The Tll-type structure of the high-pressure phase of NaBr and NaI; pressure-volume behaviour to 40 GPa

The TlI-type structure of the high-pressure phase of NaBr and NaI; pressure–volume behaviour to 40 GPa

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Abstract. NaBr and NaI have been investigated as a function of pressure to 40 GPa at room temperature by angle-dispersive x-ray powder diffraction. In both compounds, a first order transition to an orthorhombic, TlI-type structure ($Cmcm$, $Z = 4$) occurs at around 30 GPa. The structure of both the high-pressure phases of NaBr and NaI was refined by the Rietveld method. It is a compact modification of the ambient B33 TlI structure in which the layers are now in contact with one another. The cation coordination number increases from six to seven at this phase transformation. This structure is a step in the phase transition sequence between the B1 and B2 structures. These phases of NaBr and NaI are the first confirmed examples of high-pressure phases with the TlI-type structure occurring in AX compounds. The bulk moduli and their first pressure derivatives have been determined for the B1-type phases.

1. Introduction

The pressure-induced transitions in the alkali halides have been extensively studied as these compounds are representative ionic crystals and numerous theoretical calculations have been aimed at determining their high-pressure structures and pressure-induced phase transitions. Under ambient conditions, all the alkali halides crystallize in the B1 structure (NaCl type), except CsCl, CsBr and CsI, which crystallize in the B2 (CsCl type) structure. Pressure favours the B1 to B2 transformation as the packing efficiency is greater in this structure, in which the coordination number has increased from 6 to 8. No pressure-induced transformations are known for the Li halides; in contrast, at 5 GPa, all the K, Rb, Cs halides have transformed to the B2 phase [1]. The sodium halides display an intermediate behaviour, as expected from their intermediate r_c/r_a ratios of their cation and anion radii. The B1–B2 transformation occurs at 27 GPa in NaF [2] and at around 29 GPa in NaCl [3]. A phase transformation to an undetermined, non-cubic structure was found to occur for both NaBr and NaI close to 30 GPa [2, 3]. The GeS-type structure (B16), in which the cation coordination number remains 6 as in the B1 phase, was proposed for NaI, but no structure refinement was performed [2]. The structures of these unusual, high-pressure phases in alkali halides are of interest to determine the sequences of phase transitions and the pathways in these most archetypal ionic compounds. We thus performed experiments in order to determine the structures of the high-pressure phase of these two sodium halides and to look for possible intermediate structures.

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2. Experiments

High-pressure experiments were performed using diamond anvil cells. Powdered NaBr or NaI (Alfa Products, stated purity greater than 99.99%) were mixed with less than 3 volume per cent TiC to absorb Nd:YAG laser radiation. The mixture containing NaI was heated at 300 °C for two days under primary vacuum to remove any hydrate. Only the B1 phases of the sodium halides were present as confirmed by Debye–Scherrer x-ray diffraction patterns. The sample and TiC mixtures were loaded in the 150–200 μm diameter holes of T301 steel gaskets, preindented to a thickness of 120 μm, along with ruby powder as a pressure calibrant in a nitrogen dry box. In order to avoid the formation of hydrates, no pressure-transmitting medium was added. The possible anisotropic stress components which could result were, however, expected to remain small as the bulk moduli of the two compounds are low [4]. Pressures were measured based on the shifts of the ruby R_1 and R_2 fluorescence lines [5]. They were always clearly separated in spite of the absence of a pressure-transmitting medium. Heating using a 50 W Nd:YAG laser was performed at several pressures above 20 GPa in order to accelerate the phase transition kinetics and reduce anisotropic stress.

X-ray diffraction patterns were obtained on an image plate (nominal pixel size: 50 μm) placed at distances of 116.99 ($\pm$0.03) mm from the sample using molybdenum radiation from a fine focus x-ray tube [6]. The incident beam was collimated to 130 μm by crossed slits. In order to increase the incident intensity, it was not fully monochromatic due to a reduced zirconium filtering; the intensity of the $K\beta$ radiation was 4% of the $K\alpha$ radiation. Exposure times were typically 24 or 60 hours. The observed intensities were integrated over the whole pattern as a function of 2θ to give conventional one-dimensional diffraction profiles. The diffraction angles thus obtained are absolute values and do not result from the use of a standard. Rietveld refinements for the high-pressure phase were performed using the program Fullprof [7].

3. Results

The phase transition from the B1 phase began at 35 GPa for NaBr and was not complete at 40 GPa; it began at 27 GPa for NaI and was complete at 31 GPa. For the B1 phase of NaBr, the 111, 200, 311, 222, 400 and 420 diffraction lines were observed and the 220 line was observed only above 5 GPa, where it began to be separated from a gasket line. Fewer diffraction lines could be observed for NaI due to high absorption by the sample which resulted in the presence of diffraction lines by the gasket. Diffracted lines by TiC, added to permit heating under pressure, were never observed due to the low content and low diffraction scattering factors as well below or above the pressure transitions of both compounds.

The high-pressure data for the B1 phases have been analysed taking account of the presence of possible anisotropic stress components, due to the absence of a pressure-transmitting medium. In this case, a dependence of the cell parameter as a function of *hkl* [8] should be observed. No dependence was found for NaBr below 5 GPa; from 7 to 27 GPa, the same pressure dependence was observed, $a(hkl) = a(h00) + 0.04\Gamma(hkl)$ where $\Gamma(hkl) = (h^2k^2 + k^2l^2 + l^2h^2)/(h^2 + k^2 + l^2)^2$. For NaI, no difference between the cell parameters deduced from the 200 or 400 and 111 or 222 line ($\Gamma(hkl)$ minimum and maximum, respectively) was observed up to 20 GPa; above this pressure, the difference increased to 0.02 Å, while for NaBr the maximum difference amounted to 0.015 Å. This difference in the cell parameters as deduced from different diffraction lines resulted in

a volume difference of less than 1%; it persisted upon decreasing pressures down to 4 GPa. The smaller volume was systematically taken ($\Gamma(hkl) = 0$ for $h00$ lines). In the orthorhombic high-pressure phase, the anisotropic stress component could not be taken into account. The pressure variations of the cell parameters of NaBr and NaI are displayed in figures 1 and 2, respectively. The relative volumes of NaBr and NaI are plotted as a function of pressure in figures 3 and 4, respectively. The transition from the B1 to the B33 orthorhombic high-pressure (TlI-type, see below) structure is definitely first order: at the transition, there is a sudden volume decrease, 6.4 and 5.1% for NaBr and NaI, respectively; a pressure range of hysteresis is also associated to this transition.
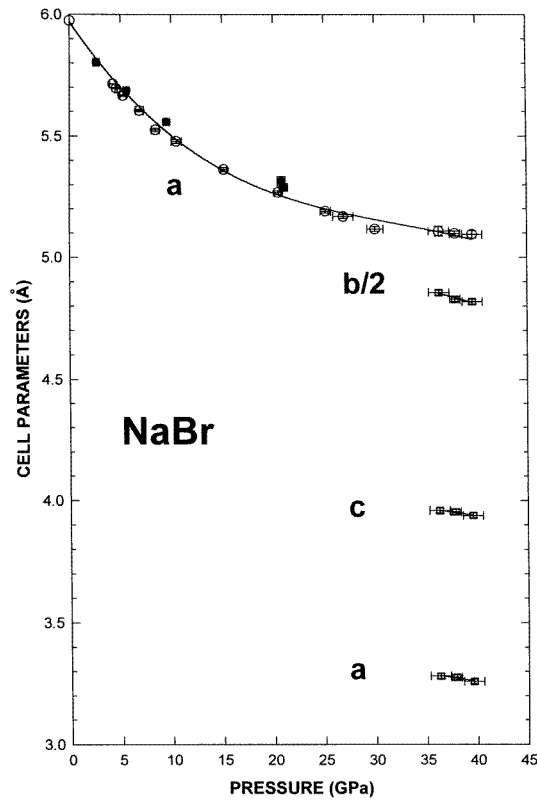
Figure 1. Cell parameters of NaBr as a function of pressure. (Open symbols: increasing pressure; filled symbols: decreasing pressure. Circles: cubic B1 phase; squares: orthorhombic B33 phase. The standard deviations are indicated.)

The P–V data for the B1 phases have been analysed using the Birch–Murnaghan equation of state [9]:

$$P = 1.5B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}][1 + 0.75(B_0' - 4))((V/V_0)^{-2/3} - 1)]$$

where V_0, B_0 and B_0' are the volume, the bulk modulus and the first pressure derivative of the bulk modulus at ambient pressure, respectively. The bulk modulus and its first pressure derivative were simultaneously refined by the least-squares method. For NaBr and NaI, the results are $B_0 = 21.0(14)$ GPa, $B_0' = 5.3(3)$ and $B_0 = 16.0(13)$ GPa, $B_0' = 5.3(4)$, respectively. These values are in excellent agreement with those previously reported [2]
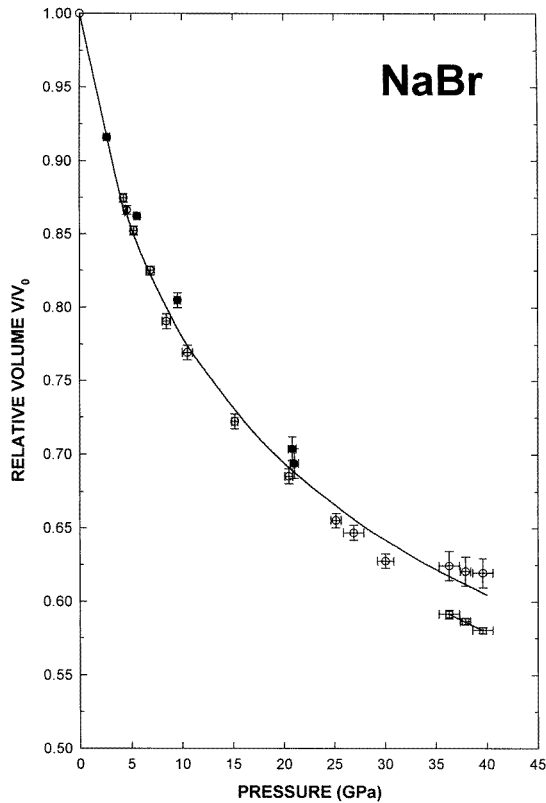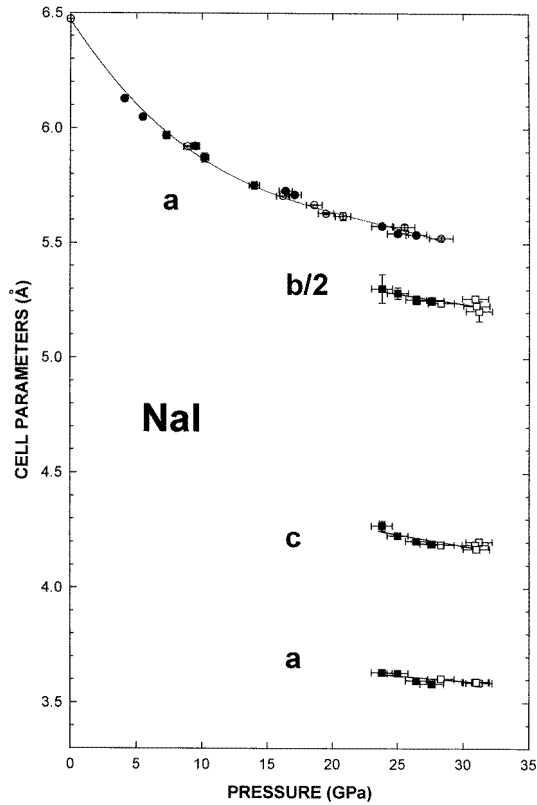
Figure 2. Cell parameters of NaI as a function of pressure (legend as for figure 1).

and with the values 21 and 17 GPa obtained from the bulk modulus–volume relationship $B_0(\text{GPa}) = 900 Z_a Z_c S^2 / V_M$ where Z_a and Z_c are the formal anion and cation charges, V_M (cm^3) the molar volume per ion pair and S^2 the ionicity parameter which is 0.75 for halides [10].

4. The structure of the high-pressure phase

Rietveld refinement of the structure of NaBr was performed at 39.6 GPa (figure 5) after heating under pressure in order to increase the amount of the high-pressure phase by accelerating the kinetics of the phase transformation. This heating was very effective as the content of the B1 phase decreased from 32% to about 7%. Two possible structures were considered at the beginning of the refinements: the GeS-type (B16) (orthorhombic, *Pnam*, $Z = 4$) and the TlI-type (B33) (orthorhombic, *Cmcm*, $Z = 4$). Starting with the space group *Pnam* and atomic positions as observed in GeS, the atomic positions converged toward significantly different values, corresponding to the TlI-type structure. Final refinements were thus made using the space group *Cmcm* which is a supergroup of *Pnam*. The same results were obtained for NaI (figure 6) for which the relative diffracted line intensities are very different as the scattering factor of iodine is much larger than that of bromine. For NaBr, the refinement included two phases: B1 and B33; for NaI the refinement included three phases: B33 NaI, ε-iron (from the gasket) and alumina (from ruby, the pressure

Figure 3. Relative volume of NaBr as a function of pressure (same symbols as for figure 1). The solid line for the B1 phase represents the Birch–Murnaghan equation of state with the parameters indicated in the text.

Table 1. Cell constants, atomic positions, agreement factors (%) and polyhedral cation–anion distances obtained from Rietveld refinements of NaBr and NaI in the high-pressure phase (*Cmcm*, $Z = 4$;. Na, I or Br on 4c sites $(0, y, 1/4)$.

	NaBr	NaI
P (Gpa)	39.6	31.0
a (Å)	3.261(1)	3.592(2)
b (Å)	9.620(4)	10.432(7)
c (Å)	3.942(1)	4.175(1)
y (Na)	0.4172(8)	0.4163(4)
y (Br or I)	0.1356(6)	0.1401(6)
R_B (%)	2.1	3.2
R_P (%)	11.8	7.6
R_{WP} (%)	9.4	6.6
Na–(Br or I)	2.608(2) × 4	2.816(1) × 4
(Å)	2.660(8) × 2	2.881(3) × 2
	2.709(10) × 1	2.945(4) × 1

marker added as a powder to the sample; it was not detected in the experiments with NaBr due to slight differences in the sample loading). Scale factors, phase amounts, line shape
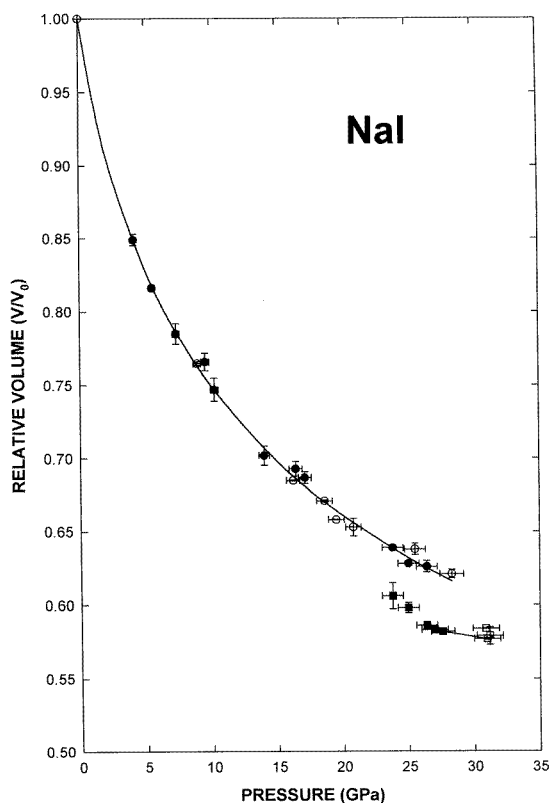
Figure 4. Relative volume of NaI as a function of pressure (legend as for figure 3).

parameters, overall thermal parameters, cell constants, atomic positions and the preferred orientation parameter (weak preferred orientation along [001] was detected, and a preferred orientation along this direction was taken into account in the refinement) were refined for the low- and high-pressure phases. The atomic positions, the cell parameters and the Na–X distances are given in table 1. The metal cations are surrounded by seven anions which lie at equal distances to within 4%. Thus, the coordination number is truly seven. The coordination polyhedron is a monocapped prism where the cation is pushed toward the square face of the prism. At ambient, the B33 TlI-type structure is a layered structure in which the cation coordination number is $5 + 2$: two of the anions which lie in the cation plane are 15% further away than the four anions lying in the square base of the prism and the remaining anion in the cation plane. The anion–anion distance between adjacent layers is 10% larger than the largest anion–anion intralayer distance. The TlI-type structure observed under pressure for NaI or NaBr is slightly different. It is a compact structure; the interlayer anion–anion distance, 3.26 Å, is shorter than the intralayer anion–anion distances, 3.37 and 3.59 Å, for NaBr. At the transition, the volume decrease is due to the greater packing efficiency induced by the increase in the coordination number from 6 to 7. In addition, the minimum Na–Na and Br–Br distances decrease from 3.60 Å in the B1 structure to 2.53 and 3.26 Å, respectively, in the B33 structure. The transition is accompanied by an increase in the average Na–X distance; for example, the Na–Br distances increase from 2.546 Å ($\times 6$) in the NaCl phase to 2.608 ($\times 4$), 2.660 ($\times 2$) and 2.709 ($\times 1$), giving an average of
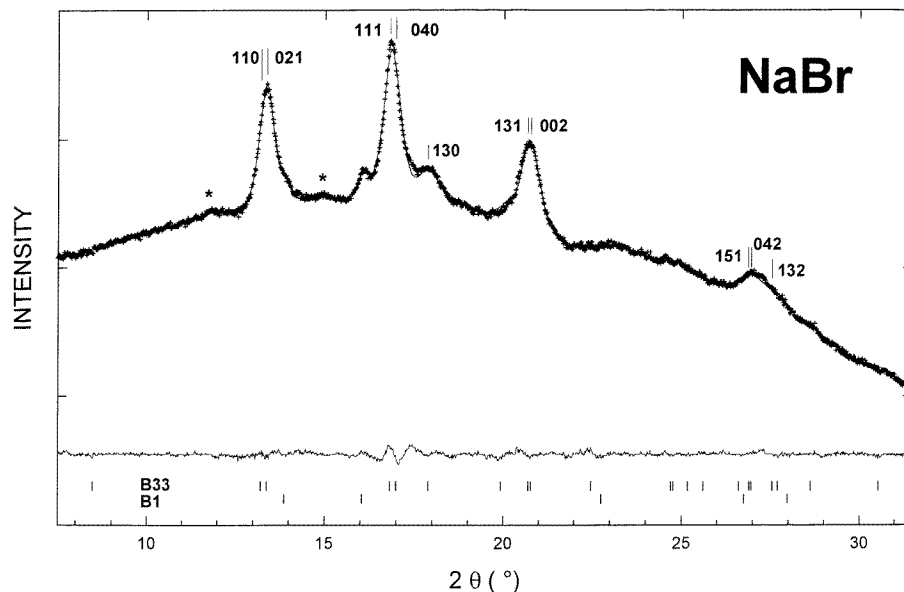
Figure 5. Experimental (symbols) and calculated (solid line) profiles from Rietveld refinement of NaBr at 39.6 GPa in the B33 structure (see table 1); the main diffracted lines ($I/I_0 > 10\%$) are indexed in the pattern. The difference profile in shown on the same scale; vertical bars indicate the positions of diffraction peaks for Kα radiation; the intense diffraction lines for the Kβ radiation are indicated by asterisks.

2.637 Å, in the B33 TlI-type structure. For NaI, similar results were obtained (see table 1). No further transition to a B2 structure was observed in the pressure range investigated for both compounds. In the B33 structure, the coordination number is 7, intermediate between those of the B1 and B2 structures and this B33 structure is an intermediate step between the B1 and the B2 structures.

This is the first demonstration by structure refinement of the occurrence of a TlI-type structure induced by high pressure in alkali halides, and more generally among the AX compounds. This phase transformation from the B1 to the B33 structure is not a progressive deformation through an intermediate structure such as B16. The B1 and B33 structures are related [11] by a simple slip on alternate (010) layers (figure 7); a second slip would yield the B2 structure.

At ambient, the occurrence of the B33 structure is not common among the AX or AX-like compounds: TlI excepted, this structure is only observed for NaOH and CsOH. This structure is observed only for materials with highly polarizable or non-spherical anions, or cations with a particular electronic structure (electron lone pair on the Tl^{+1} cation, for example). The B33 structure is a layered structure at ambient which transforms easily under pressure: TlI undergoes a structure change to the B2 structure at 0.3 GPa [1], NaOH and CsOH transform below 1 GPa to orthorhombic or monoclinic structures [12].

Under high pressure, the occurrence of the B33 structure is also rare. It has been reported for AgCl and the topological transformation from the B1 structure to the B2 structure has been described [13]: AgCl passes first through a KOH-type (monoclinic distortion of the NaCl structure) followed by the B33 structure prior transformation to the B2 structure [13]. The existence of a high-pressure B33 structure was also proposed for NaSH [14] where no
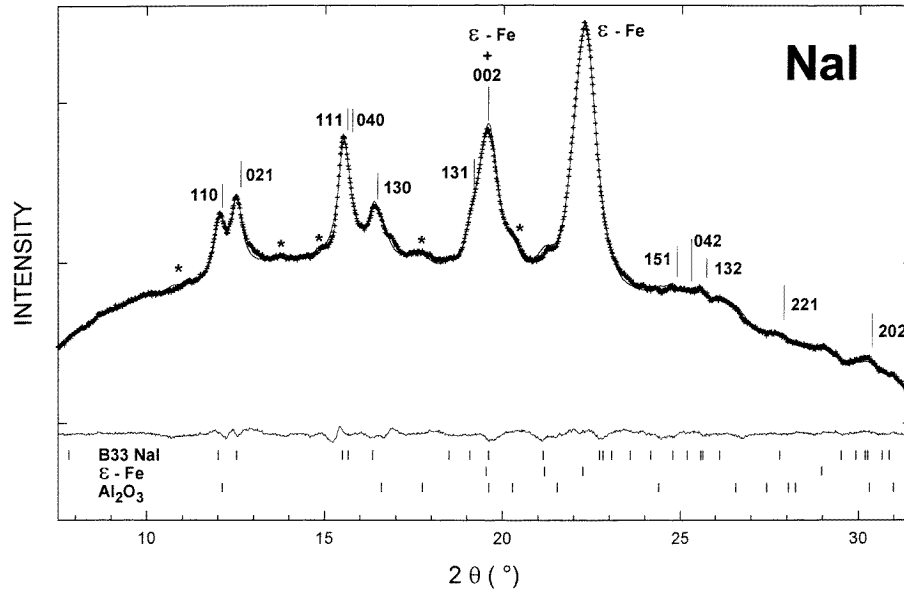
Figure 6. Experimental (symbols) and calculated (solid line) profiles from Rietveld refinement of NaI at 31 GPa in the B33 structure (see table 1); the main diffracted lines ($I/I_0 > 10\%$) are indexed in the pattern. The difference profile in shown on the same scale; vertical bars indicate the positions of diffraction peaks for Kα radiation; the intense diffraction lines for the Kβ radiation are indicated by asterisks; lines from the gasket are visible (they lie in an angular region where a low number of peaks from the B33 NaI phase are present; a small amount of alumina due to the powdered pressure marker is present).

second transformation to the B2 structure was observed up to 20 GPa. KSH also undergoes a sequence of pressure induced transitions similar to the phase sequence B1–B33–B2, but all the structures are slightly distorted [14]. The compounds SnTe, PbS, PbSe and PbTe crystallize with the B1 structure at ambient. PbS and PbSe transform under pressures of 2.2 and 4.5 GPa to an orthorhombic structure, which is probably of the B33 type [15] while PbTe [15] and SnTe [16, 17] transform at 6 GPa into a structure which is probably of the B16 type. All these chalcogenides undergo a second phase change between 13 and 32 GPa to a B2 structure. The transformation from the B1 phase to the proposed B33 phase has a small volume decrease of about 1%, while the transformation to the B2 structure occurs with a volume jump of 3–5%. In no case has the proposed B33 structure been refined and the evidence of such a structure, especially for chalcogenides, needs to be more firmly established. The II–VI and III–V semiconductors, which are zinc-blende structured at ambient, transform under high pressure into an orthorhombic structure; the space group is *Cmcm* for the II–VI semiconductors and probably also for the III–V semiconductors. In both cases, the orthorhombic structure is a slight distortion [18] of the lower-pressure B1 structure and is not of the B33 type. CuI [19] also adopts a distorted NaCl structure with the *Cmcm* symmetry under pressure. A structure of the CrB type (anti-TlI-type) was proposed for the high-pressure phases of CsH [20] and RbH [21] which transform at lower pressures from the B1 structure to the B2 structure. However, no structure refinements were performed. The appearance of such a high-pressure structure with a cation coordination number lower than that observed at lower pressure needs to be confirmed by neutron diffraction.
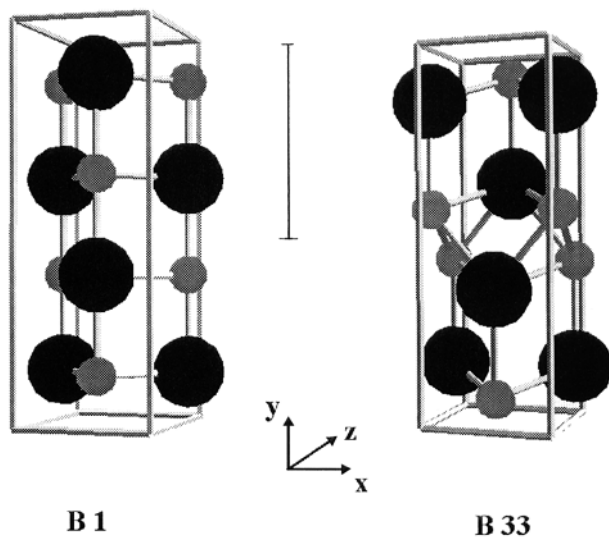
Figure 7. Perspective view of the B1 and B33 structures in the *Pnam* setting (the *Pnam* space group is a common subgroup to the $Fm\bar{3}m$ and *Cmcm* groups); the latter is obtained by a simple slip on alternate (010) layers. The layers indicated by the vertical bar slip by $a/2$.

Among the alkali halides, only NaBr and NaI adopt the B33 structure under pressure; this structure is compact and is an intermediate step prior transformation to the B2 structure. This high-pressure structure is thus found for the alkali halides where the ratio r_c/r_a is the lowest (this ratio is still lower for the Li halides, but no pressure-induced transition is yet known). Among the AX compounds, AgCl appears to undergo the B1 to B33 structure change; the ratio r_c/r_a is slightly larger; however, the presence of the d orbitals of the cation probably modifies the stability range of this structure type. In the case of AX-like compounds, NaSH and KSH also undergo this phase transition. Larger pressure ranges of stability are observed for compounds which have a deformable anion.

5. Conclusion

In contrast to all other alkali halides, which undergo a B1- to B2-type phase transition under pressure, NaBr and NaI transform from the B1-type to a B33 TlI-type structure. The high-pressure structures of both compounds have been refined by Rietveld analysis of the *in situ*, angle dispersive x-ray powder diffraction data. These are the first examples of TlI-type phases under pressure confirmed by structure refinements. In contrast to the ambient-pressure layered B33 structure, the TlI-type structure observed under high pressure is compact and the cation–anion distances are such that the cation coordination number is seven. This structure is thus an intermediate step between the B1 and B2 structures. The transformation is first order and no progressive distortion of the cubic B1 cell was observed. The transformation occurs by a simple slip on alternate (010) layers. This orthorhombic TlI-type structure is an important step in the phase transition sequence of the AX compounds under pressure which follows the usual trend of increasing coordination number. Calculations of pressure-induced transitions in AX compounds, especially Li halides, with the B1 structure at ambient should consider the possible presence of this

intermediate TlI-type structure under high pressure. The bulk moduli of the B1 phases of NaBr and NaI are in agreement with bulk modulus–volume systematics.

References

[1] Tonkov E Yu 1992 *High Pressure Phase Transformations, a Handbook* (London: Gordon and Breach)
[2] Sato-Sorensen Y 1983 *J. Geophys. Res.* **88** 3543
[3] Yagi T, Suzuki T and Akimoto S 1983 *J. Phys. Chem. Solids* **44** 135
[4] Anderson O L 1972 *The Nature of the Solid Earth* ed E C Robertson (New York: McGraw-Hill)
[5] Mao H K, Bell P M, Shaner J W and Steinberg D J 1978 *J. Appl. Phys.* **49** 3276
[6] Léger J M, Haines J and Pereira A S 1997 *Proc. 16th Int. High Pressure AIRAPT Conf. (Kyoto, 1997)* at press
      Haines J and Léger J M 1997 *Phys. Rev.* B **55** 11 144
[7] Rodriguez-Carvajal J 1990 *Satellite Meeting on Powder Diffraction, 15h Conf. Int. Union Crystallogr. (Toulouse)* p 127
[8] Singh A K and Balasingh C 1977 *J. Appl. Phys.* **48** 5238
[9] Birch F 1947 *Phys. Rev.* **71** 809
[10] Hazen R M and Finger L W 1982 *Comparative Crystal Chemistry* (New York: Wiley)
[11] Hyde B G, Andersson S, Bakker M, Plug C M and O'Keeffe M 1981 *Prog. Solid State Chem.* **12** 273
[12] Otto J W and Holzapfel W B 1995 *J. Phys.: Condens. Matter* **7** 5461
[13] Kusaba K, Syono Y, Kikegawa T and Shimomura O 1995 *J. Phys. Chem. Solids* **56** 751
[14] Haines J and Christy A G 1992 *Phys. Rev.* B **46** 8797
[15] Chattopadyay T, Werner A and von Schnering H G 1984 *Revue Phys. Appl.* **19** 807
[16] Murata K, Onodera A, Fujii Y *et al* 1985 *Solid State Physics under Pressure* ed S Minomura (Tokyo: KTK) p 141
[17] Kabalkina S S, Serebrjana N R and Malyuhitskaya Z V 1980 *High Pressure Science and Technology, Proc. 7th Int. High Pressure AIRAPT Conf. (Le Creusot, 1979)* vol 1, ed B Vodar and Ph Marteau (Oxford: Pergamon) p 566
[18] McMahon M I and Nelmes R J 1996 *Phys. Status Solidi* b **198** 389
[19] Hofmann M, Hull S and Keen D A 1995 *Phys. Rev.* B **51** 12 022
[20] Ghandehari K, Luo H, Ruoff A L, Trail S S and Disalvo F J 1995 *Mod. Phys. Lett.* B **9** 1133
[21] Ghandehari K, Luo H, Ruoff A L, Trail S S and Disalvo F J 1995 *Phys. Rev. Lett.* **74** 2264