BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 741—744 (1973)

The Bromine Nuclear Quadrupole Resonance of Two Modifications of Indium Tribromide

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(Received June 29, 1972)

The bromine nuclear quadrupole resonance study of indium tribromide has revealed that there are at least two modifications in its solid state. The high-temperature modification shows the two ^{81}Br resonance lines of 85.985 and 86.205 MHz, with the relative intensity of 1:2 at 24.5°C. This modification was stable unless the temperature was lowered to ~15°C. The low-temperature modification shows one ^{81}Br resonance line, 86.915 MHz, at -196°C and was stable up to ~30°C. The directions of the z axes of the field gradient were determined by studying the Zeeman effect on each resonance line of the two modifications at room temperature. For the two resonance lines of the high-temperature modification, one and two directions, which had the asymmetry parameters of 0.362 and 0.400 respectively, were observed. The resonance line of the low-temperature modification showed three directions with the asymmetry parameter of 0.387. The crystal structures of the high- and low-temperature modifications were, therefore, concluded to be monoclinic and hexagonal respectively, from the numbers of resonance lines and of the nonequivalent directions of the z axes. The quadrupole coupling constants and asymmetry parameters were analyzed by means of the Townes-Dailey method.

Indium trihalides, InX_3 (X: Cl, Br, I), exist as dimers in the gaseous state,[1] but their crystal structures are not always the same. According to the X-ray diffraction analysis,[2] the crystal of $InCl_3$ has a layer structure in which every indium atom is octahedrally surrounded by chlorine atoms, and its space group is C2/m as in $AlCl_3$.[3] On the other hand, the crystal of InI_3 is made up of dimer molecules joined by iodine bridges,[4]

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[1] D. P. Stevenson and V. Schomaker, *J. Amer. Chem. Soc.*, **64**, 2514 (1942).

[2] D. H. Templeton and G. F. Carter, *J. Phys. Chem.*, **58**, 940 (1954).

[3] R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York (1948).

[4] J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 63 (1964).

as in the gaseous state. As for $InBr_3$, the X-ray analysis has not yet been reported, as far as we know.

The results of the nuclear quadrupole resonance (NQR) of bromine in $InBr_3$ were reported previously by Ludwig[5] and Barnes *et al.*,[6] but they are not completely consistent. Barnes *et al.* studied extensively the NQR on the trihalides of Group IIIb elements and found that all the NQR spectra consist of a singlet on the lower-frequency side and a doublet on the higher-frequency side.[6,7] The ^{81}Br NQR spectrum of $InBr_3$ consists of the singlet of 86.912 MHz and the doublet of 106.974 and 107.428 MHz at -196°C. The former is ascribed to the bridging bromine atoms, while the latter is assinged to the terminal ones.

On the other hand, Greenwood *et al.* have reported the infrared and Raman spectra of InX_3.[8] According to their results, the spectra of $InBr_3$ are more similar to those of $InCl_3$ than those of InI_3; that is, the crystal of $InBr_3$ has a layer structure. This is contrary to the NQR results presented above.

We re-examined the ^{81}Br NQR of $InBr_3$ and, furthermore, observed the Zeeman effect on the NQR. We obtained different spectra from those reported previously; our results can be satisfactorily explained by the layer structure suggested by Greenwood *et al.*

Also, the study of the temperature dependences of the NQR frequencies revealed the existence of at least two modifications in $InBr_3$ crystals. The high-temperature modification shows two resonance lines, while the low-temperature modification shows only one resonance line. The measurements of the NQR Zeeman effect were made on these two modifications.

Experimental

The sample of $InBr_3$ was purchased from Katayama Chemical Industries Co., Ltd., and was purified by sublimation. The single crystal necessary for the study of the Zeeman effect was grown by the Bridgman-Stockbarger method.

The NQR spectrometer used in these experiments was a super-regenerative oscillator with frequency modulation; the absorption lines were observed on an oscilloscope. The resonance frequencies were determined with a VHF signal generator and a frequency counter, TR-5578, from the Takeda Riken Industry Co., Ltd. The Zeeman effect was examined by means of the zero-splitting cone method used in a low-magnetic field. The magnetic field of about 200 G was applied by means of a Helmholtz coil, and the patterns of the zero-splitting loci were determined at room temperature. The temperature dependences of the resonance frequencies were measured by using a thermostat from the Takara Kogyo Co. After the sample had been cooled or heated at a fixed temperature for 30—60 min, the resonance frequencies were determined.

Results and Discussion

The ^{81}Br NQR frequencies of $InBr_3$ observed in our experiment are presented in Table 1. Those for ^{79}Br were observed at frequencies corresponding to the frequency ratio (1.197) of $\nu(^{79}Br)/\nu(^{81}Br)$. The crystals of $InBr_3$ commercially obtained or purified by sublimation always show two closely-spaced resonance lines at room temperature. The intensity ratio of the higher line (ν_{β_2}) to the lower (ν_{β_1}) is approximately 2: 1. These results indicate that there are two kinds of non-equivalent bromine atoms in the crystal and that their abundance ratio is 2: 1. On cooling, this modification is apparently transformed to the other one, which shows only one resonance line. Tentatively we will refer to the former as the β-modification and to the latter as the α-modification.

Table 1. ^{81}Br NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES IN THE MODIFICATIONS OF INDIUM TRIBROMIDE

Modification		Resonace frequency[a] (MHz)		
		-196°C	24.5°C	49°C
α	ν_α	86.915	85.962	....
β	ν_{β_1}	....	85.985 (1)[b]	85.867 (1)
	ν_{β_2}	....	86.205 (2)	86.074 (2)

a) Experimental error is ±0.01 MHz.

b) The value in parenthesis is the relative intensity.

The resonance frequencies in Table 1 are close to that of the bridging bromine atom reported by Barnes *et al.*[6] Especially, the resonance frequency of the α-modification (ν_α) at -196°C is consistent within the limits of experimental error. We scanned carefully the frequency regions around 105 and 125 MHz, where the resonance frequencies of the terminal ^{81}Br and ^{79}Br atoms in the dimer have been reported by Barnes *et al.*,[6] but we could not detect any resonance line.[9] Therefore, we concluded that neither of the modifications observed here is composed of dimers.

The temperature dependences of the resonance frequencies were measured between -48 and 49°C, as is shown in Fig. 1. The transition point is hard to determine because of the large hysteresis. In the course of cooling the single crystal of the β-modification, an absorption line of the α-modification appeared at ~15°C. On warming, the signal of the α-modification was observed up to ~30°C. Using the powder sample, the region of the hysteresis spread as may be seen in Fig. 1. Furthermore, in the temperature range from -6 to -16°C, the absorption lines of both the α- and β-modifications were observed.

The β-Modification of Indium Tribromide. The single crystal of $InBr_3$ initially obtained had the β-modification, because it was crystallized from the melt. The patterns of zero-splitting were obtained on each resonance line. For the bromine atom (I=3/2), the

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5) G. W. Ludwig, *J. Chem. Phys.*, **25**, 159 (1956).

6) R. G. Barnes, S. L. Segel, P. J. Bray, and P. A. Cassabella *ibid.*, **26**, 1345 (1957).

7) R. G. Barnes and S. L. Segel, *ibid.*, **25**, 180 (1956). S. L. Segel and R. G. Barnes, *ibid.*, **25**, 578 (1956).

8) N. N. Greenwood, D. J. Prince, and B. P. Straughan, *J. Chem. Soc.*, *A*, **1968**, 1964.

9) The sensitivity of the spectrometer was confirmed by the detection of ^{127}I resonance line of InI_3 for 125 MHz region. The ^{79}Br resonance lines of $AlBr_3$ and also, of $InBr_3$ give the enough sensitivity for 105 MHz region.

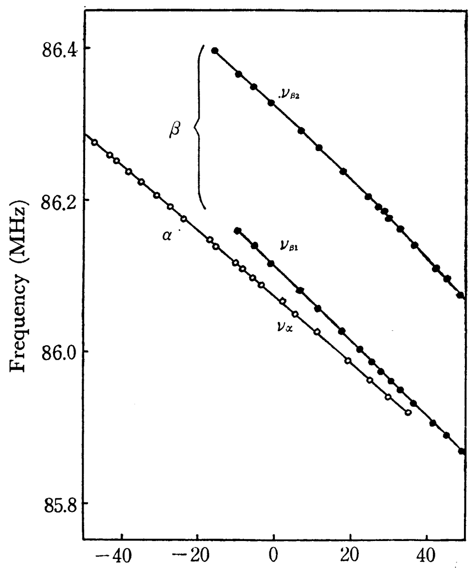

Fig. 1. Temperature dependences of ^{81}Br nuclear quadrupole resonance frequencies in indium tribromide.

zero-splitting occurs under the following conditions:[10]

$$\sin^2\theta = 2/(3-\eta\cos 2\varphi), \qquad (1)$$

where the orientation of the magnetic field is expressed by the polar coordinates (θ,φ) with respect to the coordinates of the principal axes (x, y, and z axes) of the field gradients at the resonant nuclei and where η is an asymmetry parameter of the field gradient. In this way, a cone about the z axis can be drawn by θ and φ which satisfies Eq. (1). The axes corresponding to $\varphi=0$ and $\varphi=\pi/2$ are shown by the x and y axes respectively. Only one zero-splitting pattern was obtained for $\nu_{\beta 1}$, whereas two patterns were observed for $\nu_{\beta 2}$. The experimental results are shown in Fig. 2, where Z_1, Z_{2A}, and Z_{2B} are the directions of the z axes at the bromine atoms contributing to $\nu_{\beta 1}$ and $\nu_{\beta 2}$. From the number of the z axes of $\nu_{\beta 1}$ and $\nu_{\beta 2}$, the symmetry of the β-modification must be lower than the tetragonal, but not the triclinic.[11] However, as a symmetry higher than the monoclinic is ruled out by the requirement for the angles between the z axes, it can be concluded that the β-modification belongs to the monoclinic space group. The asymmetry parameters of the field gradient were determined from Eq. (1) by the use of the least-squares method. As may be seen in Table 2, large values of η were obtained.

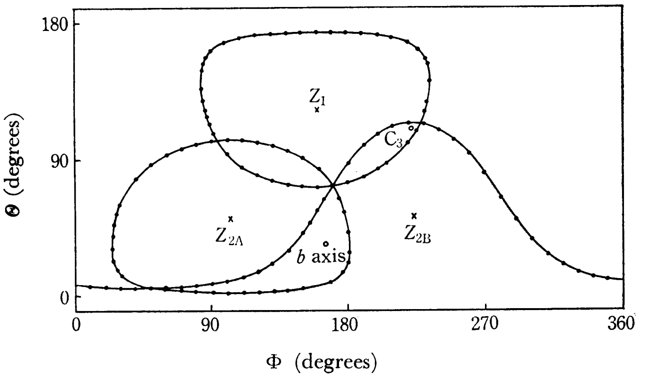

Fig. 2. Zero-splitting patterns of the Zeeman effect of the β-modification of indium tribromide. Θ and Φ are polar and azimuthal angles in the coordinates fixed to the sample respectively.

Table 2. Asymmetry parameters and quadrupole coupling constants for ^{81}Br in indium tribromide at room temperature

Modification		η	e^2Qq/h(MHz)	Up
α	(ν_α)	0.387 ± 0.005	167.79	0.2609
β	$(\nu_{\beta 1})$	0.362 ± 0.002	168.33	0.2618
	$(\nu_{\beta 2})$	0.400 ± 0.007	167.99	0.2612

Greenwood *et al.* suggested that the crystal structure of $InBr_3$ is similar to that of $InCl_3$ or $AlCl_3$.[8] In the case of the $AlCl_3$-type structure, there are two nonequivalent halogen atoms which form slightly different bridges. Therefore, the low-resonance frequencies and the large asymmetry parameters may be attributed to the bridging bromine atoms in the β-modification. Also, it is reasonable, in view of this structure, that the β-modification shows two resonance lines with the intensity ratio of 1 : 2 and that the zero-splitting patterns observed are one for $\nu_{\beta 1}$ and two for $\nu_{\beta 2}$. Table 3 shows the angles between the z axes and the b axis of the monoclinic lattice as determined by the Zeeman effect. The values in the second row are calculated from the atomic positions of $AlCl_3$,[3] because the data of X-ray analysis are not available for $InBr_3$. In this calculation, the z axis was assumed to be directed perpendicularly to the plane including M–X–M, as in the case of a bridging halogen atom of the dimer molecule.[12,13] The results of the NQR and those of the X-ray analysis are in good agreement, though the latter are derived for a related compound, $AlCl_3$. Accordingly, it seems most likely that the β-modification is isomorphous with $AlCl_3$. This conclusion is further supported by the fact that Zeeman patterns similar to those in Fig. 2 have been found in $ErCl_3$, which has an $AlCl_3$-type structure, by Carlson and Adams.[14]

Table 3. Angles between the z axes and the b axis in the β-modification of indium tribromide

	Z_1-Z_2	$Z_{2A}-Z_{2B}$	Z_1-b axis	Z_2-b axis
NQR	92°08′	88°16′	90°	44°08′
X-Ray[a]	90°27′	88°26′	90°	44°13′

a) These values were calculated from the atomic positions of $AlCl_3$. (Ref. 3).

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[10] T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Solid State Physics, Suppl. 1, Academic Press, New York (1957).

[11] K. Shimomura, *J. Phys. Soc. Jap.*, **12**, 652 (1957).

[12] G. E. Peterson and P. M. Bridenbaugh, *J. Chem. Phys.*, **51**, 238 (1969).

[13] T. Okuda, H. Terao, O. Ege, and H. Negita, *ibid.*, **52**, 5489 (1970).

[14] E. H. Carlson and H. S. Adams, *ibid.*, **51**, 388 (1969).

The α-Modification of Indium Tribromide. When the single crystal of the β-modification mounted on the apparatus was cooled to about −50°C by means of a cold stream of nitrogen gas from liquid nitrogen, it was transformed to the single crystal of the α-modification. The measurements of the zero-splitting on this modification show three different directions of the z axes, indicating that the crystal of the α-modification has a threefold axis.[15] In Fig. 2, C_3 indicates the orientation of this threefold axis of the α-modification at the same coordinates of the β-modification. The compound that possesses three nonequivalent directions of the z axes belongs, in general, to the hexagonal (point group C_3 or C_{3i}) system or, in special cases, to another hexagonal or cubic system. In this case, however, the cubic system, which has three z axes orthogonal with one another,[11] can be excluded because the observed angle between the z axes is 92°13′.

The zero-splitting patterns of the α-modification are very similar to those of the β-modification. The directions of the z axes of the α-modification deviate from the relevant axes of the β-modification to a small degree. It can, therefore, be expected that the crystal structure of the α-modification is slightly different from that of the β-modification; that is, the crystal of the α-modification may be composed of a polymeric layer lattice like $AlCl_3$. In view of these results, it is likely to be of the BiI_3-type, the structure of which is closely related to the $AlCl_3$-type[16] and which has the space group $R\bar{3}$.[17] The ^{127}I NQR of BiI_3 indicates only a resonance line and a large asymmetry parameter of the field gradient.[18] The transition may occur between monoclinic and hexagonal systems, as in the case of $CrCl_3$ reported by Morosin and Narath.[19]

The crystal of $InBr_3$ is easily cloven along the plane perpendicular to the threefold axis, which may be parallel to the c axis of the hexagonal unit cell. The b axis of the monoclinic lattice of the β-modification was perpendicular to the threefold axis of the α-modification; that is, it was parallel to the cleavage plane.

It is interesting to notice that $InBr_3$ has a higher melting point (436°C) than those of the other Group IIIb trihalides which form dimers in the crystal (*e.g.*, 210°C for InI_3[20]) and that the ratio of the ionic radii for In^{3+}/Br^- is 0.42. This value is slightly larger than the lower limiting ratio, 0.414, for the octahedral coordination of the metal atom. In view of these points, $InBr_3$ can be expected to form an infinite layer lattice, as is proposed by this experiment.

Bond Character. The analyses of the Zeeman effect of $InBr_3$ reveal a close relation between the α- and β-modifications. Such a result as above can also be seen from Tables 1 and 2, *i.e.*, the resonance frequencies and the asymmetry parameters in both modifications are almost the same.

The observed x axis of the field gradient at the bromine atom is directed nearly along the bisector of In–Br–In and the y axis is parallel to the In–In direction. The z axis is perpendicular to the plane including In–Br–In, as has been explained before. From these coordinates of the principal field gradients, we can construct the hybrid orbitals of the bromine atom to bind with two indium atoms. Using the Townes and Dailey theory and appropriate approximations, the following two equations are found to hold for the NQR parameters:[21]

$$\eta = -3\cos\alpha, \tag{2}$$

$$Up(1+\eta/3) = 2 - a, \tag{3}$$

where a is the electron population in the bonding orbital directed to the indium atom and where α is the interbond angle, ∠In–Br–In. Up is the number of unbalanced p electrons and can be determined from the observed quadrupole coupling constant, e^2Qq_{obsd}:

$$h\nu = 1/2e^2Qq_{\text{obsd}}(1+\eta^2/3)^{1/2}, \tag{4}$$

$$Up = e^2Qq_{\text{obsd}}/e^2Qq_{\text{atom}} \tag{5}$$

where e^2Qq_{atom}/h is 643.03 MHz.[22]

Substituting the observed values of η and Up into Eqs. (2) and (3), we obtain $a=1.7$ as the mean value, which gives a negative charge of 0.4e on the bromine atom. This ionic character is smaller than the 55% expected from the electronegativity difference between indium and bromine. This discrepancy may be due to the crystal field exerted by the neighboring nuclei. The angles of In–Br–In are deduced to be 96°56′~97°40′. These values are somewhat larger than the relevant angles, 94°20′ and 95°30′ for $AlCl_3$.

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[15] The NQR Zeeman analysis always introduces the center of symmetry. It is impossible to distinguish between the threefold rotation axis and the threefold inversion axis on the basis of the Zeeman analysis. (Ref. 11).

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