Phase Transitions in $CsSnCl_3$ and $CsPbBr_3$. An NMR and NQR Study

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The phase transitions in $CsSnCl_3$ and $CsPbBr_3$ have been studied by X-ray powder diffraction, by ^{81}Br-NQR and by ^{1}H-, ^{119}Sn-, and ^{113}Cs-NMR. At room temperature in air $CsSnCl_3$ forms a hydrate which can be dehydrated to the monoclinic phase II of $CsSnCl_3$. The high temperature phase I has the Perovskite structure, as the X-ray and NMR experiments show. The three phases of $CsPbBr_3$, known from literature, have been corroborated. The results are discussed in the framework of the group ABX_3, A = alkalimetal ion, B = IV main group ion, and X = Halogen ion.

Introduction

The phase transitions of solids ABX_3 with the cubic Perovskite type structure as the high temperature phase have been widely investigated within the last 40 years. There is a large family of ABX_3 compounds, in which X is a halogen (F, Cl, Br, I). Out of this family, the compounds with B = group IV element (Pb, Sn, Ge) form an interesting subgroup. Here, we focus on $B = Sn^{2+}$ and Pb^{2+}; out of these compounds, the Cesium salts have attracted considerable attention in the last 20 years.

In case of $CsSnCl_3$, the low temperature phase (phase II) is monoclinic, space group $P2_1/c$, $Z = 4$. It transforms at 380 K, and the high temperature phase (phase I) has the Perovskite-type crystal structure, space group O_h^1-Pm3m; $Z = 1$ [1]. There is some discrepancy in the literature about the reversibility of the phase transition and the structure of phase I of this compound. Poulson and Rasmussen [1] describe the transformation as an irreversible one. Scaife et al. [2] found that traces of water make the back transformation cubic → monoclinic possible and infer that water has only a catalytic effect on the phase transition. In [1] not all the observed X-ray powder diffraction lines of phase I could be indexed even by assuming two cubic lattices with cell lengths $a = 392$ pm and $a = 367$ pm, respectively. Both lattice constants are too small to adapt the Perovskite type structure, since the sum $2r(Sn^{2+}) + 2r(Cl^-) = 548$ pm, where r is the ionic radius of the concerned atom ($r(Sn^{2+}) = 93$; $r(Cl^-) = 181$ pm). Barrett et al. [3] reinvestigated phase I of $CsSnCl_3$ and accounted for all the X-ray diffraction lines with $a = 556$ pm as the lattice constant of the cubic unit cell.

$CsPbBr_3$ crystallizes in two forms. One is white and the other is orange coloured. The white form, at room temperature, belongs to the orthorhombic crystal system [4], space group D_{2h}^{16}-Pnma, $Z = 4$, and it undergoes an irreversible phase transition at 403 K into the second form. The second form is orange coloured. From the temperature dependence of the X-ray powder photographs of the orange form Møller [5] has shown that above 403 K $CsPbBr_3$ is cubic. At 403 K it is tetragonal, and a monoclinic structure ($a = b = 1165.4$, $c = 1178.2$ pm; $\gamma = 89.65°$) is found at room temperature. Cola et al. [6] have confirmed these cell constants. Therefore, a minimum of four phases are known for $CsPbBr_3$. In the following we distinguish the high temperature phase, phase I cubic, a "middle" temperature phase II which is tetragonal, and the monoclinic low temperature phase III. The white form is phase IV.

Through neutron diffraction and optical microscopic observations Hirotsu et al. [7] confirm both phase transitions in $CsPbBr_3$, I ↔ II and II ↔ III, and they characterize the transition at 361 K as of second order and the one at 403 K as of first order. These experiments unravel the mechanism of the phase transformations and they deduce the crystal structures of the lower symmetry phases from the symmetry of the condensing phonon modes. They infer that above 403 K, $CsPbBr_3$, phase I, has Perovskite-type

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structure, space group O_h^1-Pm3m, $Z=1$. As the temperature is reduced, the phonon mode M_3 becomes soft. At 403 K it is condensed. Between 361 ad 403 K, phase II, $CsPbBr_3$ has tetragonal structure, space group D_{4h}^5-P4/mbm, $Z=2$. At 361 K the phonon mode R_{25} is condensed and the room temperature phase, phase III, has orthorhombic symmetry, space group D_{2h}^{16}-Pmbn, $Z=4$.

Gesi et al. [8] studied the pressure dependence of the dielectric constant in order to understand the effect of the pressure on the phase transitions. They predicted that the volume contraction makes the R_{25} mode less stable. Hirotsu et al. [9] measured the sound velocities in this compound around 361 K and 403 K and related them to the elastic constants in each phase.

Volkov et al. [10] have carried out nuclear quadrupole resonance (NQR) measurements on ^{79}Br and ^{81}Br in the orange form of $CsPbBr_3$. They report four NQR signals between 77 K and 167 K, three between 167 K and 300 K, two between 300 K and 403 K, and no signal above 403 K. From a straight forward interpretation of this experiment the existence of four solid phases of $CsPbBr_3$ must be assumed.

In the following we report our studies on the phases I and II of $CsSnCl_3$ by X-rays and nuclear magnetic resonance (NMR), ^1H-, ^{119}Sn-, ^{133}Cs-NMR, and for $CsPbBr_3$ the temperature dependences of the ^{81}Br-NQR on polycrystalline material and an ^{133}Cs-NMR single crystal study.

Experimental

The Materials, Preparation

The starting materials CsCl (>99%), CsBr (>99%), and anhydrous $SnCl_2$ (>98%) were from Fluka AG, Switzerland and $PbBr_2$ from Merck AG, Darmstadt, Germany.

$SnCl_2$: It was dried over P_2O_5 under vacuum. About ten zones (solid-melt-solid) were passed through the commercial premelted $SnCl_2$, using a home made zone refining setup. The refined material was colourless, transparent and melted at 519 K. This compound is very sensitive to moisture and therefore was handled under the cover of dry nitrogen gas.

$CsSnCl_3$: We prepared $CsSnCl_3$ in three different ways: (a) by dissolving stoichiometric amounts of the constituents, CsCl and $SnCl_2$, in a hot solution of glycerol. Slow cooling of the solution gave colourless, needle shaped crystals. The material thus obtained was kept over P_2O_5 in a desiccator. (b) By fusing together stoichiometric amounts of dry constituents in a pyrex tube under vacuum. The material thus prepared has a light yellow colour. Ten zones were passed through this material and it was kept in a dry box after purification. Within several weeks it lost its yellow colour and turned white. (c) Stoichiometric amounts of CsCl and $SnCl_2$ were dissolved in a minimum volume of warm water, free of dissolved oxygen. White coloured crystals were obtained on slow cooling. The crystallization was carried out under the cover of oxygen free nitrogen gas. The material thus prepared turned out to be a hydrate. We shall call the products lot (a), (b), and (c), respectively.

$CsPbBr_3$: It was prepared by fusing stoichiometric amounts of the constituents, CsBr and $PbBr_2$, in a vycor tube under vacuum. The material so prepared is always orange coloured. The single crystal of $CsPbBr_3$ was grown by Bridgman crystal growth technique with an upward temperature gradient of 10 K/cm. $CsPbBr_3$ was sealed in a vycor tube of 14 mm inner diameter which was lowered at the rate of 2 mm per hour. The top of the boule contained some impurities and was removed.

The NMR and NQR measurements were carried out using a commerical Bruker CXP 200 spectrometer with homebuilt probe circuits. In the region of the phase transition, for the ^{81}Br-NQR a pulse-echo technique has been applied to observe the broad lines of about 70 kHz linewidth. In all other cases a single pulse has been applied, and the FID has been Fourier transformed to obtain the spectra.

Results and Discussion

$CsSnCl_3$

It appears that the observations regarding the reversibility of the phase transition in $CsSnCl_3$ are based only on the visual observations of the colour of this material. Phase I is light yellow and phase II is white. The material prepared, following procedure (c), is also white. Crystal structure determination by X-rays shows that it is a hydrate and has the formula $4CsSnCl_3 \cdot H_2O$, orthorhombic, space group D_{2h}^{17}-Cmcm, $Z=4$ (crystal structure to be reported). On heating, $4CsSnCl_3 \cdot H_2O$ releases water of crystallization and goes to the yellow form.

It is true that traces of water bring phase I back to phase II (the so known back transformation). In order

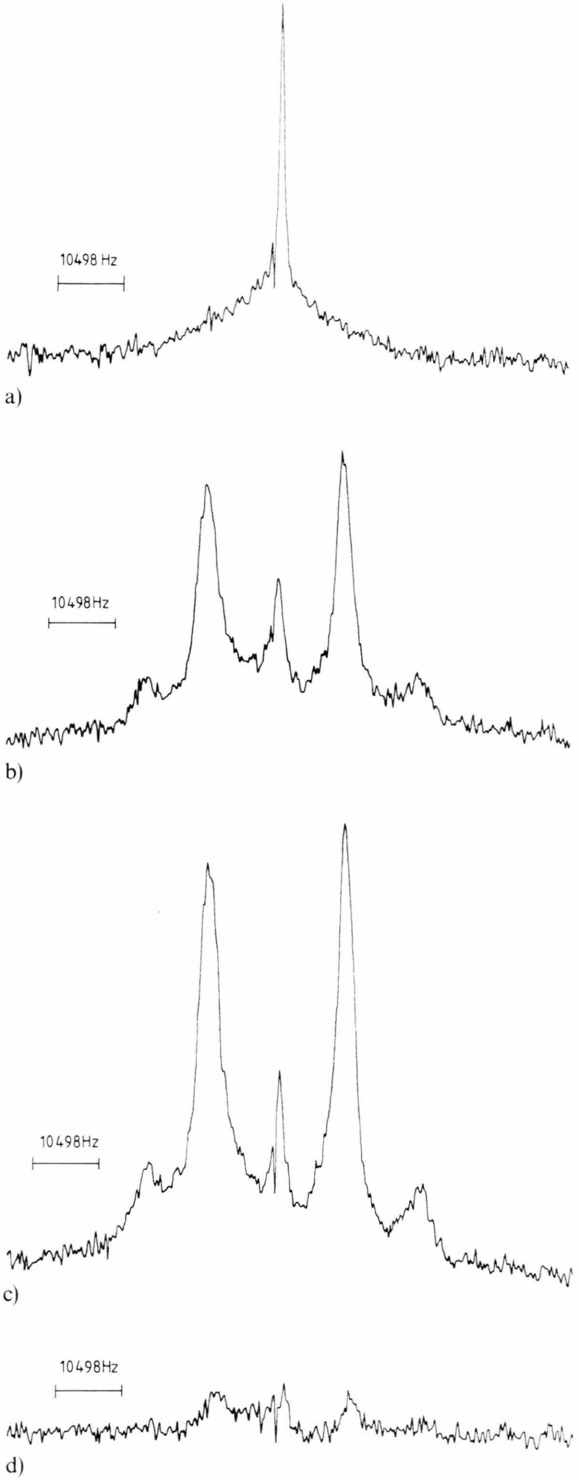

Fig. 1. Proton NMR spectrum of (a) $CsSnCl_3$ from lot a, (b) $CsSnCl_3$ exposed to the atmosphere, (c) $4\,CsSnCl_3 \cdot H_2O$, and (d) sample lot d pumped for 30 minutes at 323 K.

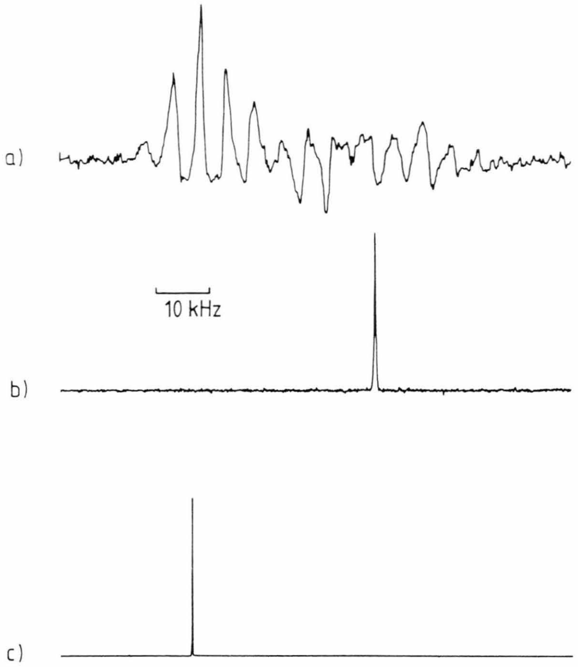

Fig. 2. (a) ^{119}Sn NMR-spectrum of the LT-phase, (b) and (c) NMR-spectra of ^{119}Sn and ^{133}Cs, respectively, of the metastable phase I of $CsSnCl_3$ taken with MAS-technique. $B_0 = 4.7$ T, $T = 296$ K.

to examine the question: Is water acting as a catalyst in the transformation phase I → phase II or is the transformation under the influence of water vapour phase I → $4\,CsSnCl_3 \cdot H_2O$, phase I was exposed to the atmosphere and left until it turned white. In the following we shall refer to it as lot (d).

We have carried out X-ray investigations on four samples, using a Guinier type camera, Cu $K\alpha_1$ radiation. Sample 1 was prepared from the material lot (a), sample 2 from the material lot (b), sample 3 from lot (d) and sample 4 from the material crystallized from water (lot (c)) which is known to be a hydrate. X-ray pictures from samples 1 and 2 were identical, from samples 3 and 4 were similar. Picture from sample 1 has no resemblance to either of the pictures 3 or 4.

Next we prepared four samples for NMR investigations, from the same materials as used for the X-ray diffraction. Sample 1 from lot (a), sample 2 from lot (d), sample 3 from lot (c) and sample 4 from lot (d) pumped for 30 minutes at 323 K. The four samples were of identical size and weight. Figures 1 a–d show the proton NMR spectra thus obtained. The first sample, Fig. 1 a, has no water. The central peak (proton peak) is due to an absorbed proton containing mate-

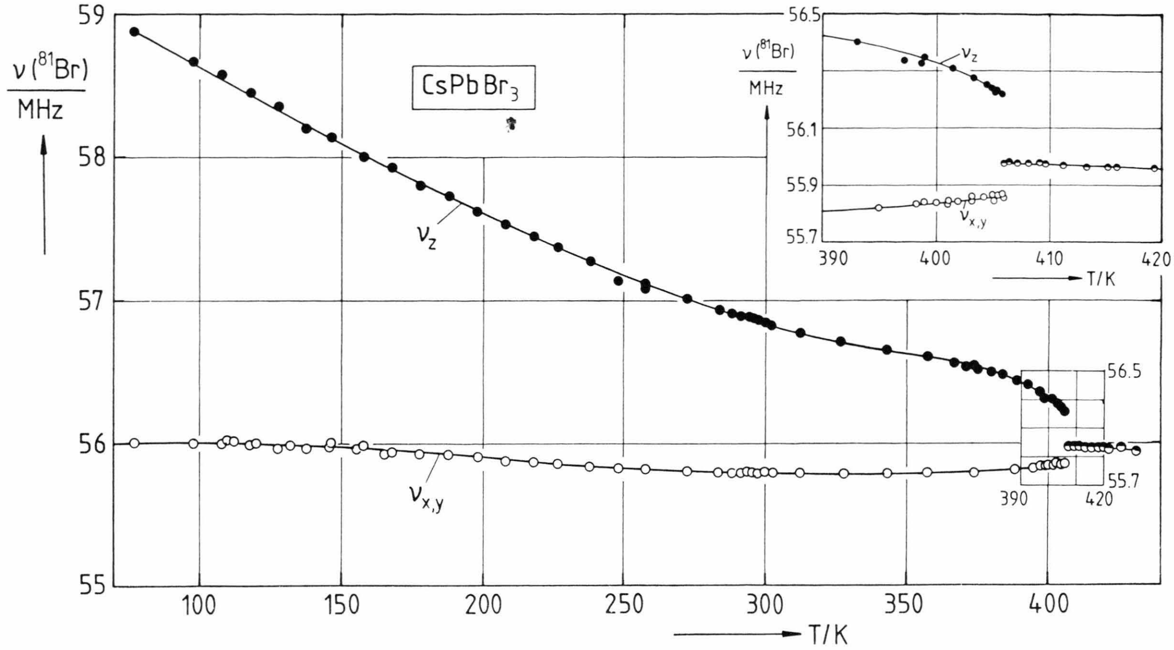

Fig. 3. Temperature dependence of the ^{81}Br NQR spectrum of $CsPbBr_3$.

rial, most probably glycerol. Figures 1 b and 1 c have remarkable similarity. They show a typical ^{1}H NMR spectrum of geometrically fixed H_2O molecules in a crystal lattice (a flipping of the molecules around their twofold axis is not excluded). If the water in the second sample (Fig. 1 b) were not fixed in the lattice it would have shown the sharp ^{1}H NMR peak of liquid H_2O in the centre of the ^{1}H NMR spectrum. Shape and intensity of the ^{1}H NMR indicate that, if the material is exposed to water vapour, it forms a hydrate. The time period for this process is several days. Figure 1 d shows the ^{1}H NMR on sample 4. It contains almost no water, indicating thereby that the water of hydration is driven out easily.

We have used magic angle spinning (MAS) NMR to study the ^{119}Sn- and ^{133}Cs-NMR signals. The ^{119}Sn spectrum (Fig. 2 a), in phase II, shows numerous spinning side bands, and the shape of the envelop indicates that the chemical shift tensor is highly anisotropic (more than 450 ppm difference in the tensor axes). The sample was spun at the rate of 5 kHz/sec. Figures 2 b and 2 c show the ^{119}Sn and ^{133}Cs spectra in the metastable phase I of $CsSnCl_3$ at room temperature. Tin as well as the cesium lines are very narrow ($\delta\nu(^{119}\text{Sn}) = 290$ Hz and $\delta\nu(^{133}\text{Cs}) = 30$ Hz, respectively). Both spectra clearly indicate that tin and cesium are occupying highly symmetric point positions in the unit cell and that there is no second phase present. The NMR has shown that phase I of $CsSnCl_3$ is definitely a single phase which has cubic structure because there is no quadrupolar structure in the ^{133}Cs-NMR.

$CsPbBr_3$: Phase I

The temperature dependence of ^{81}Br-NQR is shown in Figure 3. The DTA and NQR measurements show that the transition temperature in the material prepared by us is 406 K. Above 406 K $CsPbBr_3$ (phase I) has the cubic Perovskite-type structure, Pm3m, with Cs at (0, 0, 0), Pb at (1/2, 1/2, 1/2) and Br at (1/2, 0, 1/2), (1/2, 1/2, 0), and (0, 1/2, 1/2). The six bromines form an octahedron whose centre is occupied by lead. $PbBr_6$ octahedra are undistorted, all bromines are crystallographically equivalent and only one NQR signal is expected. Our NQR results are in agreement with this conclusion. We observe a single NQR line above 406 K (Fig. 3) which has a slope of -1.497 kHz/K.

$CsPbBr_3$: Phase II

Phase II is tetragonal, space group D_{4h}^5-P4/mbm, $Z = 2$. Positional parameters referred to the tetragonal axes *a* and *c* are [7]: $Pb^{(1)}$: (0, 0, 0), $Pb^{(2)}$: (1/2, 1/2, 0), $Cs^{(1)}$: (1/2, 0, 1/2), $Cs^{(2)}$: (0, 1/2, 1/2), $Br^{(1)}$: (0, 0, 1/2), $Br^{(2)}$: (1/2, 1/2, 1/2), $Br^{(3)}$: $(1/4+\delta, -1/4+\delta, 0)$, $Br^{(4)}$: $(1/4-\delta, 1/4+\delta, 0)$, $Br^{(5)}$: $(-1/4-\delta, 1/4-\delta, 0)$, and $Br^{(6)}$: $(-1/4+\delta, -1/4-\delta, 0)$, where $\delta=(a/2\sqrt{2})\tan\varphi$, φ is the angle of rotation of the octahedra around the *c*-axis caused by the condensation of mode M_3 and *a* is the cell length of the cubic phase. $Br^{(1)}$ and $Br^{(2)}$ (at $z=1/2$) are crystallographically equivalent but inequivalent to $Br^{(3)}$–$Br^{(6)}$, which lie in the *x*-*y*-plane, $z=0$. From the two types of bromines and their number one expects two NQR signals with an intensity ratio 1:2. Our results confirm this (see Figure 3). At 406 K the single NQR line splits into two and the intensity of the line marked $\nu_{x,y}$ is twice that of ν_z.

$CsPbBr_3$: Phase III

Moller [5] and Cola et al. [6] claim that phase III is monoclinic while Hirotsu et al. [7] infer it to be orthorhombic. We have grown single crystals of $CsPbBr_3$, with negligible twinning, and determined the crystal structure by X-rays to resolve this discrepancy. Our results (to be published) show that phase III is orthorhombic, space group: D_{2h}^{16}-Pbnm, $Z=4$, with $a=820.8(3)$, $b=825.7(3)$ and $c=1176.3(4)$ pm, in agreement with the inference of [7]. Four of the bromines occupy point symmetry m and the rest occupy the eightfold point position. Thus there are two inequivalent groups of bromines. Four equivalent bromines are located on the *z*-axis and eight equivalent bromines lie almost in the *x*-*y*-plane. Two NQR signals are again expected which should have intensities in the ratio 1:2. Our ^{81}Br NQR results confirm this (see Figure 3). Two additional lines reported by Volkov et al. [10], which are in contradiction to the crystal structure, could not be detected. We were not able to detect the phase transition at 316 K through NQR, only the line marked ν_z has a change in slope. We may mention that we could not detect this phase transition in our DTA measurements either.

Table 1. Transition temperatures, crystal structure, symmetry of soft modes and order of transition in $CsPbCl_3$, $CsPbBr_3$ and $CsSnBr_3$.

Compound	Phase	*T*/K	Space group	*Z*	Soft mode	Order	Ref.
$CsPbCl_3$	I		O_h^1-Pm3m	1			[7]
		320			M_3	first	
	II		D_{4h}^5-P4/mbm	2			[7]
		315			$(R_{25})_x$	second	
	III		D_{2h}^{17}-Cmcm	8			[7]
		310			$(R_{25})_y$	first	
	IV		D_{2h}^{16}-Pbnm	4			[17]
$CsPbBr_3$	I		O_h^1-Pm3m	1			[5, 7]
		403			M_3	first	
	II		D_{4h}^5-P4/mbm	2			[7]
		361			R_{25}	second	
	III		D_{2h}^{16}-Pmbn	4			[7]
$CsSnBr_3$	I		O_h^1-Pm3m	1			[13]
		292			M_3	first	
	II		D_{4h}^5-P4/mbm	2			[13]
		274			$(R_{25})_z$	second	
	III		D_4^2-$P42_12$	4			[13]
		274			$(R_{25})_{x,y}$	second	
	IV		monoclinic				[13]

A comparison between $CsPbBr_3$ and other double halides which have been investigated by NQR may be interesting. $CsPbCl_3$ [11, 12], $CsPbBr_3$ [10, present work], and $CsSnBr_3$ [2, 13, 14] have some common features. The parameters of interest regarding the phase transformations are listed in Table 1. They all have Perovskite-type structure in the HT-phase, transform to tetragonal structure through the condensation of an M_3 phonon mode and to an orthorhombic phase when mode R_{25} is condensed. They all have one NQR signal in the HT-phase, two in the tetragonal and orthorhombic phases, the intensities of the two signals being in the ratio 1:2; the low frequency signal, $\nu_{x,y}$, is less sensitive to the temperature variation and the high frequency signal, ν_z, changes it's slope when the material transforms from tetragonal to orthorhombic structure. In the case of $CsPbCl_3$, R_{25} is condensed in two steps (at 320 and 315 K) where the degeneracy of the $\nu_{x,y}$ line is lifted and there are three distinct signals. The temperature dependence of the NQR spectrum of all three is very similar.

The different temperature dependence of the two lines may have it's origin in the way the octahedra are connected to each other. In phase I the octahedra are undistorted and join each other through corner connection only. In phase III the halogens still have the corner connection but the angle Pb–Br–Pb in the *x*-*y*-plane is 157.5° and the bridge along the *z*-axis makes 164.2°. The different temperature dependence may come from different bridging angles.

Figure 4 shows the orientation dependence of the satellite splitting of the ^{133}Cs NMR lines in a single crystal of $CsPbBr_3$ rotated around the pseudocubic axis [001] at room temperature. An examination of this figure shows that there are two sets of signals, shifted by about 90° with respect to each other, caused by the twinning, indicating thereby that the twin walls are formed at right angles to each other. An analysis of the data yields a coupling constant of 240 kHz and an asymmetry parameter $\eta = 0.33$, for ^{133}Cs at room temperature.

Chabin and Gilletta [15, 16] have investigated the domain structure in $CsPbCl_3$, theoretically and experimentally, for the room temperature phase. Through microscopic examination they found the angle between twin walls to be 89°. Our NMR results suggest that the angle is about 90° for phase III of $CsPbBr_3$.

About 2 K away from the transition point of 407 K, from DTA experiments, we were able to observe ^{81}Br-NQR signals from two phases, phase I and phase II, simultaneously, but since the signals became broad and weak we did not investigate this phenomenon further with ^{81}Br-NQR. The disadvantage of broad lines was overcome by investigating the temperature dependence of the quadrupolar interaction of ^{133}Cs ($I = 7/2$) in a single crystal via NMR in high magnetic field (4.7 T). The satellites of the Cs-spectra are usually very sharp, due to the small quadrupole moment. We

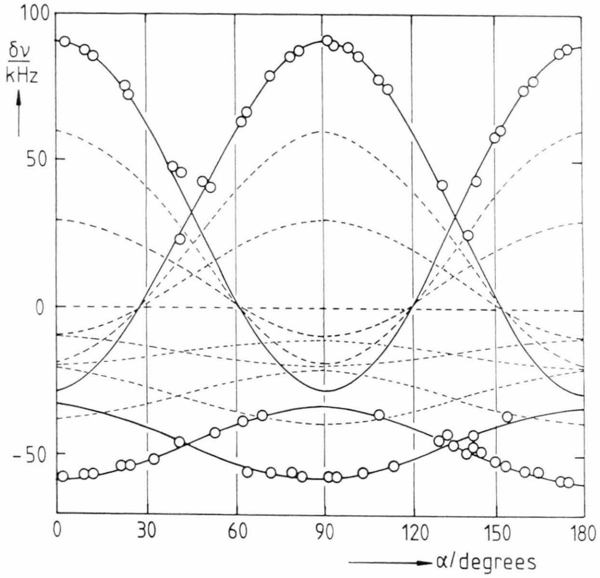

Fig. 4. Orientation dependence of the satellite splitting of ^{133}Cs-NMR of a single crystal of $CsPbBr_3$ at room temperature.

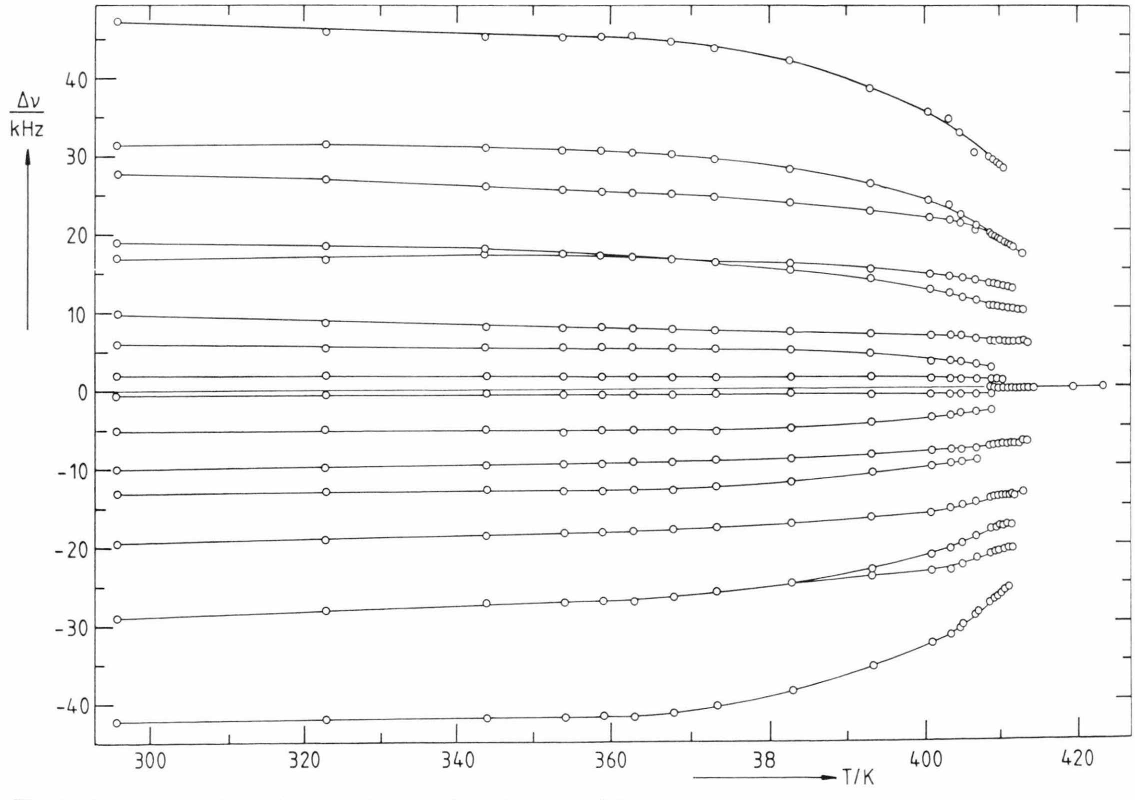

Fig. 5. Temperature dependence of the satellite splitting of ^{133}Cs, in a fixed orientation, of a single crystal of $CsPbBr_3$. $B_0 = 4.7$ T.

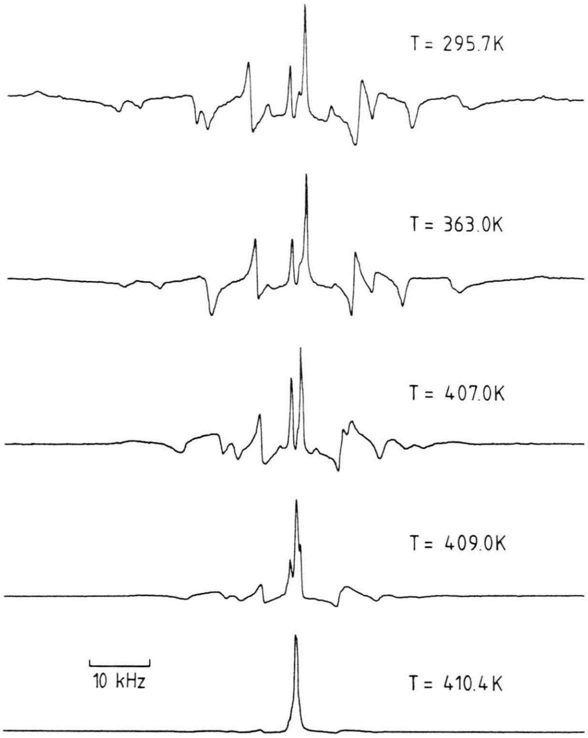

Fig. 6. A few representative spectra of the satellite splitting in $CsPbBr_3$ at various temperatures.

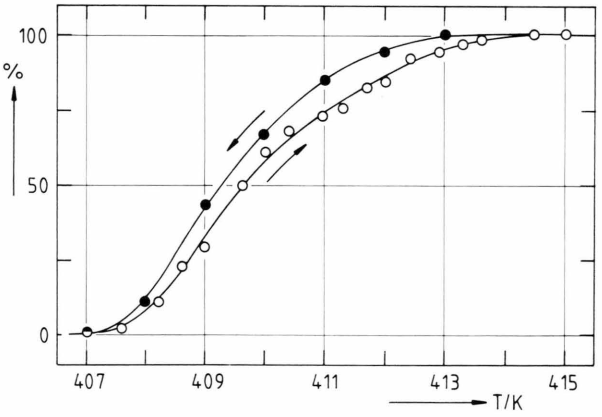

Fig. 7. Phase transformation from tetragonal-cubic in $CsPbBr_3$.

have kept the crystal orientation fixed and varied the temperature. Figure 5 shows the temperature dependence of the satellite splitting. Again, the second order phase transition at about 363 K cannot be detected by NMR although there is supposed to be a small displacement of Cs atoms with the freezing of the mode R_{25}. From 363 K upwards the satellite splitting has strong temperature dependence. This holds for all satellites, indicating that the point positions of the Cs atoms are heading towards a higher symmetry. At temperatures above 407 K there is only one line in the middle of the spectrum, which indicates the HT-phase to be cubic. The crystal has been oriented in a way that (i) good resolution of the satellites was achieved and (ii) the single line of the cubic phase did appear at a different position than the $1/2 \leftrightarrow -1/2$ transition of the tetragonal phase. It turned out that $\alpha = 0$ (Fig. 4) fulfilled both conditions.

Some representative spectra of Cs satellites, in the fixed orientation, at various temperatures are shown in Figure 6. It has two features: (a) the splitting becomes smaller with rising temperature and (b) above 407 K a new line appears in the middle of the spectrum, which gains in intensity at the expense of the satellites on increasing the temperature, and finally the satellites disappear and this line stays on. In order to follow the growth of the cubic phase as a function of temperature we have measured the ratio of the intensities of all "old" lines, belonging to the noncubic phase, to the intensity of the new line by integrating all lines. Figure 7 shows the percentage of the cubic phase as a function of the temperature. It is seen that the cubic phase grows over a temperature interval of about 6 K. This process is reversible, with a slight hysteresis of less than 1 K. The onset temperature coincides with that of the peak in the DTA experiments and the temperature interval with that of the width of the peak. No dependence on time could be observed. If the temperature is kept constant for hours, the ratio of the cubic phase does not change. A possible explanation is that various twin domains make a spontaneous transformation to the cubic phase at individual temperatures, depending on size and internal stress of the domains. The reversibility of the process may have the reason that always the same size distribution is obtained by going back into the tetragonal phase. This may be due to impurities and/or a defect distribution which cannot be annealed.

Acknowledgement

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