

## Isotropic compression of the linear-chain perovskite-type CsCdBr<sub>3</sub> up to 20 GPa

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Powder x-ray-diffraction experiments have been performed on 2*H*-CsCdBr<sub>3</sub> at room temperature up to 20 GPa. Although this compound is usually considered as quasiunidimensional, such a characteristic could not be evidenced for its elastic bulk properties under pressure. No phase transformation occurs in this pressure range, and the *a* and *c* lattice parameters steadily decrease with pressure; their ratio lowers by only 2%. As for the bulk modulus, its first and second pressure derivatives have been calculated using Birch's equation of state. The bulk modulus is low (21.3 GPa) and is in good agreement with the bulk-modulus-volume systematics for usual ionic compounds. The value of the first pressure derivative is also typical of ionic compounds. Above 5 GPa increasing intensities of a few diffraction lines were observed; they are consistent with a shift of the bromine anions inside the cell that leaves the structure unchanged. This is also supported by the variations of the Raman frequencies with volume.

### INTRODUCTION

Compounds with the general chemical formula *ABX*<sub>3</sub> form an extensive class of structurally related compounds<sup>1</sup> where *A* is a large cation, *B* a smaller one, and *X* is O, S, F, Cl, or Br. The structures found in this class can all be described by a stacking of ordered close-packed *AX*<sub>3</sub> layers that avoid near-neighboring *A* cations everywhere; the *B* cations fill all the anionic octahedral sites between these layers. Two types of stacking of the *AX*<sub>3</sub> layers fulfill these requirements: cubic or hexagonal. If there is only cubic stacking, the *B*-filled octahedra share only corners in three dimensions to form the well-known perovskite structure. If there is only hexagonal stacking, the *B*-filled octahedra share faces and form infinitely long chains parallel to the *c* axis. An infinite number of ordered sheets, each having a different ratio of cubic-to-hexagonal stacking, are theoretically possible but only three intermediate structures have been observed. The known structures are 2*H*, 9*R*, 4*H*, 6*H*, and 3*C* (conventional labeling: the number indicates the number of layers in the unit cell along the *c* axis while the letters designate the hexagonal, rhombohedral, or cubic structures, respectively). The type of stacking depends on the tolerance factor

$$t = (r_A + r_X) / 2^{1/2} (r_B + r_X),$$

where the *r* are the ionic radii of Shannon and Prewitt<sup>2</sup> which depend on the coordination number. High values of *t* lead to the 2*H* hexagonal stacking while lower values, close to 1 in oxides, are found for the ideal cubic perovskite structure. In general, the *A*—*X* bond length decreases more rapidly with pressure than the *B*—*X* bond length.<sup>3</sup> This means that pressure decreases the tolerance factor and therefore stabilizes cubic rather than hexagonal stacking. This is also consistent with pressure stabilizing preferentially the more dense phase since, in

the 3*C* polytype, an *A* cation has twelfold coordination, whereas in the hexagonal polytypes, some or all of the *A* cations have this coordination reduced from 12 to (6+6) by deviations of the *c/a* ratio from its ideal value.

After simultaneous treatment at high pressure and high temperature,<sup>3,4</sup> the following sequence of structures with increasing density has been effectively observed: 2*H*-9*R*-4*H*-6*H*-3*C* with the following stacking sequences: *ab*, *ababcac*, *abac*, *abcacb*, *abc*. The *c/aN* ratio (*N* is the number of *AX*<sub>3</sub> layers in the unit cell) slightly decreases at each transformation to reach  $\frac{1}{3}$  in the cubic cell. For example, BaMnO<sub>3</sub> is obtained in normal conditions in the 2*H* structure (*c/aN*=0.415, *V/Z*=65.6 Å<sup>3</sup>). After treatment under pressures of 3–7.5 GPa and temperatures of 850–1350°C followed by quenching, it is transformed into the 9*R* structure (*c/aN*=0.411, *V/Z*=64.7 Å<sup>3</sup>); a treatment at still higher pressures and temperatures, at about 9 GPa and 1200°C, allowed for the retention of the 4*H* structure in normal conditions (*c/aN*=0.410, *V/Z*=63.9 Å<sup>3</sup>). A small increase of density is observed: it only amounts to +1.6% and +1.2% at these two transitions.<sup>4</sup> These transformations have not been observed at room temperature in this 9-GPa range and their hysteresis fields could be considerable.

At room temperature, the relative stabilities of these structures are unknown as the previous transformations have been induced by use of conjugated high-pressure and high-temperature treatments. In addition, very few high-pressure compression experiments have been conducted on this class of compounds and the bulk moduli, as well as their pressure derivatives, are lacking.

CsCdBr<sub>3</sub> belongs to the 2*H* structure, just as BaMnO<sub>3</sub> at normal pressure; this structure is of the BaNiO<sub>3</sub> type with the space group (*D*<sub>6h</sub>)<sup>4</sup>-*P*6<sub>3</sub>/*mmc*.<sup>5</sup> For the bromine compounds, the tolerance factors are higher than for oxides (*t*=0.956, *r*<sub>Cs, XII</sub>=1.88 Å, *r*<sub>Cd, VI</sub>=0.88 Å, *r*<sub>Br</sub>=1.96 Å for CsCdBr<sub>3</sub>) and should decrease under

high pressure, leading to the more dense ideal perovskite structure.

Raman experiments at room temperatures have already been performed as a function of pressure up to 25 GPa but were inconclusive as for the presence of phase transformations.<sup>6</sup> Indeed, in this pressure range, no discontinuity of the Raman frequencies could be detected, which would have shown the presence of first-order transformations. However, the pressure shifts of the Raman lines could be fitted either by straight lines with slope changes at 2 and 10 GPa or by continuous higher-order polynomial expressions, and therefore no definite conclusion about the presence of an eventual second-order transformation could be derived.

However, there is no report about the elastic bulk properties under high pressure for this compound, although it would be highly desirable to correlate these Raman shifts with volume variations. In addition, there is no report on the behavior of the elastic properties of such linear-chain compounds. Thus, we investigated the structural behavior of CsCdBr<sub>3</sub> as a function of pressure up to 20 GPa at room temperature.

#### EXPERIMENTAL PROCEDURE

The sample was prepared by the Bridgman method in a bromine atmosphere.<sup>7</sup> The amount of impurities detected by chemical methods was less than 5 ppm. A single crystal was crushed into powder for the x-ray experiments under high pressure. It was mixed with sodium chloride which simultaneously acted as the pressure marker and pressure transmitting medium.

Powder x-ray-diffraction experiments on CsCdBr<sub>3</sub> were performed in a diamond anvil press with the angular dispersive method ( $4\theta=80^\circ$ ) using the zirconium-filtered molybdenum radiation from a fine focus tube. The beam was collimated down to 150  $\mu\text{m}$  by crossed slits and impinged onto the sample which filled the cavity 250  $\mu\text{m}$  in diameter drilled in the inconel gasket. The diffraction patterns were recorded on planar films placed 24.3 mm away from the sample, and exposure times were approximately 24 h. The diameters of the Debye rings were measured with a low-magnification microscope ensuring a sensitivity of 10  $\mu\text{m}$ .<sup>8</sup>

The cell parameter of NaCl was calculated as the average of the values given by the (111), (200), (220), and (222) lines. No systematic dependence on this cell parameter as a function of

$$\Gamma(hkl) = (h^2k^2 + k^2l^2 + l^2h^2) / (h^2 + k^2 + l^2)^2$$

( $h$ ,  $k$ , and  $l$  denote Miller indices) could be evidenced, indicative of low anisotropic stress components. Actually, it has been demonstrated on stress-sensitive compounds<sup>9</sup> that NaCl is a convenient pressure-transmitting medium under high pressure, especially above 10–12 GPa, a pressure range in which all the pressure media are solid. The pressure was calculated from the cell parameter of NaCl using Decker's equation of state.<sup>10</sup> The uncertainty of the pressure is estimated to be approximately 0.4 GPa at 10 GPa.

The cell parameters of 2H-CsCdBr<sub>3</sub> were determined

from the more intense lines, which were the only ones observable under high pressure: (110), (002), (201), (202), (220), (203), and (401). These lines persisted over the whole pressure range, up to 25 GPa. The data have been recorded at increasing or decreasing pressure; no volume difference could be noticed.

At 5 GPa, a diffraction line appeared on the pattern and at higher pressure the (201) seemed to broaden. These phenomena were found to be perfectly reversible without noticeable hysteresis when pressure decreased, and their origins will be discussed in the next section.

#### RESULTS

At normal pressure and room temperature, the cell parameters of 2H-CsCdBr<sub>3</sub> are  $a=7.675$  Å,  $c=6.722$  Å,  $Z=2$ , and  $V/Z=171.45$  Å<sup>3</sup>, in excellent agreement with published results.<sup>5</sup>

Under high pressure, these cell parameters, as calculated from the above-listed lines, decreased smoothly up to 25 GPa, the highest investigated pressure. Thus, no transition to a different structure could be evidenced in this pressure range.<sup>11</sup>

The  $a$  and  $c$  parameters decreased in the same way (Fig. 1). The ratio  $c/a$  remained nearly constant: only a slight decrease by about 2%, from 0.876 to 0.860 was observed up to 20 GPa. This demonstrates that the

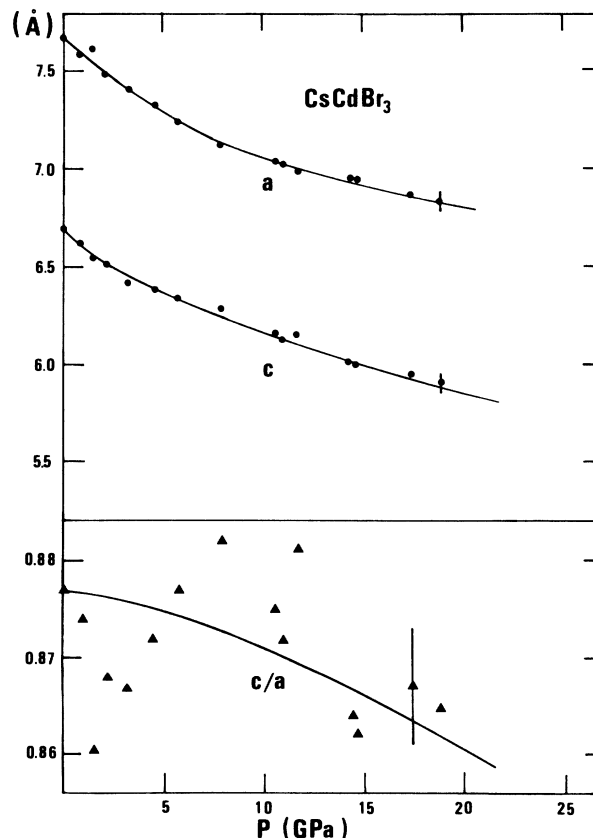


FIG. 1. Variations of the  $a$  and  $c$  lattice parameters and the  $c/a$  ratio for 2H-CsCdBr<sub>3</sub> as a function of pressure.

compression of  $\text{CsCdBr}_3$  is isotropic; furthermore, the  $c$  axis is slightly more compressible than the  $a$  axis by 2%.

The volume decreased very rapidly with pressure (Fig. 2): the relative volume is reduced to 0.65 at 25 GPa. For example, the volume compression is larger than for NaCl, a soft ionic compound. With such a high compression, the data have been fitted to the second-order equation of state of Birch:<sup>12</sup>

$$P = \frac{3}{2}B_0x(1+x)^{5/2}(1+\alpha x + \beta x^2)$$

with

$$x = [(V/V_0)^{-2/3} - 1],$$

$$\alpha = \frac{3}{4}(B'_0 - 4),$$

and

$$\beta = \frac{3}{8}(B_0B''_0 + B_0'^2 - 7B'_0 + \frac{143}{9}).$$

$B$  is the bulk modulus,  $B'$  and  $B''$  are its first and second pressure derivatives; the subscript zero refers to values at normal pressure.

The fits to the data yield  $B_0 = 21.2 \pm 0.2$  GPa,  $B'_0 = 4.93 \pm 0.15$ ,  $B''_0 = -0.25 \pm 0.05$  GPa<sup>-1</sup>.

Another equation of state has recently been proposed by Vinet *et al.*<sup>13</sup> from an expression of the cohesive energy which was found to depend exponentially on the interatomic spacings. Only two parameters,  $B_0$  and  $B'_0$ , are then involved, and the equation of state takes the follow-

ing form:

$$P = 3B_0[(1-y)/y^2][\exp\delta(1-y)]$$

with  $y = (V/V_0)^{1/3}$  and  $\delta = 1.5(B'_0 - 1)$ . In these conditions, the bulk modulus and its pressure derivatives take the values  $B_0 = 21.44 \pm 0.05$  GPa and  $B'_0 = 5.1 \pm 0.15$ . We thus adopt for  $B_0$  the value 21.3 GPa, but for the different  $B'_0$  the meanings are not exactly identical and depend on the equation of state which is used.

One of the main results of this study was, first of all, the isotropic compression of  $2H\text{-CsCdBr}_3$ . In addition, it sustains a larger compression than NaCl without undergoing any phase change. The compression is so large that under high pressure the Cd-Cd distances are shorter than in cadmium metal at normal pressure but no evidence of a metallic behavior is then found.

Another important result was the emergence under pressure, above 5 GPa, of a diffraction line ( $d = 2.348$  Å at 5.7 GPa) which remained at the highest pressure; with decreasing pressure, this line vanished at about the same pressure without any noticeable hysteresis. The line whose intensity sharply increases with pressure and which could not be observed at lower pressures, actually is the (210) line. In the same way, another diffraction line, the (211), with  $d$  close to 2.1 Å also seemed to appear under pressure but it was weaker and possibly mixed with the strongest line from the gasket at the highest pressures.

All the lines observed at lower pressure remained clearly visible all along the investigated pressure range, and thus we tentatively attributed the increasing intensities of some lines to a change in the structure itself and not to a new structure. In order to test this hypothesis, we performed intensity calculations of the powder x-ray diagram. The only changes we allowed was a variation of the  $x$  parameter which gives the positions of the bromine atoms in the cell. We increased  $x$  from 0.166 to 0.190. This, indeed, accounted very well for the observed intensity variations. The intensity of the (210) line is increased fivefold and then it can be seen; a similar increase is observed for the (211) line which corresponds to  $d = 2$  Å and can overlap with the strongest line from the gasket. Furthermore, the intensity of the (102) line which is close to the strongest (201) line, also increases; this was actually detected as an enlarged width of the (201) line. All other lines showed minor intensity variations (see Table I).

## DISCUSSION

Generally, the phase changes induced by pressure lead to structures which do exist at normal pressure with larger cations. Under pressure, it is thus considered that the relative sizes of the cations with respect to the anions increase rather than decrease. This is also similar to the general increase of the cation coordination number under high pressure. Our above-mentioned x-ray results concerning the isotropic compressibility of  $\text{CsCdBr}_3$  and the shift of the bromine anions inside the cell, sustain this well-documented trend.

In  $2H\text{-CsCdBr}_3$ , the  $\text{CsBr}_3$  close-packed layers, in the

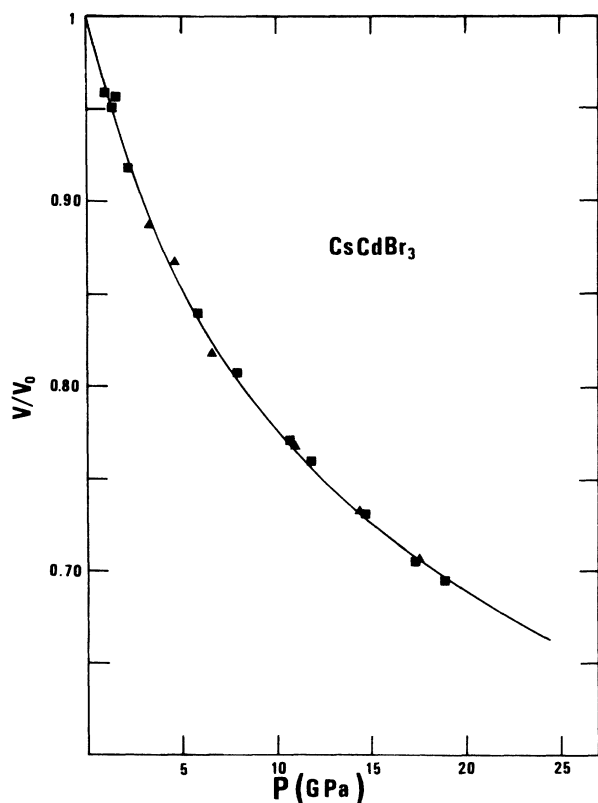


FIG. 2. Relative volume of  $2H\text{-CsCdBr}_3$  as a function of pressure (■: increasing pressure; ▲: decreasing pressure).

TABLE I. Observed and calculated powder diffraction patterns for 2H-CsCdBr<sub>3</sub> in the BaNiO<sub>3</sub>-type structure for molybdenum radiation. Unit-cell contents of the CsCdBr<sub>3</sub> perovskite (atom, point symmetry, coordinates, number of positions): Cs, 6m2, ( $\frac{1}{3}, \frac{2}{3}, \frac{3}{4}$ ), 2; Cd, 3m, (0,0,0), 2; Br, mm, ( $x, x, \frac{1}{4}$ ), 6. *S*: strong, *M*: medium, *W*: weak, *VW*: very weak. +Inc: overlap with line from the inconel gasket. +NaCl: overlap with line from the NaCl marker. \*: wide line (102+201 overlapping).

<i>P</i> =1.97 GPa		<i>x</i> =0.166			<i>P</i> =17.4 GPa		<i>x</i> =0.190	
<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>obs</sub>	<i>I</i> <sub>calc</sub>	<i>h k l</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>obs</sub>	<i>I</i> <sub>calc</sub>
3.745	3.758	<i>M</i>	23	1 1 0	3.444	3.469	<i>M</i>	32
3.280	3.260	<i>M</i>	14	0 0 2	2.956	2.957	<i>M</i>	16
	2.915		18	1 0 2		2.653	*	33
2.906	2.912	<i>S</i>	100	2 0 1	2.664	2.678	<i>S</i> *	100
	2.460		4	2 1 0	2.289	2.271	<i>VW</i>	17
2.309	2.303	<i>W</i>	45	2 0 2	1.996	2.107	<i>M</i> +Inc	47
	2.302		2	2 1 1	2.108	2.119	<i>W</i>	10
1.872	1.879	<i>W</i>	33	2 2 0	1.712	1.735	<i>W</i>	29
1.800	1.807	<i>VW</i>	26	2 0 3	1.647	1.648	<i>VW</i>	25
1.585	1.579	<i>W</i>	17	4 0 1	1.469	1.456	<i>M</i> +NaCl	13
	<i>a</i> =7.517 Å					<i>a</i> =6.939 Å		
	<i>c</i> =6.520 Å					<i>c</i> =5.914 Å		

sequence *ab*, are separated by Cd planes. The relative sizes of the ions are such that the bromine anions represent more than  $\frac{3}{4}$  of the volume. Therefore, the bulk compression properties are mostly due to these ions. As they become relatively smaller and smaller under pressure, they are able to come closer and closer in the CsBr<sub>3</sub> planes; this movement can be described by an increase of the *x* position parameter. A variation of *x* from 0.166 to 0.190 effectively accounted quite well for the experimental results as stated above. The effect of increasing this *x* parameter, at constant lattice cell (see Table II), is to increase the shortest Cd-Br distances and thereby enhance the size of the small (CdBr<sub>6</sub>)<sup>4-</sup> octahedra. The Cs-Br distances in the bromine planes practically remain constant while the Cs-Br out-plane distances are strongly reduced and become nearly equal to the in-plane distances (see Table II). The rhombododecahedral Cs<sup>+</sup> cages are then smaller but much more symmetrical, and the coordination of the cesium cation increases from (6+6) to 12. This increase of the *x* position parameter allows the *c* parameter to decrease more rapidly with pressure than without this shift of the bromine anions. Although no large deformation of the structure occurs, a slight decrease of 2% of the *c/aN* ratio from 0.438 to 0.430 is observed. This trend is consistent with the decrease of the *c/aN* ratio, which is observed with increasing density in

the polytypes, but in the case of CsCdBr<sub>3</sub> it still remains higher than the value found in BaMnO<sub>3</sub> at the phase transition (0.415).

The low value of the bulk modulus of CsCdBr<sub>3</sub>, *B*<sub>0</sub>=21.3 GPa, can be accounted for from the bulk modulus versus volume systematics. Anderson<sup>14</sup> has pointed out that

$$B_0 V_0 / S^2 Z_1 Z_2 = \text{const}.$$

In this expression *S* is the ionicity, less than one; it is close to 1 for halides and 0.7 for oxides. *Z*<sub>1</sub> and *Z*<sub>2</sub> are the formal charges of the cations. *V*<sub>0</sub> is the mean molar volume of an atomic pair; it is thus defined as *V*<sub>0</sub>=2(*d*<sub>0</sub>)<sup>-1</sup>*M*/*n*, where *M* is the mean atomic weight of a pair, *n* the number of atomic pairs, and *d*<sub>0</sub> the density in normal conditions. The constant, from published results, is close to 700 GPa cm<sup>3</sup>.

Application to CsCdBr<sub>3</sub> yields *V*<sub>0</sub>=41.3 cm<sup>3</sup> and thus *S*=0.793, a value between those found for halides or oxides, as could be expected because of the partly covalent Cd-Br bonding. The value of the bulk modulus of CsCdBr<sub>3</sub> is thus normal.

From oxides and silicates, Hazen and Finger<sup>15</sup> derived a generalized relationship which they also applied to halides, sulphides, selenites, tellurides, phosphides, ar-

TABLE II. Effect of increasing the *x* position parameter of the bromine atoms on the polyhedral distance (Å) at constant lattice cell (*a*=7.675 Å and *c*=6.722 Å at *P*=0; *a*=6.83 Å, and *c*=5.87 Å at *P*=20 GPa).

<i>x</i>	<i>d</i> (Cd-Br) (Å)	<i>d</i> (Cs-Br) (Å)		<i>d</i> (Br-Br) (Å)	<i>P</i>
		in Br plane	out Br plane		
0.166	2.77	3.84	4.03	3.85	
0.190	3.03	3.85	3.86	3.30	0
0.166	2.45	3.42	3.53	3.43	
0.190	2.68	3.43	3.39	2.94	20 GPa

senides, antimonites, and carbides:

$$(B_P d^3)/(S^2 Z_A Z_C) = 750 \pm 20 \text{ GPa } \text{Å}^3.$$

In this expression  $B_P$  is the polyhedral bulk modulus,  $d$  is the mean cation-anion distance,  $Z_A$  and  $Z_C$  are the formal anion and cation charges, and  $S$  is an empirical term for the relative ionicity of the bond, defined as 0.7 for  $R^{2+}$ -O bonds in oxides, 0.87 for halides. This relationship yields the bulk modulus of the various cation coordination polyhedra.

In the case of  $2H\text{-CsCdBr}_3$ , the cation-anion distances are very different:  $d_{\text{Cd-Br}} = 2.77 \text{ Å}$ ,  $d_{\text{Cs-Br}} = 3.96 \text{ Å}$ . Using  $S^2 = 0.75$ , as proposed for halides, the above relation leads to small and incompressible ( $B_0 = 53 \text{ GPa}$ ) Cd-Br face-sharing octahedra linked by large and soft ( $B_0 = 9 \text{ GPa}$ ) Cs-Br isododecahedra. In this compound, there is no possible polyhedra tilting and so this relation should allow for calculating the bulk compression. A value of about 12.5 GPa is then obtained, nearly two times smaller than the experimental result. The previous relation was stated to be only applicable when no polyhedral tilting occurred, but the present results show that, in addition, no change of the relative atomic positions in a given structure should occur; this furthermore restricts the range of application.

The smooth shift of the  $x$  position parameter of the bromine anions allows the Cd-Br distances to decrease much more slowly with pressure than the Cs-Br distances; this increases the compressibility of the Cd polyhedra along the  $c$  axis without appreciably changing the Cd-Br distance and reduces the compressibility of the Cs polyhedra. Otherwise, without a shift of the  $x$  parameter with pressure, important distortions in the structure would result and this was not observed.

The value of the first pressure derivative of the bulk modulus was calculated to be 4.93 when using Birch's equation of state to the second order. This value compares well with the value reported for NaCl, 5.7. Again, the elastic properties of  $2H\text{-CsCdBr}_3$  are very close to those of a typical fully three-dimensional ionic compound.

The pressure derivative of the bulk modulus and the macroscopic acoustic Gruneisen constant at normal pressure are connected through the relation  $\gamma_0 = B'_0/2 - \text{const}$ . This constant depends on the models and has values between 0 and  $\frac{5}{6}$ . For a Born-Mayer potential, this constant is equal to  $\frac{5}{6}$  which yields a  $\gamma_0$  value of 1.67, close to the optical values deduced from the Raman experiments, 1.2–2.0, as shown below.

The macroscopic Gruneisen constant of a solid decreases with volume in such a way that  $d \ln \gamma / d \ln V$  is equal to +1 as has been established from a continuum model;<sup>16</sup> the same trend was also obtained from an ionic model. This has been experimentally confirmed for example,  $d \ln \gamma / d \ln V \approx 1.3$ , for NaCl.<sup>17</sup> Actually, the variations of the Gruneisen constant are related to the volume, or to be more precise, mainly to the cation-anion distance:<sup>16</sup> with compression, the Gruneisen constant decreases with this distance but, at a phase transition, it increases because the shortest cation-anion distance then

increases with the coordination number.

In  $\text{CsCdBr}_3$  there is no discontinuous phase transition, but the x-ray-diffraction experiments performed under pressure show that the position of the bromine ions shifts inside the cell with pressure which induces an effect opposite to the lone volume compression for the Cd-Br distance in the  $(\text{CdBr}_6)^{4-}$  octahedra (see above). Thus, there are two competing effects which counteract, the volume compression and the shift of the bromine anions inside the cell. These opposite effects should give a slower variation of the Gruneisen constant with volume. Such a smaller variation with volume is consistent with the shifts of the Raman frequencies which have been determined as a function of pressure.<sup>6</sup>

Only five active Raman modes are allowed:  $1A_{1g} + 1E_{1g} + 3E_{2g}$ . The cadmium atom motion does not give rise to any active Raman mode; the  $E_{1g}$  and  $E_{2g}^b$  modes involve  $\text{Br}^-$  motions in the  $z$  and  $x$ - $y$  directions, respectively. The  $A_{1g}$  and  $E_{2g}^c$  modes are attributed to symmetric and antisymmetric breathing of the  $(\text{CdBr}_6)^{4-}$  octahedra in the  $x$ - $y$  plane; the  $E_{2g}^a$  mode only involves  $\text{Cs}^+$  ion displacements, perpendicular to the  $c$  axis. The line intensities showed different pressure variations: the intensities of the  $A_{1g}$  and  $E_{2g}^c$  modes remained constant with pressure, the intensity of the  $E_{2g}^a$  mode increases over the whole pressure ranges while the remaining lines  $E_{1g}$  and  $E_{2g}^b$  have decreasing intensities. No conclusive evidence concerning the presence of second-order phase transformations around 2 and possibly at 10 GPa could be reached from the pressure shifts of the Raman frequencies.<sup>6</sup>

With the present pressure-volume results, it is now possible to derive the variations of the Raman frequencies with volume (Fig. 3). These are very smooth, and there is no longer any discontinuous slope change. This comes from the large and highly nonlinear variation of the volume with pressure. Thus, there are no second-order transitions at 2 and 10 GPa.

In addition, from these results it is also possible to calculate the mode Gruneisen constants  $\gamma_i = -d \ln \sigma_i / d \ln V$  (Fig. 4). At normal pressure, their values are equal to 2 and 1.6 for the  $E_{1g}$  and  $E_{2g}^b$  modes, 1.4 for the  $A_{1g}$  and  $E_{2g}^c$  modes, and 1.2 for the  $E_{2g}^a$  mode. For a solid with bonds of only one type, the theoretical values of the Gruneisen constants are 2.2 for an ionic bonding and 1 for a covalent bonding. The values thus found are indeed in this range.

With increasing pressure, the Gruneisen constants of the  $A_{1g}$  and  $E_{2g}^c$  modes, as well as the intensities of these two modes, remain constant. The latter are actually attributed to the vibrations of the  $(\text{CdBr}_6)^{4-}$  octahedra whose dimensions remain essentially unchanged; actually, the corresponding mode Gruneisen constants remain nearly constant. The larger mode Gruneisen constants decrease slightly, from 1.6–2 down to 1.1–1.2; thus, they all become nearly equal indicating a much more symmetrical environment as already deduced from the shift of the bromine anions shown from the x-ray experiments. This is also confirmed by the intensity of the  $E_{2g}^a$  mode which increases with pressure, in opposition to the  $E_{1g}$

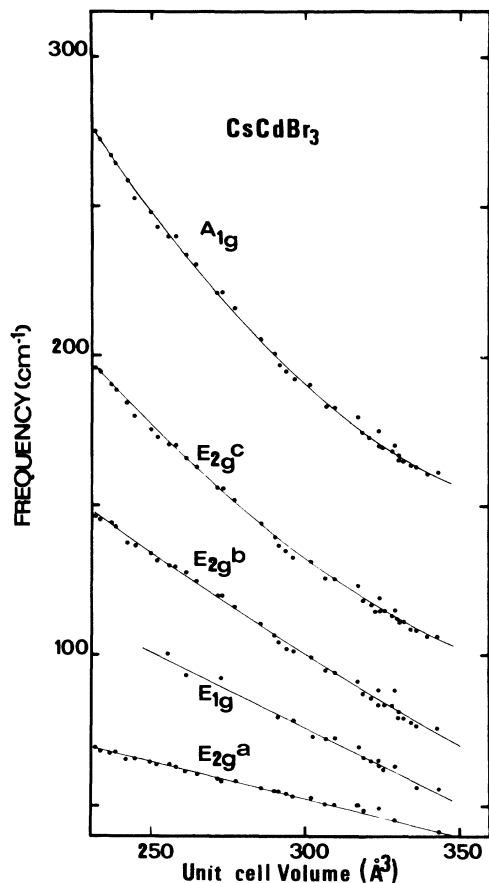


FIG. 3. Raman frequencies of  $2H\text{-CsCdBr}_3$  as a function of the lattice cell volume ( $\text{\AA}^3$ ).

and  $E_{2g}^b$  modes. Actually, the  $E_{2g}^a$  mode corresponds to the motion of the Cs atom which is perpendicular to the  $c$  direction, and which becomes larger as the environment becomes more symmetrical. Above 2 GPa, the volume variations become slower as the bulk modulus increases very rapidly, and the shift of the bromine anions is sufficient to make the Gruneisen constants to remain constant for all the modes: the mode Gruneisen constants do not further decrease with volume.

The Raman shifts and the x-ray-diffraction patterns under pressure are in very good agreement, and both indicate that the bromine anions move inside the lattice cell. However, it is only at 5 GPa that this displacement is sufficient to induce enough high intensities of some x-ray diffracted lines to be detected.

### CONCLUSION

$2H\text{-CsCdBr}_3$  has been studied by powder x-ray diffraction at room temperature as a function of pressure

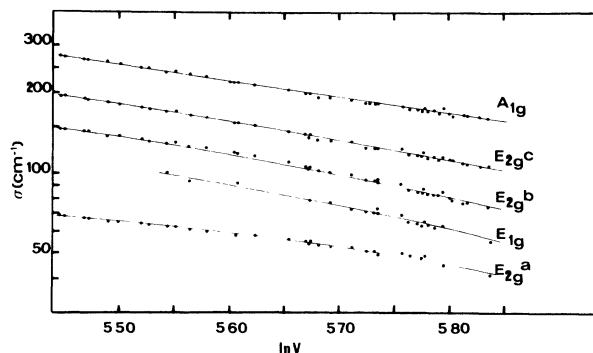


FIG. 4. Raman frequencies of  $2H\text{-CsCdBr}_3$  as a function of the cell volume ( $\ln\text{-ln}$  plot); the slopes are the Gruneisen constants of the different modes.

up to 20 GPa in a diamond anvil cell. No change of structure could be evidenced in this pressure range, although the volume reduction is quite large; the relative volume actually decreased down to 0.65 at 25 GPa. The bulk modulus, its first pressure derivative, and also its second pressure derivative of Birch's equation of state to the second order, have been derived from the volume compression.

The bulk modulus is low, 21.3 GPa, and is in excellent agreement with values derived from ionic compounds as a function of the mean atomic volume and the formal cation charges. The first pressure derivative is also in excellent agreement with those of usual three-dimensional ionic compounds. The bulk modulus of  $\text{CsCdBr}_3$  cannot be inferred from the polyhedral bulk moduli of the two cations, although there is no polyhedral tilting. The linear chains formed by the small face-sharing  $\text{CdBr}_6$  tetrahedra do not induce bulk unidimensional properties although the Cd-Cd distances are very short and give rise to unidimensional magnetic properties in  $\text{CsCdBr}_3:M^{3+}$  ( $M=\text{Cr, Ni, Fe, . . .}$ ). Actually, the  $c$  axis is as compressible as the  $a$  axis because the cation polyhedra undergo some deformations under pressure as the positions of the bromine anions shift inside the lattice cell. This is shown by the variations of relative intensities of the x-ray diffracted lines. No evidence of unidimensional behavior for the bulk elastic properties can be evidenced in  $\text{CsCdBr}_3$ , a typical linear-chain perovskite-type compound. The experimental pressure-volume experiments allowed us to calculate the mode Gruneisen constants from the pressure shifts of the Raman frequencies. These Gruneisen constants essentially remain constant above 4 GPa because of two competing effects, the volume shrinkage with pressure and the shift of the bromine anions inside the structure.

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