Phase Transition in Cesium Enneabromodibismuthate(III), $Cs_3Bi_2Br_9$; an [81]Br and [209]Bi NQR Study

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The [81]Br and [209]Bi NQR spectra of $Cs_3Bi_2Br_9$ have been studied over a wide temperature range ([81]Br-NQR: $77 \leq T/K \leq 383$; [209]Bi-NQR: $77 \leq T/K \leq 310$). Therefrom a phase transition in the compounds is found which is probably of second order.

Introduction

The crystal structure of $Cs_3Bi_2Br_9$ is built up by colligated $Bi_2Br_9^{3-}$ anion layers in which the octahedra $BiBr_6$ share three cis-vertices with three neighboring octahedra [1]. The Cs^+ cations reside in highly symmetric vacancies with hexagonal site symmetry. So far it has been found that $(CH_3NH_3)_3Sb_2Br_9$ [2] and $(CH_3NH_3)_3Bi_2Br_9$ [3] are isomorphous with $Cs_3Bi_2Br_9$ at room temperature. The three named compounds make an interesting series of phase transitions [4]: It has been observed that $(CH_3NH_3)_3Bi_2Br_9$ undergoes three successive transitions at 188, 140, and 101.5 K. These transitions are connected with librational motions of the methylammonium cation [5]. In $(CH_3NH_3)_3Bi_2Br_9$ the third, low temperature phase transition is an improper ferroelectric transition. No corresponding transition has yet been found in $(CH_3NH_3)_3Sb_2Br_9$, though it is not excluded that such a transition may appear at $T < 80$ K. Therefore, it seemed to be interesting to investigate whether an analogous phase transition scheme holds for the isomorphous cesium enneabromodibismuthate(III).

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NQR (nuclear quadrupole resonance) has often presented valuable information on solid state phase transitions because of the high sensitivity of NQR frequencies to the electronic state around the resonant nucleus. Previous work [6] (crystal structure and NQR studies) on $(CH_3NH_3)_3Sb_2Br_9$ and $(CH_3NH_3)_3Bi_2Br_9$ has presented information concerning the phase transitions in these compounds. However, a third, low temperature phase transition in $(CH_3NH_3)_3Sb_2Br_9$ could not be detected because no NQR signal was observed below $T = 168$ K, probably due to low signal intensity. In this paper we report on [81]Br and [209]Bi NQR spectroscopy on $Cs_3Bi_2Br_9$ and the detection of a low temperature phase transition of this solid.

Experimental

Very small, powdery, yellow crystals of $Cs_3Bi_2Br_9$ are obtained from a dilute HBr solution of stoichiometric amounts of $Bi(OH)_3$ and CsBr. The crystal size can be improved by extracting the powdery solid with the HBr solution in a Soxhlet extractor. A considerable enhancement of the NQR signal intensities is reached by this procedure. Chemical analysis confirms the composition $Cs_3Bi_2Br_9$ (found/calc.; weight%: Bi: 27.03/27.22; Br: 46.49/46.82).

The NQR signals were observed on a superregenerative type spectrometer. The accuracy of frequency measurement was estimated to ± 10 kHz unless otherwise noted. The temperature was measured via a copper-constantan thermocouple to ± 1 K.

Results and Discussion

In Table 1 the [81]Br and [209]Bi NQR frequency values found at 77 K and at room temperature are listed. The assignment of the Br NQR frequencies given to the isotope [81]Br was confirmed by observing the corresponding [79]Br NQR frequencies, too. For [209]Bi only one signal could be observed within the searched range 8.3 to 22.4 MHz at room temperature and 7.0 to 10.3 MHz at 77 K. Therefore we have not been able to assign the observed resonance to an appropriate transition $m \leftrightarrow m \pm 1$ between the [209]Bi ($I = 9/2$) levels.

The NQR spectrum at room temperature is consistent with the crystal structure of $Cs_3Bi_2Br_9$ at room temperature [1] which reveals two kinds of bromine
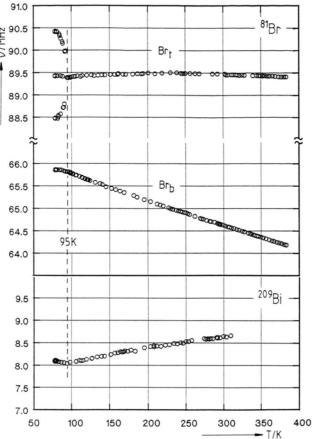
Fig. 1. Temperature dependence of NQR frequencies of $Cs_3Bi_2Br_9$; upper part: ^{81}Br, Br_t and Br_b denote terminal and bridging bromine atoms, respectively; lower part: ^{209}Bi.

Table 1. ^{81}Br and ^{209}Bi nuclear quadrupole resonance frequencies in $Cs_3Bi_2Br_9$. S/N is the signal to noise ratio observed with lock in technique and recorder.

Nucleus	v/MHz		Assignment
	77 K (S/N)	[Room temp./K] (S/N)	
^{81}Br	90.43 [a] (20)	89.48 [293] (50)	terminal
	89.44 [a] (7)		terminal
	88.49 [a] (17)		terminal
	65.87 [a] (20)	64.66 [293] (20)	bridging
^{209}Bi	8.10 (4)	8.62 [292] (6)	

[a] ± 0.02 MHz.

atoms, terminal Br_t at the point position 6i, bridging Br_b at the point position 3e and one kind of bismuth atoms at the point position 2d in the space group $P\bar{3}m1$, $Z = 1$. The bond distances found are 271.3 pm and 297.9 pm for $d(Bi-Br_t)$ and $d(Bi-Br_b)$, respectively. From theory the electric field gradient tensor principal axes are proportional to $1/r^3$, i.e. $\Phi_{zz} = a \cdot 1/(d(Bi-Br))^3$. Therefrom we conclude that the higher ^{81}Br NQR frequency belongs to the shorter distance $d(Bi-Br_t)$.

Additionally, this is confirmed by the intensity ratio: the higher frequency line is about twice as intensive as the lower frequency line. Both, frequencies and intensities allow a safe assignment to the crystallographic positions and thereby to the bond properties of the bromine atoms.

The temperature dependence of the ^{81}Br and ^{209}Bi NQR frequencies is shown in Figure 1. It is noticed

that the ^{81}Br NQR singlet of the terminal bromines split at $T_c = 95 \pm 1$ K into a triplet. The splitting grows continuously out of the singlet line, as one recognizes from the central line of the triplet. The very steep slope of $dv(^{81}Br)_t/dT$ of the upper and lower triplet components prohibits observation very near to T_c. It is observed that the central line of the triplet has lower intensity ($\approx 1/3$) compared to the upper and lower component. Also the triplet line widths have broadened below T_c compared to Δv above T_c. No line splitting is observed for the ^{81}Br NQR line assigned to the bridging bromine. A slight change of the curvature $v(^{81}Br)_b = f(T)$ is, however, observed at T_c. Raising the temperature through T_c is accompanied by a minor enhancement in signal intensity and narrowing of the resonance line.

Throughout the temperature range covered the ^{209}Bi NQR spectrum is a singlet. $v(^{209}Bi) = f(T)$ shows a small change at T_c and above T_c $dv(^{209}Bi)/dT$ is positive. Above T_c the line width is slightly smaller, the intensity somewhat higher compared to the range $T < T_c$.

From the NQR spectrum one learns that the phase transition at T_c must be a structural one. The symmetry changes: the atoms Br_t become crystallographically inequivalent in the low temperature phase. It may well be, that the phase transition is of similar nature as that of the third, low temperature transition in $(CH_3NH_3)_3Bi_2Br_9$. The continuous change of the curves $v = f(T)$ suggests that the transition is of second order. It is difficult to explain why the $v(^{81}Br_t) = f(T)$ curve of the terminal bromines exhibits a very small maximum around 220 K. Also the slopes in $dv(^{81}Br_b)/dT$ and $dv(^{209}Bi)/dT$ are slightly changing, probably due to excitations of certain librational motions within the anion $Bi_2Br_9^{3-}$.

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