperature phase of CCB possesses a unit cell of $P\bar{1}$ symmetry, with unit-cell volume multiplication, and that the soft mode is caused by the phonon softening on the boundary of the Brillouin zone of phase I.

The latent phase concept allows one to describe the situation in CCB as follows. The order parameter Q describing the $P6_3/mmc \rightarrow Pnma$ PT transforms unambiguously according to the threefold degenerate representation M_4 from the M point ($k_{12} = \frac{1}{2}b_1$) of the hexagonal Brillouin zone (Shiozaki *et al* 1977); in phase I, only one component of this threefold-degenerate mode (say, $q_1 \neq 0$, $q_2 = 0$, $q_3 = 0$) condenses. The incommensurate phase II appears with $q_x \simeq 0.15a_x^*$ and locks in to phase III ($P2_1/n11$, with $q_x = 0$) at about 230 K. The soft branch symmetry is thus Σ_2^0 (for $q_x \neq 0$) and B_{3g}^0 for the Γ^0 point (several possibilities for branches of such symmetry exist).

Inspection of table 4 shows that there are the following translational (t) and librational (l) modes of the M_4 symmetry in the latent phase: $t(BX_4)$, $l(BX_4)$, $t(A^I)$ and $2t(A^{II})$. For the first mode, our estimate yields its frequency to be about 12 cm^{-1} (cf figure 2). Unfortunately,

there is no trivial way to estimate the frequency limits for the librational branches

$$E_{2u}^h - \begin{bmatrix} \Sigma_2^h - M_2^h \rightarrow B_{3g}^o \\ \Sigma_4^h - M_4^h \rightarrow A_g^o \end{bmatrix}.$$

From the symmetry point of view, the E_{2u}^h mode softening must lead to softening of the $E_{2u}^h - \Sigma_4^h - M_4^h$ branch. This branch, in turn, when meeting on its way the $A_6^h - \Sigma_4^h - M_4^h$ (acoustic) branch, will give it its softness so that the M_4 phonon of $A_{2u}^h - \Sigma_4^h - M_4^h$ can become the soft mode of the $P6_3mmc \rightarrow Pnma$ PT. The M_2^h phonon from $E_{2u}^h - \Sigma_2^h - M_2^h$ will fold into the B_{3g}^o phonon of the Brillouin zone centre; its further softening must then lead to the ferroelastic $Pnma \rightarrow P2_1/n11$ PT. The $B_{3g}^o - \Sigma_2^o - X_2^o$ branch can interact (i.e. anticross) with branches of analogous symmetry, originating from $E_{2w}^h - \Delta_6^h - A_3^h$ or from one of the $M_i^h - U_i^h - L_i^h$ branches which, because the Brillouin zone folds at the $P6_3/mmc \rightarrow Pnma$ PT, has become the Σ_2^o branch of phase I (*Pnma*). The I→II PT to the incommensurate phase thus occurs as a consequence of an interaction of the two Σ_2^o modes. The last-mentioned mechanism has been proposed by Plesko *et al* (1981) when studying PTs in CHB. In the PT to the triclinic phase V without the (phase I) unit-cell volume multiplication, shear deformations u_{xy} and u_{xz} have to take part, but the PT to the triclinic phase (with unit-cell volume multiplied) is probably caused by coupling of the M_4^h (original) soft mode with other modes.

Recently, this idea has been confirmed by Quilichini *et al* (1991) who studied the low-temperature PT in Rb₂ZnCl₄ and K₂ZnCl₄ by inelastic neutron scattering. In the ferroelectric phase III of these crystals, there are soft optical modes at the T point $\frac{1}{2}(b^* + c^*)$ of the Brillouin zone of the orthorhombic phase *Pnma* (this is equivalent to the M point of the latent phase that we propose for CCB). For Rb₂ZnCl₄, these soft modes are underdampled near the PT.

In K₂ZnCl₄, the situation is more complex. The soft branch in the $(\mu b^* + \frac{1}{2}c^*)$ direction has a minimum near the T point which demonstrates the appearance of a new incommensurate phase modulated along *b* prior to phase IV.

There is a possibility that such a situation takes place in CCB as well. If it were so, an analogous PT to the incommensurate phase would appear before the last low-temperature phase with the cell multiplication. Indirect evidence for this assumption might be some broadening of the Rayleigh line, preceding the underdamping of the soft mode, as is seen in the CCB spectra. Further investigations, however, are necessary to test our conclusions.

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