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## Study of the Incommensurately Modulated Structure of Cs<sub>2</sub>CdBr<sub>4</sub> by Single-Crystal Diffraction

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### Abstract

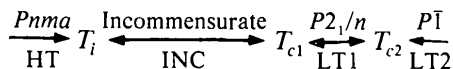
Three thermotropic phase transitions have been detected in Cs<sub>2</sub>CdBr<sub>4</sub>: a second-order orthorhombic to incommensurate transition at  $T_i = 252$  K, a first-order incommensurate to monoclinic transition at  $T_{c1} = 237$  K and a second-order monoclinic to triclinic transition at  $T_{c2} = 156$  K. The incommensurate phase of Cs<sub>2</sub>CdBr<sub>4</sub> has been studied by single-crystal X-ray diffraction. Main reflections and first-order satellites were measured at 245 K. Based on extinction rules for the diffracted intensities, the superspace group could be determined unambiguously. The modulation vector could be precisely measured as  $\mathbf{q} = 0.170(3)\mathbf{a}^*$ . The incommensurately modulated structure is characterized by a rotation of the CdBr<sub>4</sub> tetrahedra around  $\mathbf{a}$  in addition to a slight translational component along  $\mathbf{b}$ . In the monoclinic phase the rotation of the tetrahedra is 'locked' and the structure analysis shows the existence of two twinning domains. Crystal data: dicaesium tetrabromocadmate, Cs<sub>2</sub>CdBr<sub>4</sub>,  $M_r = 697.9$ . At 245 K:  $Pnma$ ,  $a = 10.205(4)$ ,  $b = 7.887(3)$ ,  $c = 13.925(7)$  Å,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $R = 0.054$  for 578 reflections. At 200 K:  $P2_1/n$ ,  $a = 10.200(3)$ ,  $b = 7.844(4)$ ,  $c = 13.958(9)$  Å,  $\alpha = 90.0(1)^\circ$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $R = 0.042$  for 1739 reflections.

### 1. Introduction

The room-temperature phase of Cs<sub>2</sub>CdBr<sub>4</sub> is isomorphous with  $\beta$ -K<sub>2</sub>SO<sub>4</sub> (orthorhombic space group  $Pnma$ ) with  $a = 10.228(7)$ ,  $b = 7.931(4)$  and  $c = 13.966(8)$  Å and four formula units per unit cell

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(Altermatt, Arend, Gramlich, Niggli & Petter, 1984). With decreasing temperature the crystal undergoes a displacive-type structural phase transition at  $T_i = 252$  K into an incommensurate phase as evidenced by the presence of satellite reflections on diffractograms. Two additional phase transitions take place at  $T_{c1} = 237$  K, a first-order phase transition, and at  $T_{c2} = 156$  K, a second-order phase transition:



Studies based on <sup>81</sup>Br nuclear quadrupolar resonance measurements (Plesko, Kind & Arend, 1980) revealed the existence of the above phase-transition sequence. Their results were also in agreement with the symmetry detected by X-ray diffraction for the normal and commensurate phases. No ferroelectric phase occurs for Cs<sub>2</sub>CdBr<sub>4</sub> as it does in other  $A_2BX_4$ -type compounds like K<sub>2</sub>SeO<sub>4</sub> (Izumi, Axe & Shirane, 1977) and Rb<sub>2</sub>ZnCl<sub>4</sub> and Rb<sub>2</sub>ZnBr<sub>4</sub> halides (Sawada, Shiroishi, Yamamoto, Takashige & Matsuo, 1978; Arend, Muralt, Plesko & Altermatt, 1980) for example. Studies by Maeda, Honda & Yamada (1983) showed that by lowering the temperature, the intensity of the satellite reflection 0311 behaves like  $I \propto (T_i - T)^\beta$  with  $\beta = 0.29$ . In addition, they detected a linear decrease of the  $q$  value from 0.15 to 0.20 with decreasing temperature. The superspace group of the INC phase discussed by other authors seemed to be controversial (Maeda *et al.*, 1983; Altermatt *et al.*, 1984).

No structural study of the incommensurate phase of this compound has been performed. The small value of  $q$  causes the satellites to be very close to the main reflections. This fact together with the low intensities of the satellite reflections and the high absorption

coefficient of the compound do not facilitate the analysis of the INC phase by single-crystal diffraction. In the present work, the preparation of a spherical crystal and the utilization of Cu  $K\alpha$  X-ray radiation allowed the structure of the incommensurate phase to be solved. The presence of satellite intensities could be confirmed in the temperature range 250–238 K, both on precession diffractograms and on a four-circle diffractometer. The modulation vector  $\mathbf{q} = 0.170(3)\mathbf{a}^*$  was precisely measured at 245 K and the superspace group determined as  $P\bar{P}nma_{1s}$ . These results are at variance with the previous study by Altermatt *et al.* (1984).

The diffracted intensities of the LT1 phase were also measured. Its structure determination revealed the existence of two twinning domains in accordance with previous studies (Altermatt *et al.*, 1984; Maeda *et al.*, 1983). This phase is paraelectric and the structure is monoclinic with space group  $P2_1/n$ .

## 2. Experimental

Single crystals of  $\text{Cs}_2\text{CdBr}_4$  were grown from a melt using the Bridgman technique. The X-ray intensities were measured on a CAD-4 four-circle diffractometer using a graphite monochromator. The  $\theta$ – $2\theta$  technique was used. The samples were cooled by a stream of nitrogen gas (modified Enraf–Nonius system). The temperature control was monitored by a thermocouple placed a few millimeters from the crystal. The temperature stability was better than 0.3 K. For the modulated phase the temperature was 245 K, and 200 K for the LT1 phase. Cu  $K\alpha$  and Mo  $K\alpha$  radiations were used for INC and LT1 phases respectively. Table 1 gives a summary of the data-collection parameters.

A local set of computer programs compatible with the XRAY72 system (Stewart, Kundell & Baldwin, 1972) was developed for the data reduction with four-indices reflections and for the preparation of a unique set of data to be used in the REMOS85.0 (Yamamoto, 1982) refinement. Atomic scattering factors were calculated from Cromer & Mann (1968).

### 2.1. INC phase

A 0.15 mm diameter spherical crystal was prepared for the collection of the reflections. Intensities were measured from 2 to 60° ( $2\theta$ ) using an intensity-dependent scan speed ranging from 0.08 to 0.21° min<sup>-1</sup>. From precession diffractograms the modulation wavevector was measured as 0.17 $\mathbf{a}^*$ . Owing to the very low intensities of the satellite reflections, it was impossible to center them automatically on the diffractometer. However, a careful search of the maximum intensity of some satellites monitored manually allowed precise measurement of the modulation wavevector at 245 K. The lattice

Table 1. *Data collection*

	INC phase	LT1 phase
Scan width (°)	0.5 + 0.14tan $\theta$	0.5 + 0.34tan $\theta$
Scan speed (° min <sup>-1</sup> )	0.08 to 0.21	0.30 to 1.37
(Sin $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.543	0.596
Range of $hklm$	$-1 \leq h \leq 11; -7 \leq k \leq 7;$ $0 \leq l \leq 14; -1 \leq m \leq 1$	$-1 \leq h \leq 12; -9 \leq k \leq 9;$ $-16 \leq l \leq 16$
Collected reflections	3244	5745
Non-equivalent reflections	992	2122
Observed reflections	386 main 192 satellites [ $I_o \geq 5\sigma(I_o)$ ]	1739 [ $I_o \geq 3\sigma(I_o)$ ]
Internal consistency	0.0365 (all); 0.0355 (main); 0.109 (satellites)	0.033

constants of the basic structure were  $a = 10.205(4)$ ,  $b = 7.887(3)$  and  $c = 13.925(7)$  Å. A spherical absorption correction was applied with the linear absorption coefficient  $\mu = 941$  cm<sup>-1</sup>. At least two symmetrically equivalent reflections were collected for every independent  $hkl$ . Their internal consistency gave  $R_{\text{int}}$  values of 0.036 and 0.109 for main and satellite reflections respectively. A total of 578 independent reflections with  $I_o \geq 5\sigma(I_o)$  (including 192 satellites) was used in the refinement.

### 2.2. LT1 phase

At 237 K a first-order phase transition takes place. A crystal with a parallelepiped shape was used for data collection. The measurements were performed at 200 K. A total of 5745 reflections were collected with  $2\theta$  ranging from 2 to 50° resulting in 2122 nonequivalent reflections, 1739 of which were considered as observed [ $I_o \geq 3\sigma(I_o)$ ]. Internal consistency calculations gave  $R_{\text{int}} = 0.033$ . At this temperature the lattice constants were  $a = 10.200(3)$ ,  $b = 7.844(4)$ ,  $c = 13.958(9)$  Å and  $\alpha = 90.0(1)^\circ$ .

## 3. Superspace-group determination

From the systematic absences, the space group for the main reflections could be identified as  $Pnma$ . According to Landau theory for second-order phase transitions, this should also be the space group for the basic structure in the incommensurate phase since  $\mathbf{q}$  is parallel to  $\mathbf{a}^*$  (Heine & Simmons, 1987). As a consequence, the superspace group in a four-dimensional space must be one of the following (de Wolff, Janssen & Janner, 1981):

$$P\bar{P}nma_{111} \quad P\bar{P}nma_{11s} \quad P\bar{P}nma_{1sa} \quad P\bar{P}nma_{1ss}$$

From precession diffractograms and the analysis of diffracted intensities collected with the diffractometer, the superspace group  $P\bar{P}nma_{1ss}$  could be unambiguously determined. The following systematic absences were observed:

$$k + l = 2n + 1 \text{ for } 0k0l \Rightarrow \left(\frac{n}{1}\right)$$

$$m = 2n + 1 \text{ for } h0lm \Rightarrow \left(\frac{m}{s}\right)$$

$$h + m = 2n + 1 \text{ for } hk0m \Rightarrow \left(\frac{a}{s}\right)$$

Fixing the origin of the four-dimensional cell on the inversion center, *i.e.*  $I \equiv (\bar{1}10000)$ , the symmetry equivalent positions can be generated by the following four operators:

$$\begin{aligned} (\varepsilon) &\equiv (110000); & (\eta) &\equiv (m_x | \frac{1}{2}\frac{1}{2}\frac{1}{2}0); \\ (m) &\equiv (m_y | 0\frac{1}{2}0\frac{1}{2}); & (\alpha) &\equiv (m_z | \frac{1}{2}0\frac{1}{2}\frac{1}{2}). \end{aligned}$$

#### 4. Model for the structure in the INC phase

A displacive incommensurate structure can be described as a modulated distortion of a basic structure. In a four-dimensional lattice the atomic positions  $\mathbf{r}^\mu$  are given by the basic structure  $\bar{\mathbf{r}}^\mu$  and a modulation displacement field  $\mathbf{U}$ . For a one-dimensional modulation vector the coordinates  $x_i^\mu$  can be written as:

$$x_i^\mu = \bar{x}_i^\mu + U_i^\mu(\bar{x}_4^\mu) \quad (1)$$

where  $U_i^\mu$  are the atomic modulation displacements from  $\bar{x}_i^\mu$ . This is a periodic function of the fourth coordinate  $\bar{x}_4^\mu$ , which is expressed by:

$$\bar{x}_4^\mu = q_1\bar{x}_1^\mu + q_2\bar{x}_2^\mu + q_3\bar{x}_3^\mu + t \quad (2)$$

where  $t$  is the intrinsic phase.

Expanding  $U_i^\mu(\bar{x}_4^\mu)$  as a Fourier series one has:

$$U_i^\mu(\bar{x}_4^\mu) = \frac{1}{2} \left[ \sum_{n=-\infty}^{\infty} U_{i,n}^\mu \exp(2\pi i n \bar{x}_4^\mu) \right]. \quad (3)$$

In the general case  $2n + 1$  modulation displacement parameters should be used for each atom. However, atoms in special positions are subject to restrictions on their harmonic components. Thus for atoms located on mirror planes one has:

$$\begin{aligned} (m_y | 0\frac{1}{2}0\frac{1}{2}) U_i(\bar{x}_4) &= \begin{cases} U_i(\bar{x}_4 + \frac{1}{2}) & \text{for } i = 1; 3 \\ -U_i(\bar{x}_4 + \frac{1}{2}) & \text{for } i = 2 \end{cases} \\ &\equiv U_i(\bar{x}_4) \end{aligned} \quad (4)$$

which implies the following restrictions:

$$U_{x,n} = U_{z,n} = 0 \quad \text{for } n \text{ odd} \quad (5a)$$

$$U_{y,n} = 0 \quad \text{for } n \text{ even.} \quad (5b)$$

The Fourier expansion (3) can be truncated beyond harmonic terms of an order equal to the highest order of the measured satellite reflections (van Aalst, den Hollander, Peterse & de Wolff, 1976). In the present work only first-order satellites could be collected. Considering that  $\mathbf{q}$  is parallel to  $\mathbf{a}^*$ , (1) reduces to:

$$\begin{aligned} x_i^\mu &= \bar{x}_i^\mu + u_{i0}^\mu + u_{i1}^\mu \cos[2\pi(q\bar{x}_1^\mu + t)] \\ &\quad - u_{i2}^\mu \sin[2\pi(q\bar{x}_1^\mu + t)]. \end{aligned} \quad (6)$$

Nine modulation displacement parameters should be refined for atoms in general positions and four for those on special position *.m.*

No modulation function was postulated for displacement parameters  $U_{ij}$ . Occupation probability was fixed to unity for all the atoms in the cell.

To avoid confusion between 'modulation displacement parameters'  $u_{i0,1,2}^\mu$  and 'displacement parameters'  $U_{ij}$  ( $B_{ij}$  or  $\beta_{ij}$ ) the former will be, hereafter, referred to simply as 'modulation parameters'.

#### 5. Refinement of the structures

##### 5.1. INC phase

The program *REMOS85.0* was used for the refinement of the incommensurate structure. The function minimized was  $\sum w(|F_o - F_c|)^2 / \sum w|F_o|^2$  with unit weights. The phase integral appearing in the four-dimensional description of the structure factors of modulated phases (Yamamoto, 1982) was calculated numerically with eight divisions. The refinement of the average structure, resulting from the use of main reflections only, converged to  $R = 0.046$  with anisotropic displacement parameters and secondary-extinction correction.

Of the seven atoms in the Cs<sub>2</sub>CdBr<sub>4</sub> unit, five are placed on a mirror and the remaining two are related by symmetry. According to (5) and (6), the total number of positional parameters to be refined amounts to 27. Neglecting the modulation of the displacement parameters, the complete set of atomic parameters amounts to 56.

The atomic positions of the refined average structure were used as the starting point for the refinement of the modulated structure; isotropic displacement parameters were used in the initial stage.

After some initial step-by-step adjustments of the starting parameters, the structure converged in a few refinement cycles including secondary-extinction correction with  $g = 0.063$  (6) (Becker & Coppens, 1975). No geometrical constraints had to be applied. The final calculated  $R$  values are 0.054, 0.045 and 0.146 for all, main and satellite reflections respectively. For comparison, main reflections with intensities comparable to those of satellites gave an  $R$  value of 0.137. Moreover,  $|F_o - F_c|$  values for satellites are of the same order as for main reflections; their relative errors are however high owing to the small  $|F_o|$ . The final positional parameters are reported in Table 2\* and the basic structure is shown in Fig. 1. A comparison between the anisotropic displacement ellipsoids in the average and basic structure is given in Table 3.  $\Delta/\sigma = 0.02$ .

\* Lists of structure factors for the INC and LT1 phases have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51229 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional parameters in the INC phase with e.s.d.'s in parentheses

<i>i</i>	$\bar{x}_i$	$u_{i0}$	$u_{i1}$	$u_{i2}$
Cs(1)	<i>x</i>	0.1233	0.0000 (2)	0.0000
	<i>y</i>	0.2500	0.0000	0.0076 (11)
	<i>z</i>	0.0976	0.0000 (2)	0.0000
Cs(2)	<i>x</i>	-0.0165	0.0000 (2)	0.0000
	<i>y</i>	0.2500	0.0000	0.0074 (9)
	<i>z</i>	0.6759	0.0000 (1)	0.0000
Cd	<i>x</i>	0.2224	-0.0001 (2)	0.0000
	<i>y</i>	0.2500	0.0000	-0.0026 (8)
	<i>z</i>	0.4238	0.0000 (1)	0.0000
Br(1)	<i>x</i>	-0.0253	0.0001 (4)	0.0000
	<i>y</i>	0.2500	0.0000	0.0021 (21)
	<i>z</i>	0.4125	0.0001 (3)	0.0000
Br(2)	<i>x</i>	0.3219	0.0000 (4)	0.0000
	<i>y</i>	0.2500	0.0000	0.0296 (20)
	<i>z</i>	0.5925	0.0001 (3)	0.0000
Br(3)	<i>x</i>	0.3196	0.0000 (3)	0.0046 (11)
	<i>y</i>	-0.0083	0.0000 (5)	-0.0170 (12)
	<i>z</i>	0.3413	-0.0001 (3)	0.0188 (6)

Table 3. Diagonalized displacement ellipsoids (Å<sup>2</sup>): a comparison between average and basic structure

	Average structure			Basic structure		
	$U_{11}$	$U_{22}$	$U_{33}$	$U_{11}$	$U_{22}$	$U_{33}$
Cs(1)	0.1256	0.0897	0.0267	0.1240	0.0831	0.0239
Cs(2)	0.0354	0.0833	0.0263	0.0336	0.0768	0.0235
Cd	0.0206	0.0528	0.0290	0.0195	0.0519	0.0280
Br(1)	0.0265	0.1676	0.0744	0.0227	0.1580	0.0713
Br(2)	0.0328	0.1866	0.0540	0.0305	0.1470	0.0509
Br(3)	0.0565	0.0444	0.2487	0.0406	0.0537	0.1899

based on this model converged to  $R = 0.042$  with a twin volume ratio of approximately 1:2.5. The weight function  $1/\sigma^2(F)$  was applied in this refinement. The final parameters are reported in Table 4.  $\Delta/\sigma_{\max} = 0.04$ .

5.2. LT1 phase

In this phase the lattice angles are, within e.s.d.'s, equal to 90°. The extinction rule for the glide plane  $..a$  is no longer fulfilled. The disappearance of this extinction rule ( $hk0: h = 2n$ ) can be interpreted as a lock-in of  $q$  at  $q = 0$ : the satellite reflections at the  $hk0m$  projected plane with  $m = 1$  become main reflections with  $h = 2n + 1$  (Fig. 2). Two monoclinic domains, twinned by the mirror plane  $..m$ , explain the pseudo-orthorhombic symmetry. The structure refinement

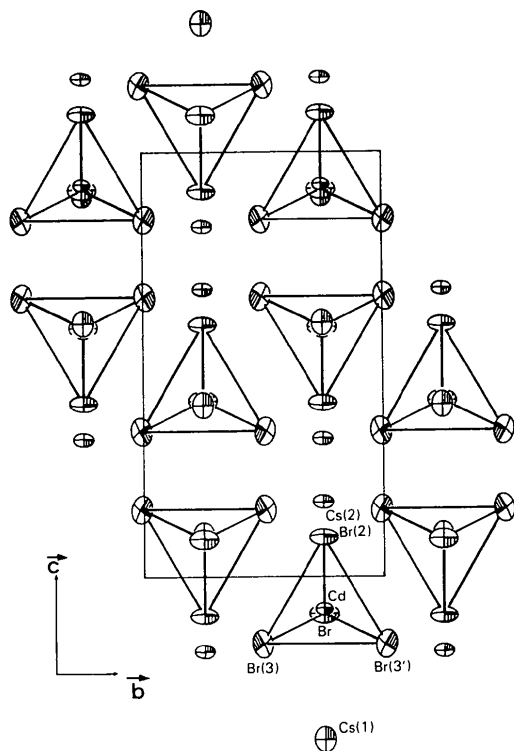


Fig. 1. Basic structure of the incommensurate phase resulting from the refinement of main and satellite reflections. Modulation displacements are not represented.

6. Description of the structures

The wavelength of the modulation is about six times the lattice parameter  $a$  ( $q^{-1} \approx 6$ ). As a consequence, two

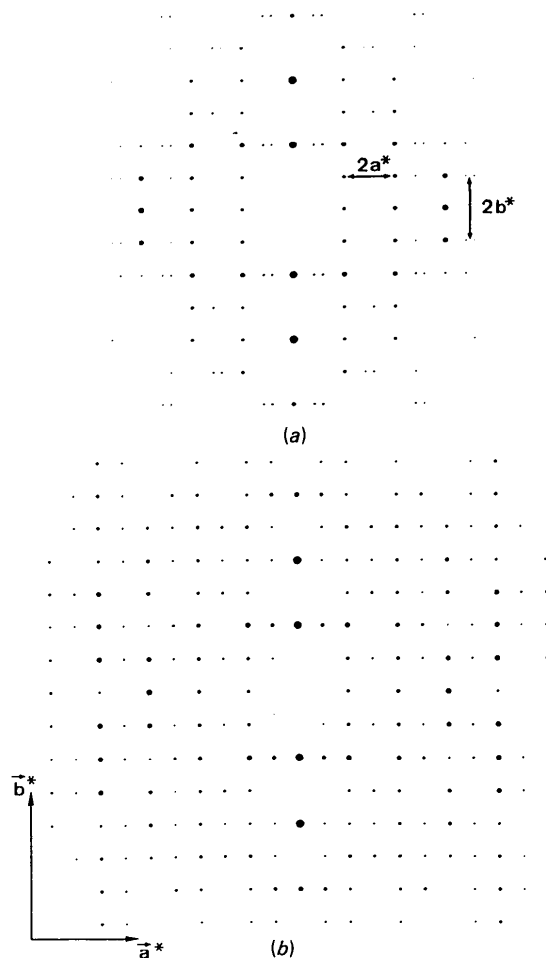


Fig. 2. Representation of diffracted intensities collected on a four-circle diffractometer, in reciprocal lattice planes (Yamamoto, 1987): (a)  $hk0m$  plane in the INC phase, reflections with  $h+m = 2n+1$  are absent; (b)  $h0k$  plane in the LT1 phase, reflections with  $h = 2n+1$  are present.

Table 4. Positional parameters and diagonalized ellipsoid components ( $\text{\AA}^2$ ) in the LT1 phase

	$x$	$y$	$z$	$U_1$	$U_{11}$	$U_{111}$
Cs(1)	0.1213	0.2598	0.1002	0.0483	0.1171	0.0249
Cs(2)	-0.0156	0.2602	0.6758	0.0497	0.0246	0.0273
Cd	0.2225	0.2473	0.4245	0.0322	0.0268	0.0240
Br(1)	-0.0265	0.2579	0.4143	0.0528	0.1124	0.0194
Br(2)	0.3231	0.2885	0.5920	0.0214	0.0382	0.0711
Br(3)	0.3235	-0.0318	0.3628	0.0386	0.0219	0.1028
Br(3')	0.3131	0.4832	0.3172	0.1148	0.0270	0.0381

translation-equivalent atoms on the basic structure, in the  $i$ th and in the  $i$ th + 3 unit cells have approximately antiphase displacement when the modulation is considered. Calculating the modulation displacement for each atom in different unit cells and varying the intrinsic phase  $t$  from 0 to 1 one can find all the possible atomic configurations resulting from the modulation (Fig. 3 shows the atomic modulation displacement  $U_i^u$  from the basic position  $\bar{x}_i^u$  as a function of  $t$ ). The interatomic distances can thus be found for each configuration (Fig. 4). The range of distances for each pair of atoms can be seen in Table 5. From this table, two main characteristics can be observed. First,  $\text{CdBr}_4$  can be treated as a rigid body. (The tetrahedra are slightly distorted as in the HT phase.) Second, there is an antiphase movement between Br(3), Br(3') and Cs(1) and an in-phase movement between Cs(2) and Br(2). The Cs ion displacements are closely related to the rotation of the  $\text{CdBr}_4$  tetrahedra. Electrostatic interactions between Br(3), Br(3') and Cs(1), and between Br(2) and Cs(2), are responsible for their antiphase and in-phase movement respectively.

Analyses of the modulation displacements for different values of the intrinsic phase show that the maximal rotations take place at  $t \approx t_r$  and  $t_r + 0.5$  with  $t_r = 0.45$ . Both configurations are shown in Fig. 5. This corresponds to a rotation of the tetrahedra of about  $7^\circ$ .

According to the model of McConnell & Heine (1984) the incommensurate structure can be described as an average structure plus two component structures  $C_1$  and  $C_2$ , oscillating  $\pi/2$  out of phase:

$$\begin{aligned} (\text{INC structure}) = & (\text{average structure}) + C_1 \cos(\mathbf{q} \cdot \bar{\mathbf{r}}) \\ & + C_2 \sin(\mathbf{q} \cdot \bar{\mathbf{r}}). \end{aligned}$$

Looking at the structure configuration at  $t = t_r \pm 0.25$  it is clear that the rotational part is negligible whereas a slight translation in the  $\mathbf{b}$  direction can be identified.  $C_1$  can be assigned to the rotational component structure corresponding to an amplitude of about  $7^\circ$  and  $C_2$  to the (small) translational component. The space groups of  $C_1$  and  $C_2$  can be easily identified as  $P2_1/n$  and  $P2_12_12_1$  respectively as indeed they should be according to Heine & Simmons (1987).

The LT1 phase can be interpreted as a lock-in structure of the modulated phase. In this phase the atomic coordinates correspond to the maximum modulated atomic displacement in the INC phase as

can be seen in Fig. 6. The quality of the experimental data and the lower temperature of the intensity measurements collected explain the difference in the displacement ellipsoids as compared to those in the INC phase.

## 7. Concluding remarks

The previous results (Altermatt *et al.*, 1984) obtained from the studies of the INC phase of the  $\text{Cs}_2\text{CdBr}_4$  can be attributed to the difficulties associated with the small value of the modulation vector  $\mathbf{q}$  and to the strong absorption of X-rays. The use of  $\text{Cu K}\alpha$  radiation increases the resolution of the satellite reflections but, on the other hand, also increases the absorption coefficient. Nevertheless, a data collection performed with a low-speed scan and using a spherical crystal provided a set of diffracted intensities reliable enough to be used in the structure determination.

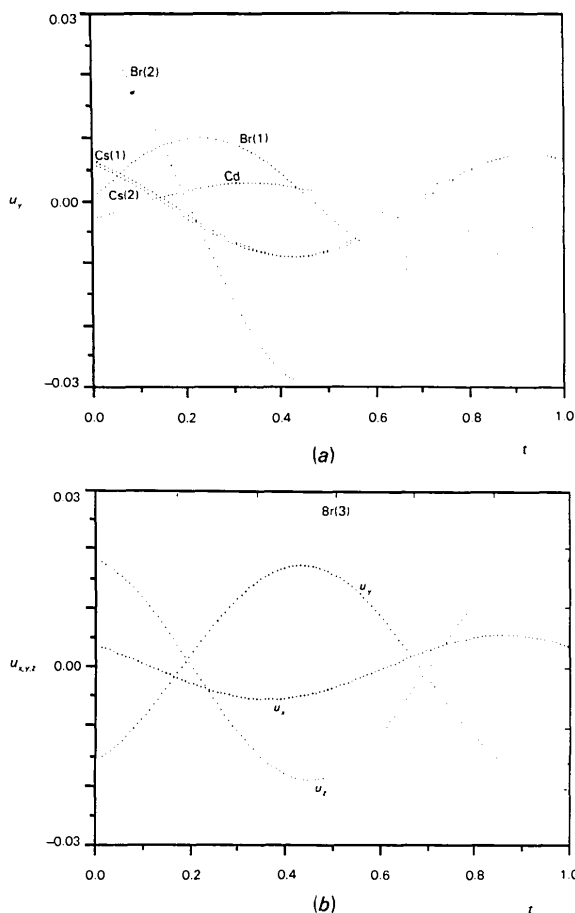


Fig. 3. Modulation displacement  $u_i^u \cos[2\pi(q\bar{x}_i^u + t)] - u_i^u \sin[2\pi(q\bar{x}_i^u + t)]$  from the basic positions  $\bar{x}_i^u$  at different values of the intrinsic phase  $t$ : (a) the atoms in special position and (b) the Br(3) atom with three displacement components. At  $t \approx 0.45$  and  $0.95$  the  $\text{CdBr}_4$  units exhibit their maximal rotation.

Based on the observed extinction rules other authors suggested that the superspace group of the INC phase should be  $P\bar{1}2_1/a$ . According to the Landau symmetry theorem, such a superspace group could only be assigned if an additional phase transition were assumed to have occurred. This is apparently not the case. Thus the  $P\bar{1}2_1/a$  superspace-group assignment is more appropriate as confirmed by the experimental results and the structure refinement presented here.

The calculated  $R$  value for the satellite reflections (0.146) can be considered as acceptable. It is interesting to point out here that, by eliminating 8 of the 192 satellite reflections for which  $|F_o - F_c|$  was very high, the  $R$  value decreases to 0.124.

The main characteristic of the modulation is a rotation of the  $\text{CdBr}_4$  tetrahedra around the  $a$  direction (amplitude of  $7^\circ$ ), the movement of Cs(1) and Cs(2) being strongly related to this rotation. This model is compatible with a decomposition of the modulated structure as an average structure plus two difference structures  $C_1$  and  $C_2$  which are out of phase by a factor  $\pi/2$ .

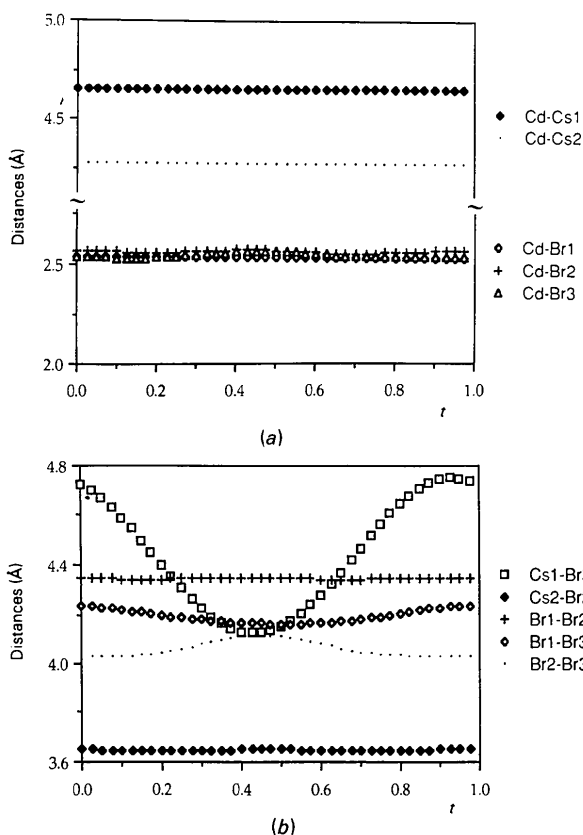


Fig. 4. Characteristic interatomic distances as a function of the intrinsic phase  $t$ . In (a) the distances between any atom and Cd are nearly constant and in (b) a small variation is observed between the Br distances inside the tetrahedron and a great variation in Cs(1)-Br(3) distances due to their antiphase movement.

Table 5. Possible interatomic distances (Å)

First and second rows: minimum and maximum distances; third row: difference between distances. The values on the diagonal correspond to the displacement from the basic positions.

	Cs(1)	Cs(2)	Cd	Br(1)	Br(2)	Br(3)
Cs(1)	0.000 0.065 0.065					
Cs(2)	8.178 8.178 0.000	0.000 0.066 0.066				
Cd	4.653 4.654 0.001	4.275 4.276 0.001	0.000 0.032 0.032			
Br(1)	4.640 4.642 0.002	3.669 3.671 0.002	2.535 2.536 0.001	0.000 0.090 0.090		
Br(2)	7.183 7.185 0.002	3.646 3.650 0.004	2.559 2.572 0.013	4.343 4.350 0.008	0.000 0.228 0.228	
Br(3)	4.125 4.751 0.626	6.033 6.252 0.218	2.532 2.568 0.036	4.161 4.234 0.073	4.028 4.114 0.086	0.037 0.297 0.260

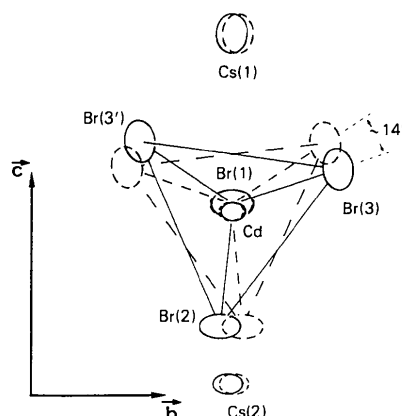


Fig. 5. Two configurations for a  $\text{Cs}_2\text{CdBr}_4$  unit corresponding to maximal rotation values in the INC phase. They are half a wavelength out of phase which is equivalent to nearly  $3a$ . The rotation amplitude is about  $7^\circ$ .

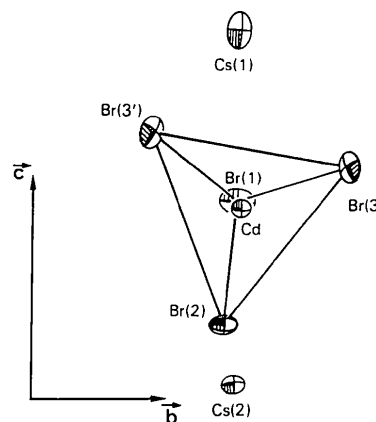


Fig. 6. A  $\text{Cs}_2\text{CdBr}_4$  unit configuration at LT1 phase. This corresponds to the lock-in of one of the configurations shown in Fig. 5.

The LT1 (paraelectric) phase can be considered as a lock-in of the modulated structure. The presence of twinning domains, with the twin plane (010), is due to two energetically equivalent configurations. The symmetry of this phase is the symmetry of the rotational structure component  $C_1$  and could correspond to a nonpolar soft-mode phase transition.

The incommensurate phase of Cs<sub>2</sub>CdBr<sub>4</sub> can be compared with the corresponding modulated phase of K<sub>2</sub>SeO<sub>4</sub> (Yamada & Ikeda, 1984) which is stable between 130 and 93 K. In the oxide compound,  $\mathbf{q}$  is approximately twice as large as in the bromide. In addition, the SeO<sub>4</sub> groups have been shown to rotate around  $\mathbf{b}$  (perpendicular to  $\mathbf{q}$ ) whereas the CdBr<sub>4</sub> groups rotate around  $\mathbf{a}$  (parallel to  $\mathbf{q}$ ). In the 'lock-in' phase, K<sub>2</sub>SeO<sub>4</sub> is ferroelectric with orthorhombic symmetry while Cs<sub>2</sub>CdBr<sub>4</sub> has monoclinic symmetry with a center of inversion. Although the structures are completely isomorphous in the high-temperature phase (same space group and same site symmetries), the comparison indicates the independent evolution of the systems up to the 'lock-in' at low temperature.

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## Structural and Thermal Dependence of Normal-Mode Condensations in K<sub>2</sub>TeBr<sub>6</sub>

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### Abstract

The structural thermal dependence in K<sub>2</sub>TeBr<sub>6</sub> resulting from the condensation of normal modes at the monoclinic-to-tetragonal and at the tetragonal-to-cubic phase transitions has been investigated over the temperature range 20 to 430 K. Both single-crystal and powder-profile-fitting structure refinement methods were used, with  $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$  and  $\mu = 22.76 \text{ mm}^{-1}$ .  $M_r = 685.22$ . Phase III is monoclinic,  $P2_1/n$ , with two K<sub>2</sub>TeBr<sub>6</sub> per unit cell and  $a^{295 \text{ K}} = 7.4908 (10)$ ,  $b^{295 \text{ K}} = 7.5492 (7)$ ,  $c^{295 \text{ K}} = 10.6984 (11) \text{ \AA}$ ,  $\beta^{295 \text{ K}} = 90.307 (6)^\circ$ ,  $V =$

$604.98 (23) \text{ \AA}^3$ ,  $D_m = 3.68$ ,  $D_x = 3.761 \text{ g cm}^{-3}$ ,  $F(000) = 600$ ; phase II is tetragonal,  $P4/mnc$ , with two K<sub>2</sub>TeBr<sub>6</sub> per unit cell and  $a^{410 \text{ K}} = 7.5755 (10)$ ,  $c^{410 \text{ K}} = 10.7702 (22) \text{ \AA}$ ,  $V = 618.1 (3) \text{ \AA}^3$ ; and phase (I) is cubic,  $Fm\bar{3}m$ , with  $a^{435 \text{ K}} = 10.7456 (14) \text{ \AA}$ ,  $V = 1240.8 (7) \text{ \AA}^3$  and four K<sub>2</sub>TeBr<sub>6</sub> per unit cell. In phase III at 295 K  $wR = 0.0563$  for 1221 independent averaged  $F_m^2 > 4\sigma(F_m^2)$ , in phase II at 418 K  $wR = 0.0312$  for 302 independent averaged  $F_m^2 > \sigma(F_m^2)$  and in phase I at 435 K  $wR = 0.0310$  for 58 independent averaged  $F_m^2 > \sigma(F_m^2)$ . The powder-profile-fitting refinements gave  $0.046 \leq R_f \leq 0.086$  over the entire temperature range. The TeBr<sub>6</sub><sup>2-</sup> octahedron is very regular, with Te–Br distances of 2.699 (6)  $\text{ \AA}$  at 295 K, 2.707 (5)  $\text{ \AA}$  at 418 K and 2.695 (3)  $\text{ \AA}$  at 453 K after

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