Phase Transition in Cesium Enneabromodibismuthate(III), Cs$_3$Bi$_2$Br$_9$; an $^{81}$Br and $^{209}$Bi NQR Study

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Z. Naturforsch. 47a, 1259–1261 (1992); received September 24, 1992

The $^{81}$Br and $^{209}$Bi NQR spectra of Cs$_3$Bi$_2$Br$_9$ have been studied over a wide temperature range ($^{81}$Br-NQR: 77 ≤ T/K ≤ 383; $^{209}$Bi-NQR: 77 ≤ T/K ≤ 310). Therefrom a phase transition in the compounds is found which is probably of second order.

Introduction

The crystal structure of Cs$_3$Bi$_2$Br$_9$ is built up by colligated Bi$_2$Br$_6^-$ anion layers in which the octahedra Bi$_6$ share three cis-vertices with three neighboring octahedra [1]. The Cs$^+$ cations reside in highly symmetric vacuums with hexagonal site symmetry. So far it has been found that (CH$_3$NH)$_2$Sb$_2$Br$_9$ [2] and (CH$_3$NH)$_3$Bi$_2$Br$_9$ [3] are isomorphous with Cs$_3$Bi$_2$Br$_9$ at room temperature. The three named compounds make an interesting series of phase transitions [4]: It has been observed that (CH$_3$NH)$_3$Bi$_2$Br$_9$ 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$_3$NH)$_3$Bi$_2$Br$_9$ the third, low temperature phase transition is an improper ferroelectric transition. No corresponding transition has yet been found in (CH$_3$NH)$_2$Sb$_2$Br$_9$, 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).

Results and Discussion

In Table 1 the $^{81}$Br and $^{209}$Bi NQR frequency values 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 from 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 $m$ ↔ $m$ ± 1 between the $^{209}$Bi ($I = 9/2$) levels.

The NQR spectrum at room temperature is consistent with the crystal structure of Cs$_3$Bi$_2$Br$_9$ at room temperature [1] which reveals two kinds of bromine...
atoms, terminal \(\text{Br}_t\) at the point position 6i, bridging \(\text{Br}_b\) 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 \(d(\text{Bi}–\text{Br}_t)\) and \(d(\text{Bi}–\text{Br}_b)\), respectively. From theory the electric field gradient tensor principal axes are proportional to \(1/r^3\), i.e. \(\Phi_{zz} = a \cdot 1/(d(\text{Bi}–\text{Br}))^3\). Therefrom we conclude that the higher \(\text{Br}^8\) NQR frequency belongs to the shorter distance \(d(\text{Bi}–\text{Br}_t)\).

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 \(\text{Br}^8\) and \(\text{Bi}^{209}\) NQR frequencies is shown in Figure 1. It is noticed that the \(\text{Br}^8\) 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 \(dv(\text{Br}^8)/dT\) 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 \(\Delta T\) above \(T_c\). No line splitting is observed for the \(\text{Bi}^{209}\) NQR line assigned to the bridging bromine. A slight change of the curvature \(v(\text{Bi}^{209})/T\) 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 \(\text{Bi}^{209}\) NQR spectrum is a singlet. \(v(\text{Bi}^{209})=f(T)\) shows a small change at \(T_c\) and above \(T_c\) \(dv(\text{Bi}^{209})/dT\) 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 \(\text{Br}_t\) 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 \((\text{CH}_3\text{NH}_2)_3\text{Bi}_2\text{Br}_9\). The continuous change of the curves \(v=f(T)\) suggests that the transition is of second order. It is difficult to explain why the \(v(\text{Br}^8)=f(T)\) curve of the terminal bromines exhibits a very small maximum around 220 K. Also the slopes in \(dv(\text{Br}^8)/dT\) and \(dv(\text{Bi}^{209})/dT\) are slightly changing, probably due to excitations of certain librational motions within the anion \(\text{Bi}_3\text{Br}_3^3\).

### Table 1. \(\text{Br}^8\) and \(\text{Bi}^{209}\) nuclear quadrupole resonance frequencies in \(\text{Cs}_5\text{Bi}_3\text{Br}_9\). S/N is the signal to noise ratio observed with lock in technique and recorder.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>(v)/MHz</th>
<th>[Room temp./K]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Br}^8)</td>
<td>90.43 (20)</td>
<td>89.48 (293) (50)</td>
<td>terminal</td>
</tr>
<tr>
<td></td>
<td>89.44 (7)</td>
<td>64.66 (20) (293)</td>
<td>bridging</td>
</tr>
<tr>
<td>(\text{Bi}^{209})</td>
<td>8.10 (4)</td>
<td>8.62 (292) (6)</td>
<td>bridging</td>
</tr>
</tbody>
</table>

\(\pm 0.02\) MHz.