主論文

Structural Studies on Bismuth Trihalides by Means of the Nuclear Quadrupole Resonance

Yoshihiro FURUKAWA

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Structural Studies on Bismuth Trihalides by Means of the Nuclear Quadrupole Resonance

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The nuclear quadrupole resonance (NQR) due to ^{35}Cl, ^{81}Br, ^{127}I, and ^{209}Bi were observed in bismuth trihalides. The NQR Zeeman effect on bismuth trichloride was measured at room temperature using the single crystal. The bond angles of bismuth trichloride were found to be 85.5°, 92.3°, and 92.3°. The asymmetry parameters of the field gradients were calculated to be 0.431 and 0.178 for two non-equivalent chlorine atoms. On the other hand, three ^{81}Br NQR frequencies of bismuth tribromide were newly observed and the Zeeman effect was examined on each resonance line: the quadrupole coupling constants and asymmetry parameters were 205.01 MHz and 0.077, 225.39 MHz and 0.424, and 240.17 MHz and 0.152 respectively, and the crystal had a monoclinic symmetry. A different spectrum of ^{209}Bi from that reported previously was observed: e^2Qq_{ZZ}/h = 266.6 MHz and η = 0.822. Two NQR frequencies due to ^{127}I in bismuth triiodide were in good agreement with the literature values. The NQR parameters obtained were discussed in terms of the bond nature of intra- and intermolecular bonds between the bismuth and halogen atoms on the basis of the Townes-Dailey theory.

It would be of interest to study the nuclear quadrupole resonance (NQR) of bismuth trihalides except bismuth trifluoride since the halogen and bismuth atoms have nuclear quadrupole moment (eQ) and provide informations on the crystal and molecular structures as well as the bond character by the NQR measurements on both nuclei. However, the NQR studies on bismuth trihalides are not seen so frequently as compared with those on the trihalides of the other Group VA elements. The crystal structures of bismuth trihalides are not the same: the chloride has been shown to form the molecular crystal by X-ray diffraction1) and the iodide to form the layer lattice.2) This makes a direct comparison of the NQR parameters of the halides meaningless.

Robinson has reported the NQR frequencies of ^{35}Cl and ^{209}Bi in bismuth trichloride; two resonance frequencies due to ^{35}Cl and a set of four resonance frequencies due to ^{209}Bi.3) However, he did not discuss about the results in detail, because the asymmetry parameters of the field gradients of the chlorine atoms were not determined and the crystal structure of this compound was not available at that time. It was decided, therefore, to measure the NQR frequencies of ^{35}Cl and ^{209}Bi, and the temperature dependence of each resonance frequency of bismuth trichloride. Furthermore, the NQR Zeeman effect on its single crystal was measured at room temperature.

On the other hand, for bismuth tribromide only the ^{209}Bi NQR frequencies have been reported.4) The bromine NQR frequencies have not been given until the present experiment, as far as we know. Three ^{81}Br NQR frequencies were found for the first time and were assigned to the non-equivalent bromine atoms in its crystal. The ^{209}Bi NQR spectrum observed in the present experiment was different from that reported previously, and the quadrupole coupling constant and the asymmetry parameter were derived from four allowed transition frequencies for ^{209}Bi nucleus.

Crystal Structure

The crystal structure of bismuth trichloride by means of X-ray diffraction has been recently published by Nyburg, Ozin, and Szymanski.1) Figure 1 shows the projection along the c axis of the crystal lattice. The space group is an orthorhombic $Pn2_1a$ with four molecules in a unit cell, the dimensions of which are

$a=7.641$, $b=9.172$, and $c=6.291$ Å .

It is confirmed that the bismuth trichloride crystal is made up of discrete, distorted pyramidal molecules, although in gaseous state it has a complete C_{3v} symmetry. The Bi-Cl bond distances are 2.518, 2.513, and 2.468 Å, among which those for Cl(1) and Cl(1)' atoms in Fig. 1 are nearly equal. There are shorter intermolecular distances between bismuth and chlorine atoms than the sum of the van der Waals radii of relevant atoms. Accordingly, the bismuth atom is surrounded by five neighboring chlorine atoms besides three intramolecular chlorine atoms. These intermolecular Bi···Cl distances are 3.22 and 3.45 Å for the Cl(1) atom, 3.26 and

3.40 Å for the Cl(1)' atom, and 3.22 Å for the Cl(2) atom. The unit cell dimension becomes smaller than that of antimony trichloride, which also suggests that there are strong intermolecular bondings between the bismuth and chlorine atoms.

The crystal structure of bismuth tribromide has been little known so far. According to the information obtained by X-ray diffraction analysis the bismuth tribromide crystallizes into the $P2_13$ lattice isomorphous with incorrect bismuth trichloride structure.5)

Bismuth triiodide has a hexagonal layer lattice, in which all the iodine atoms occupy the equivalent sites and have bridge structures between two bismuth atoms.2) The distance between the bismuth and iodine atoms is 3.1 Å in every site.

Experimental

Material. Commercial bismuth trichloride, of which it is impossible to detect any NQR absorption line due to either chlorine or bismuth atom, was purified by normal freezing method. After the central parts of several ampoules of bismuth trichloride were collected, the single crystal was prepared by means of the Bridgman-Stockbarger method. It was succeeded to detect the resonance absorptions and to examine the NQR Zeeman effect.

Bismuth tribromide was parchased from the same origin as bismuth trichloride, of which no NQR absorption was able to be detected. We purified the compound and obtained its single crystal by the same procedure as above.

Bismuth triiodide from commercial origin was purified by removal of excess iodine under reduced pressure and subjected to the NQR measurements.

Apparatus. The NQR spectrometer used in these experiments was a self-quenching super-regenerative oscillator with frequency modulation, and absorption lines were displayed on an oscilloscope. Resonance frequencies were measured with a standard signal generator and a universal frequency counter by matching a zero-beat on the oscilloscope. A Zeeman magnetic field of about 200 G was applied to the sample by a Helmholtz coil. The crystal was rotated about the sample axis (Φ) and the Helmholtz coil was rotated in the plane parallel to the sample axis (Θ). For the measurements of the temperature dependence of the resonance frequency the temperature was controlled by sending a cold stream of nitrogen gas from liquid nitrogen and its value was determined using a copper-constantan thermocouple.

Results

Bismuth Trichloride. The NQR frequency, ν, for a nucleus having a nuclear spin of $I=3/2$ as ^{35}Cl and ^{81}Br is given as the following equation:6)

$$\nu = e^2Qq_{ZZ}/2h\ (\ 1 + \eta^2/3\ )^{\frac{1}{2}}, \qquad (1)$$

where e^2Qq_{ZZ}/h is a quadrupole coupling constant of the atom under consideration and η is an asymmetry parameter of the field gradients defined as $\eta = (eq_{XX}-eq_{YY})/eq_{ZZ}$ and $|eq_{ZZ}| >$

$|eq_{YY}| > |eq_{XX}|$. Since Eq. (1) involves only one observable value, ν, we cannot determine e^2Qq_{ZZ}/h and η separately in an ordinary case. In such a case we must observe the NQR Zeeman effect to find the two parameters.

For bismuth trichloride, two ^{35}Cl frequencies were observed as reported by Robinson.3) These frequencies at liquid nitrogen and room temperatures are presented in Table 1. When the polycrystalline sample was used, the lower absorption (designated as ν_1) is about twice as intense as the higher one (ν_2). These results indicate that there are two kinds of chlorine atoms in the crystal and that the abundance ratio is 2:1.

Since bismuth atom has a nuclear spin $I = 9/2$, it shows four NQR absorptions. Then, the e^2Qq_{ZZ}/h and η values can be determined from the resonance frequencies. Four allowed frequencies are expressed by the following relations.

$$\nu_i = r_i(\eta)\ e^2Qq_{ZZ}/24h\ , \qquad (2)$$

where i = 1, 2, 3, 4 and $r_i(\eta)$ is a relative frequency factor including η. Since in this case the secular equation for nuclear electric quadrupole interaction cannot be solved precisely, the value of $r_i(\eta)$ are evaluated by the Cohen's table, in which the eigen value is tabulated for any value of η in intervals of 0.1 from 0 to 1.7) The bismuth resonance frequencies and assigned transitions are listed in Table 1.

In order to determine the asymmetry parameter for the chlorine atom by the NQR Zeeman effect, the zero-splitting method is generally used. This method gives the directions of the principal field gradients as well as the asymmetry parameters. The condition under which the zero-splitting occurs for nuclear spin I=3/2 is given[8)] by

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

where θ and φ are the polar and azimuthal angles for the Zeeman magnetic field with respect to the coordinates of the principal axes (X, Y, and Z axes) of the field gradient at the resonant nucleus. Thus the asymmetry parameter was determined from Eq. (3) by the use of the least-square method. Once the asymmetry parameter is obtained, the quadrupole coupling constant and the unbalanced p electron number, Up, can be determined from Eqs. (1) and (4).

$$Up = (e^2Qq_{ZZ}/h)\ /\ (e^2Qq_{ZZ}/h)_{atom}. \qquad (4)$$

$(e^2Qq_{ZZ}/h)_{atom}$ is 109.746 MHz for ^{35}Cl[9a)] and 643.03 MHz for ^{81}Br.[9b)] The values of η , e^2Qq_{ZZ}/h, and Up at room temperature are listed in Table 2.

Four zero-splitting patterns were deduced from ν_1, whereas two patterns from ν_2, as is shown in Fig. 2. These results indicate that there are four different directions for the chlorine atoms, Cl(1), contributing to ν_1 and two directions for the chlorine atoms, Cl(2), contributing to ν_2 in a unit cell. The Zeeman effect on the bismuth absorption was also measured on the $5/2 \leftrightarrow 7/2$ transition, since it was more intense than the others. Two zero-splitting patterns were observed and shown in Fig. 3 at the same coordinates as those in Fig. 2. The crystal must be of the Laue symmetry of D_{2h} and therefore, belongs to the orthorhombic lattice.[10] The Cl(2) and bismuth atoms occupy the special positions in the lattice.

Temperature dependences of ν_1 and ν_2 were measured between 77 and 373 K as Fig. 4 shows. It is noticed that ν_2 shows a normal negative temperature gradient, whereas ν_1 behaves abnormally. These features suggest that the Cl(1) atom is in an unusual situation which is indicated also in a lower resonance frequency. The temperature dependences of the e^2Qq_{ZZ}/h and η of the ^{209}Bi atom were derived from the 5/2 ↔ 7/2 and 7/2 ↔ 9/2 transitions as is seen in Fig.5.

Bismuth Tribromide. As for bismuth tribromide three resonance frequencies due to ^{81}Br have been newly observed. Table 3 shows these resonance frequencies at room temperature where those due to ^{79}Br are omitted because they have correct isotope frequency ratio. The Zeeman effect on each resonance line was measured at room temperature. Two zero-splitting patterns were obtained from each line. These features of the bromine NQR indicate that the crystal structure of bismuth tribromide is apparently different from that of bismuth trichloride. The quadrupole coupling constant and asymmetry parameter are listed in Table 3. On the other hand, the ^{209}Bi NQR spectrum observed in this experiment is different from that reported by Swiger et al.[4] Four resonance frequencies were observed and ascribed to a kind of bismuth atom in the lattice. The quadrupole coupling constant and asymmetry parameter were calculated using the Cohen's table as Table 3 shows. Only one zero-splitting pattern was observed on either

$5/2 \leftrightarrow 7/2$ or $7/2 \leftrightarrow 9/2$ transition of ^{209}Bi at room temperature. However, there should be another zero-splitting pattern because the crystal has a twofold symmetry which is revealed by the bromine Zeeman effect. This pattern must have been missed, because the Z axis of the field gradient makes a small angle with the rf field and the resonance is too weak to be detected. The observed zero-splitting angles of the $5/2 \leftrightarrow 7/2$ and $7/2 \leftrightarrow 9/2$ transitions were in good agreement with the calculated ones on condition $\eta = 0.82$.[11] The angles among the Z axes of the bromine and bismuth atoms are listed in Table 4.

Discussion

Bismuth Trichloride. As mentioned before the crystal of bismuth trichloride contains two kinds of chemically non-equivalent chlorine atoms and one kind of bismuth atom in the orthorhombic unit cell; the abundance ratio (Cl(1): Cl(2)) in the crystal may be 2:1 according to the relative intensity of two resonance lines due to ^{35}Cl. Furthermore, the Cl(1) atoms have four non-equivalent directions and the Cl(2) atoms have two directions. The unit cell axes of the orthorhombic lattice appear as three twofold axes perpendicular to each other, which may be easily determined by the relations of the Z axes in Figs. 2 and 3.

Nyburg et al. have discussed on the ambiguity of the space group of bismuth trichloride; which is either $Pn2_1a$ or Pnma.[1] If it belongs to Pnma, the molecule in the crystal must have a mirror plane (or a center of symmetry). On the other hand, if it belong to $Pn2_1a$, the molecule need not have any symmetry. They elucidated on the basis of the structure analysis that the correct space group is $Pn2_1a$. The $Pn2_1a$ structure contains three kinds of chlorine atoms in a unit cell as may be seen in Fig. 1. The NQR spectrum of this structure may be composed of three resonance lines due to ^{35}Cl having nearly equal intensity and a set of the bismuth resonance lines. Also, each resonance line must split into four zero-splitting components when a magnetic field is applied. The observed number of the resonance lines and the Zeeman patterns are in disagreement with these expectations on the $Pn2_1a$ structure. These disagreement between the results of the NQR and X-ray methods is originated from whether the molecule has a mirror plane or not, which may appear at $y=\frac{1}{4}$ in Fig. 1. The NQR results suggest apparently that the molecule has the mirror plane so that its space group is Pnma. This structure is isomorphous with that of antimony trichloride and the NQR spectra of these compounds are also similar to each other. In any event, the crystal may be composed of distorted pyramidal molecules. ν_1 is assigned to the chlorine atoms out of the mirror plane and ν_2 to those in the plane. The interatomic distance of the Bi-Cl(2) bond is shorter than that of the Bi-Cl(1) bond. This is an expected tendency from the NQR frequencies since the NQR frequency becomes generally higher as the bond length is shortened.

Table 5 shows the angles between the Z axes and the crystal axes determined by means of the NQR Zeeman effect.[10] The values in the second row were calculated from the $Pn2_1a$

structure by assuming that the Z axes lie on the relevant Bi-Cl bonds. The numerical agreement is good except the difference of the crystal symmetry. Therefore, the directions of the Z axes of the chlorine atoms may be taken to be nearly consistent with the directions of the Bi-Cl bonds in spite of their large asymmetry parameters, although the small deviation of the Z axis from the bond direction may occur as will be mentioned later. Thus, the bond angle can be derived from the directions of the Z axes by considering the molecular symmetry and its pyramidal structure. Table 6 presents the interbond angles thus obtained, along with those by means of the X-ray method.

The difference in the crystal structures proposed by means of the NQR and X-ray analyses is suggestive of the presence of modifications in bismuth trichloride crystal. This is the case in antimony tribromide; that is, there are the $P2_12_12_1$ and Pnma structures which were confirmed by the X-ray and NQR methods.[12)] However, the study of the temperature dependence of the NQR frequency indicates no evidence for such a phase transition in the temperature range concerned as is seen in Figs. 4 and 5.

Although the molecular structure in the Pnma lattice deviates slightly from that in the $Pn2_1a$ lattice, the NQR parameters will be discussed on the basis of the crystal structure of Nyburg et al.

There are strong intermolecular interaction or bonds between the chlorine and bismuth atoms in the solid state as revealed by the X-ray analysis. These intermolecular bonds may affect on the observed quadrupole coupling constants and asymmetry parameters of the chlorine atoms as well as the bismuth atoms. Thus, the large asymmetry parameters may be caused to some extent by these intermolecular bonds, although they are rather weaker compared with the intramolecular bonds, because the Z axis on the chlorine atom is directed along the intramolecular Bi-Cl bond. If halogen atom makes the bridge bonds with equal or comparable strength as is seen in the dimer molecule of Group ⅢA trihalides, the Z axis on the atom becomes to be oriented along any direction other than the bond axis.

As Fig. 6 shows, three bismuth atoms around the Cl(1) atom, which has a larger asymmetry parameter and a lower quadrupole coupling constant, are almost co-planar and the intramolecular Bi-Cl bond makes nearly equal angles with two intermolecular Bi···Cl bonds. Since the intermolecular bond may be formed by transfer of the p_π electrons of the chlorine atom to the empty orbital of the bismuth atom, the quadrupole coupling constant will become lower due to the decrease in the p_π population and the asymmetry parameter will become larger due to the unbalance between p_x and p_y populations.

To explain the observed NQR parameters we will use a method similar to that by Townes and Dailey which accounts for the large asymmetry parameter of the solid iodine in terms of the intermolecular bonds.$^{13)}$ The axially symmetric field gradient, eq, is placed on each of the three bismuth-chlorine bonds around the Cl(1) atom. To simplify the problem two intermolecular bonds are assumed to be equivalent, and the fractional contribution to the total field gradient was denoted by π as the sum of two. That of the intramolecular bond which contains a small s character is represented by σ. The Z axis is placed in the intramolecular Bi-Cl(1) bond and the X and Y axes are found to lie parallel and perpendicular to the plane of the bridge.

Thus, each component of the field gradients can be expressed as follows;

$$
\begin{aligned}
eq_{XX} &= \left\{-\tfrac{1}{2}\sigma + \tfrac{1}{2}\pi(\,3\sin^2\theta - 1)\right\} eq, \\
eq_{YY} &= -\tfrac{1}{2}\,(\,\sigma + \pi\,)\; eq\;, \qquad (5) \\
eq_{ZZ} &= \left\{\sigma + \tfrac{1}{2}\pi(\,3\cos^2\theta - 1)\right\} eq\;,
\end{aligned}
$$

where θ is the angle between the intra- and intermolecular bonds. The ionic character of the Bi-Cl bond, i_σ, is represented by the usual equation: $\sigma = (1-s)\,(1-i_\sigma)$, where s is the s character of the σ bond assumed to be 0.15.[6] Substituting the observed values listed in Table 2 and replacing eq by eq_{atom} for ^{35}Cl, Eq. (5) may be solved; π=0.09 and i_σ=0.63.

It is simply thought from the value of π that the 0.09e charge is transferred from the Cl(1) atom to the bismuth atom as the result of formation of the intermolecular bonds, but most of p_π electrons are localized on the side of the Cl(1) atom. The intramolecular Bi-Cl bond has rather higher covalency, 0.37, than that of the intermolecular σ bond. This reflects the difference between the two interatomic distances. Since the total charge on the Cl(1) atom is defined as $-I = i_\sigma - \pi$, it is reduced to be -0.54e.

Strictly speaking, the contributions of two intermolecular bonds are not the same. For this reason, the Z axis will no longer direct along the Bi-Cl(1) bond and Eq. (5) is no longer held due to the lack of the C_2 symmetry. The degrees of the deviation of the Z axis from the bond axis are dependent on the gap between two contributions, which may be small by considering their interatomic distances. Thus, the assumption of the C_2 symmetry around the Cl(1) atom is not far from the truth, and it is the reason why the Z axis retains the direction along the bond in spite of such large asymmetry parameter as 0.431.

On the other hand, when Eq. (5) is applied to the bonding of the Cl(2) atom, we need consider the contribution of only one intermolecular bond. However, unfortunately the direction of the Z axis is ambiguous because the XZ component of the field gradient, eq_{XZ}, at the bridge system does not vanish due to the lack of C_2 symmetry as mentioned above, which is given by the following;

$$eq_{XZ} = -3/2\ \pi \sin\theta \cos\theta\ eq. \qquad (6)$$

To diagonalize the field gradients we must rotate the coordinates only about the Y axis. This is simply made and diagonalized components of the field gradient are

$$\begin{aligned} eq_{XX'} &= \left[\tfrac{1}{4}(\sigma + \pi) - 3/4\ \left\{(\sigma+\pi)^2 - 4\sigma\pi\sin^2\theta\right\}^{\frac{1}{2}}\right] eq \\ eq_{ZZ'} &= \left[\tfrac{1}{4}(\sigma + \pi) + 3/4\ \left\{(\sigma+\pi)^2 - 4\sigma\pi\sin^2\theta\right\}^{\frac{1}{2}}\right] eq, \end{aligned} \qquad (7)$$

where eq_{YY} remains unchanged from Eq. (5) as well as its direction because the field gradient is unchanged by rotation about own axis. The Z' axis is no longer directed along the

Bi-Cl(2) bond.

Substituting the observed values into Eq. (7), we obtain the following values: $\pi = 0.07$, $i_\sigma = 0.60$, and $I = -0.53e$. These are reasonable compared with those of the Cl(1) atom. On the other hand, the rotational angle α is readily deduced to be about 5° from that $\tan 2\alpha = 2eq_{XZ}/(eq_{XX} - eq_{ZZ})$. Thus, the direction of the Z axis is within 5° from the bond as far as the above model is concerned.

The ionic character of the Bi-Cl(2) bond, 0.60, is somewhat smaller than that of the Bi-Cl(1) bond. It is accordance with the shorter bond distance of the former by 0.05 Å. On the other hand, the ionic character is estimated to be 0.58 according to the Gordy's relation which is based on electronegativity difference between bismuth and chlorine.14) This is fully consistent with the ionic character of the σ bond rather than with total electronic charge, which is nearly constant in spite of the large difference of their NQR parameters.

Thus, the quadrupole coupling constants and asymmetry parameters of the Cl(1) and Cl(2) atoms can be, qualitatively, interpreted by means of the Townes-Dailey method.

The positive temperature dependence of the NQR frequency as is seen for ν_1 is interpreted in terms of one of the following reasons; (i) the d_π-p_π bonding in the metal-chlorine bond,15) (ii) the hydrogen bonding of the chlorine atom,16) and (iii) the intermolecular bonding of the chlorine atom.17) Apparently, neither (i) nor (ii) is concerned with the present case. Since the intermolecular π bond is formed by transfer of p electrons from the chlorine atom to the bismuth atom as mentioned above, it may be broken down by the increased amplitude of librational motions as the temperature raises. This effect increases the pπ population of the chlorine atom and consequently, the resonance frequency. Also, the thermal expansion of the crystal may weaken the intermolecular bond, and hence increase the resonance frequency. The librational motion always lowers the frequency by averaging the field gradient and this is given by the following relation.[18)]

$$\nu = \nu_0\left[1 - 3h/8\pi^2 \sum_i 1/I_i \nu_i \left\{\tfrac{1}{2} + 1/(e^{h\nu_i/kT} - 1\right\}\right] \quad , (8)$$

where $i = x, y, z$ and the symbols used are referred to the original. Thus, the observed temperature dependence appears as the combined result of the two counteracting effects. If the former effect overcomes the latter, the positive temperature coefficient will be observed. This is the case for ν_1 of bismuth trichloride. Accordingly, the intermolecular bond of the Cl(1) atom should be stronger than that of the Cl(2) atom. Assuming that ν_2 is representable by Eq. (8) in spite of its sizable asymmetry parameter and that the term of temperature dependence is set nearly equal for ν_1 and ν_2, ν_1 may be lowered by about 0.6 MHz from the observed frequency at 298 K by the librational motion. This gap is simply thought due to the increased pπ electrons of the chlorine atom. Using Eq. (5), $\Delta\pi$ is calculated to be about 0.03 under the constant σ, from which the asymmetry parameter at 0 K is about 0.6. The temperature dependences of e^2Qq_{ZZ}/h and η of the bismuth atom will be affected by the intermolecular bond as well. However, the theoretical explanation would be hardly made because of the difficulty to estimate these effects including temperature.[17, 19)] From the temperature dependences of the central atoms in arcenic, antimony, and bismuth trichlorides it is seen generally that the intermolecular bonds between the central and chlorine atoms reduce the quadrupole coupling constant of the central atom as well as that of the chlorine atom.

Bismuth Tribromide. The crystal structure of bismuth tribromide is little known. The features of the NQR spectra of ^{81}Br and ^{209}Bi observed in this experiment support that the crystal of this compound is composed of discrete bismuth tribromide molecules. This is in agreement with the results of Raman spectrum of this compound by Oertel et al.20) They also showed that the spectrum was well interpreted if the molecule had a Cs symmetry; this Cs symmetry of the molecule is nearly acceptable in terms of the NQR frequencies. The absorption lines due to ^{209}Bi and three lines due to ^{81}Br may be ascribed to a molecular species in the solid state. However, the spectrum is slightly different from those of bismuth trichloride and the trichlorides of the other Group VA elements which form the molecular crystal. Those spectra are composed of a closely-spaced doublet or a singlet with larger intensity on the lower-frequency side, and a singlet on the higher-frequency side. On the other hand, the spectrum of bismuth tribromide is composed of a doublet on the higher-frequency side and a singlet on the lower-frequency side. Three kinds of NQR spectra have been observed on antimony tribromide by several authors.21) The first two have the characteristics stated above. The third observed by Ogawa, however, resembles to that of bismuth tribromide. Unfortunately, no X-ray diffraction study on this modification has not been established as far as we know.

Since two zero-splitting patterns were observed for each of the three resonances due to ^{81}Br, the crystal was found to belong to monoclinic lattice.10) This is apparently in disagreement with the space group $P2_13$ assumed from the X-ray method.5) The crystal b axis (twofold axis) of the monoclinic lattice could be oriented at the coordinates fixed the sample. The relative orientations of the Bi-Br(1), Bi-Br(2), and Bi-Br(3) bonds with respect to the b axis are 23.3°, 75.9°, and 66.4° respectively. Therefore, only one pattern of ^{209}Bi is erroneous and another direction of the Z axis was calculated in view of its twofold symmetry.

The Z axis of the Br(1) and Br(3) atoms at which the asymmetry parameters are rather small may be directed along the relevant Bi-Br bonds. Although that of the Br(2) atom is unable to be directed straightforwardly along the Bi-Br(2) bond as is shown by its large asymmetry parameter, we assumed its direction to be along the bond as the case of the Cl(1) atom in bismuth trichloride. Furthermore, we assumed that the Z axis of the bismuth atom was directed inside the triangle made by the three Z axes of the bromine atoms in a molecule and the bond angle $\angle$Br-Bi-Br is near 90°. There are two possible atomic arrangements to satisfy above conditions as seen in Fig. 7. It cannot be determined by means of the NQR Zeeman effect only which is really the case. In gaseous state the bond angle is found to be $100° \pm 4°$,22) and hence it becomes smaller than 100° upon solidification. This may be required by molecular packing and intermolecular interaction.

The Bi-Br bonds in the solid state show a wide distribution of the NQR parameters. At 77 K, the resonance frequencies were observed at 98.958, 117.530, and 121.521 MHz. It is noticed that ν_1' has a positive temperature coefficient. The lowest quadrupole coupling constant is likely due to a strong intermolecular bond or a high ionicity of the σ bond of the Bi-Br(1). It is presumed that the larger asymmetry parameter for the Bi-Br(2) bond is caused by the strong intermolecular bond as seen for the Cl(1) atom in bismuth trichloride.

Since the crystal structure is unknown, we will use the following, well-known relations in order to deduce the bond character.

$$\begin{aligned} &(1-s)\,(1-i_\sigma) = \mathrm{Up}\,(1+\eta/3), \\ &\pi = 2/3\,\eta\,\mathrm{Up}, \end{aligned} \qquad (8)$$

where the symbols, s and i_σ, are of the same meaning as before and π is the decreased p_π electrons of the bromine atom. If we introduce 90° as θ in Eq. (5), then above equations becomes identical with Eq. (5). From the observed values of Up and η, we obtained the following: $\pi=0.02$, $i_\sigma=0.62$ for the Br(1) atom, $\pi=0.10$, $i_\sigma=0.53$ for the Br(2) atom, and $\pi=0.04$, $i_\sigma=0.54$ for the Br(3) atom. Thus the ionic charge on the bromine atom is deduced to be -0.60e, -0.43e, and -0.50e. One of the reasons for this inconsistency may be due to the disregard for the angular dependence of the intermolecular bond on the NQR parameters. If we take the intermolecular bond as the origin for the lowest coupling constant of ν_1',

π is obtained to be 0.16 and I is -0.39e under the assumption that i_σ of the Bi-Br(1) bond is 0.53. We qualitatively concluded that the intermolecular interactions in bismuth tribromide crystal are comparable with those in bismuth trichloride crystal. The ionicity of the σ bond is compared with 0.53 which is derived from the electronegativity difference.

Swiger et al. have observed the NQR due to ^{209}Bi of this compound. Their values of e^2Qq_{zz}/h and η were 340.5 MHz and 0.553 respectively. The higher value of e^2Qq_{zz}/h than that of bismuth trichloride was interpreted in terms of the increased s character of the bonding orbitals and of the widened $\angle$Br-Bi-Br angles compared with those in bismuth trichloride. The bond angle deduced by Swiger et al. is 93.4° by assuming the value of η to be zero.

On the other hand, we obtained another NQR parameter of ^{209}Bi as listed in Table 3: e^2Qq_{zz}/h =266.6 MHz and η= 0.822. The value of e^2Qq_{zz}/h is lowered from that of bismuth trichloride as expected from the electronegativity difference between bromine and chlorine. The ratio of quadrupole coupling constants of bismuth tribromide to bismuth trichloride is 0.84, which is comparable to the relevant ratio of antimony trihalides. This is reasonable in view of the discrete molecular structure of bismuth tribromide in the solid state. The large asymmetry parameter, 0.822, may not reflect the distortion of the molecule from C_{3v} symmetry but the wide distribution in bond nature of the Bi-Br as indicated in the bromine NQR parameters, that is, the asymmetry parameter is much more affected by the charge distribution rather than the geometric distortions around the atom concerned.[23)] At 77 K, e^2Qq_{ZZ}/h and η were 276.5 MHz and 0.865 respectively.

Bismuth Triiodide. The ^{127}I NQR spectrum of bismuth triiodide was consisted of two resonance lines of 106.833 and 197.144 MHz at 298 K, which were assigned to $1/2 \leftrightarrow 3/2$ and $3/2 \leftrightarrow 5/2$ transitions respectively; these are in good agreement with the values reported previously.[24)] The Z axis of the iodine atom has been shown to be directed perpendicularly to the Bi-I-Bi plane on the basis of the sign of quadrupole coupling constant by means of ^{129}I Mössbauer effect.[25)] In this case, the following relations given by Lucken are used to interpret the bond nature.[6b)]

$$\begin{aligned} 2 - A &= Up\,(1 + \eta/3), \\ \eta &= -3\cos\theta, \end{aligned} \qquad (9)$$

where A is an electron population of the Bi-I bridging bond and θ is an interbond angle, ∠Bi-I-Bi. From the observed values, $Up=0.2925$ and $\eta=0.258$, we obtained the following values: $A=1.68$ and $\theta=95^\circ$.

Thus, the Bi-I bond in the bridge is seen to have larger ionic character of the σ bond, 0.68, than that of the Bi-Cl or Bi-Br bond. It is likely that the Bi-I bond is weakened by formation of two equivalent bridge bonds, that is, the bridge bonding increases the ionic character of the σ bond. This is found from the increased bond distance, 3.1 Å, in comparison with 2.92 Å for the normal single bond in $Bi_2I_9^{3-}$ ion.[26)] The total electronic charge on the iodine atom which is $-0.36e$ is, however, affected by the decrease of electronegativity in the order of chlorine, bromine, and iodine.

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References

1) S. G. Nyburg, G. A. Ozin and J. T. Szymanski, Acta Crystallogr. B27, 2298 (1971); B28, 2885 (1972).

2) J. Trotter and T. Zobel, Z. Kristallogr. 123 , 67 (1966).

3) H. G. Robinson, Phys. Rev. 100, 1731 (1955).

4) E. D. Swiger, P. J. Green, G. K. Mckown and J. D. Graybeal, J. Phys. Chem. 69, 949 (1965).

5) G. M. Wolter and S. W. Mayer, Acta Crystallogr. 11, 739 (1958).

6) (a) T. P. Das and E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy, Solid State Phys. Suppl. 1 (Academic Press Inc., New York, 1958). (b) E. A. C. Lucken, Nuclear Quadrupole Coupling Constants (Academic Press Inc., New York, 1969).

7) M. H. Cohen, Phys. Rev. 96, 1278 (1954).

8) C. Dean, ibid. 96, 1053 (1954).

9) (a) V. Jaccarino and J. G. King, ibid. 83, 471 (1951); (b) J. G. King and V. Jaccarino, ibid. 94, 1610 (1954).

10) K. Shimomura, J. Phys. Soc. Jap. 12, 652 (1957).

11) N. Inoue, J. Sci. Hiroshima Univ. Ser. A 24, 619 (1960).

12) (a) D. W. Cushen and R. Hulme, J. Chem. Soc. 1962, 2218; 1964, 4162. (b) T. Okuda, H. Terao, O. Ege and H. Negita, Bull. Chem. Soc. Jap. 43, 2398 (1970).

13) C. H. Townes and B. P. Dailey, J. Chem. Phys. 20, 35 (1952).

14) W. Gordy, W. V. Smith and R. F. Trambarulo, Microwave Spectroscopy (John Wiley and Sons, Inc., New York, 1953)

15) T. Okuda, Y. Furukawa and H. Negita, Bull. Chem. Soc. Jap. 44, 2083 (1971).

16) A. Sasane, T. Matuo, D. Nakamura and M. Kubo, J. Mag. Resonance 4, 257 (1971).

17) H. Chihara, N. Nakamura and H. Okuma, J. Phys. Soc. Jap. 24, 306 (1968).

18) H. Bayer, Z. Phys. 130, 227 (1951).

19) G. C. Gillies and R. J. C. Brown, Can. J. Chem. 50, 2576 (1972).

20) R. Oertel and R. Plane, Inorg. Chem. 8, 1188 (1969).

21) Ref. (12b) and references therein.

22) H. H. Skinner and L. V. Sutton, Trans. Faraday Soc. 36, 681 (1940).

23) R. F. Schneider and J. V. DiLorenzo, J. Chem. Phys. 47, 2343 (1967).

24) R. G. Barnes and P. J. Bray, ibid. 23, 1177 (1955).

25) H. Sakai, J. Sci. Hiroshima Univ. Ser. A 36, 47 (1972).

26) O. Lindqvist, Acta Chem. Scand. 23, 2943 (1968).

Department of Chemistry
Faculty of Science
Hiroshima University
Hiroshima

TABLE 1. NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES OF ^{35}Cl AND ^{209}Bi IN BISMUTH TRICHLORIDE AT LIQUID NITROGEN AND ROOM TEMPERATURES

		Resonance frequency,[a] MHz	
		77 K	294 K
^{35}Cl	ν_1	15.826	15.952[b]
	ν_2	19.544	19.173[b]
^{209}Bi	$1/2 \leftrightarrow 3/2$	33.550	31.865
	$3/2 \leftrightarrow 5/2$	25.941	25.132
	$5/2 \leftrightarrow 7/2$	37.915	37.362
	$7/2 \leftrightarrow 9/2$	52.743	51.776

a) Experimental error is within ±0.005 MHz for ^{35}Cl and ±0.01 MHz for ^{209}Bi.

b) Measured at 291 K.

TABLE 2. ASYMMETRY PARAMETERS, QUADRUPOLE COUPLING CONSTANTS, AND UNBALANCED p ELECTRON NUMBERS OF ^{35}Cl AND ^{209}Bi IN BISMUTH TRICHLORIDE AT ROOM TEMPERATURE

	η	e^2Qq_{ZZ}/h, MHz	Up
^{35}Cl(1)	0.431	30.960	0.2821
^{35}Cl(2)	0.178	38.145	0.3476
^{209}Bi	0.555	318.9	

TABLE 3. NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES, ASYMMETRY PARAMETERS, AND QUADRUPOLE COUPLING CONSTANTS FOR ^{81}Br AND ^{209}Bi IN BISMUTH TRIBROMIDE AT ROOM TEMPERATURE (25°C)

		ν, MHz[a)]	η	e^2Qq_{zz}/h, MHz
^{81}Br	ν_1'	102.606	0.077	205.01
	ν_2'	116.021	0.424	225.39
	ν_3'	120.547	0.152	240.17
^{209}Bi	$1/2 \leftrightarrow 3/2$	35.391	0.822	266.6
	$3/2 \leftrightarrow 5/2$	24.315		
	$5/2 \leftrightarrow 7/2$	29.050		
	$7/2 \leftrightarrow 9/2$	41.902		

a) Experimental error is within ±0.01 MHz.

TABLE 4. THE ANGLES AMONG THE Z AXES OF THE FIELD GRADIENT OF THE BROMINE AND BISMUTH ATOMS IN BISMUTH TRIBROMIDE

	Br(1A)	Br(1B)	Br(2A)	Br(2B)	Br(3A)	Br(3B)	Bi(A)
Br(1B)	133.39°						
Br(2A)	64.45°	90.75°					
Br(2B)	90.87°	64.37°	151.89°				
Br(3A)	93.46°	47.48°	94.57°	96.55°			
Br(3B)	47.57°	93.40°	96.49°	94.71°	47.19°		
Bi(A)	61.53°	55.25°	42.31°	116.77°	44.43°	104.90°	
Bi(B)[a]	(55.0°)	(61.8°)	(117.1°)	(43.1°)	(105.4°)	(45.0°)	(69.4°)

a) These were calculated through the twofold symmetry of this crystal lattice.

TABLE 5. THE ORIENTATIONS OF THE PRINCIPAL Z AXES OF THE FIELD GRADIENT WITH RESPECT TO THE CRYSTAL AXES IN BISMUTH TRICHLORIDE

	Cl(1A)	Cl(1B)	Cl(2)	Bi
NQR	(107.17°, 45.25°)	(107.17°, -45.25°)	(20.47°, 0°)	(68.40°, 0°)
X-ray[a)]	(108.60°, 44.77°)	(106.41°, -44.93°)	(18.70°, -0.33°)	.....

a) These values were calculated from the $Pn2_1a$ structure assuming that the Z axis coincides with the relevant Bi-Cl bond.

TABLE 6. THE BOND ANGLES ∠Cl-Bi-Cl IN BISMUTH TRICHLORIDE

	Cl(1)-Bi-Cl(1)	Cl(1)-Bi-Cl(2)	Cl(1)-Bi-Cl(2)
NQR	85.5°	92.3°	92.3°
X-ray	84.5°	93.2°	94.9°

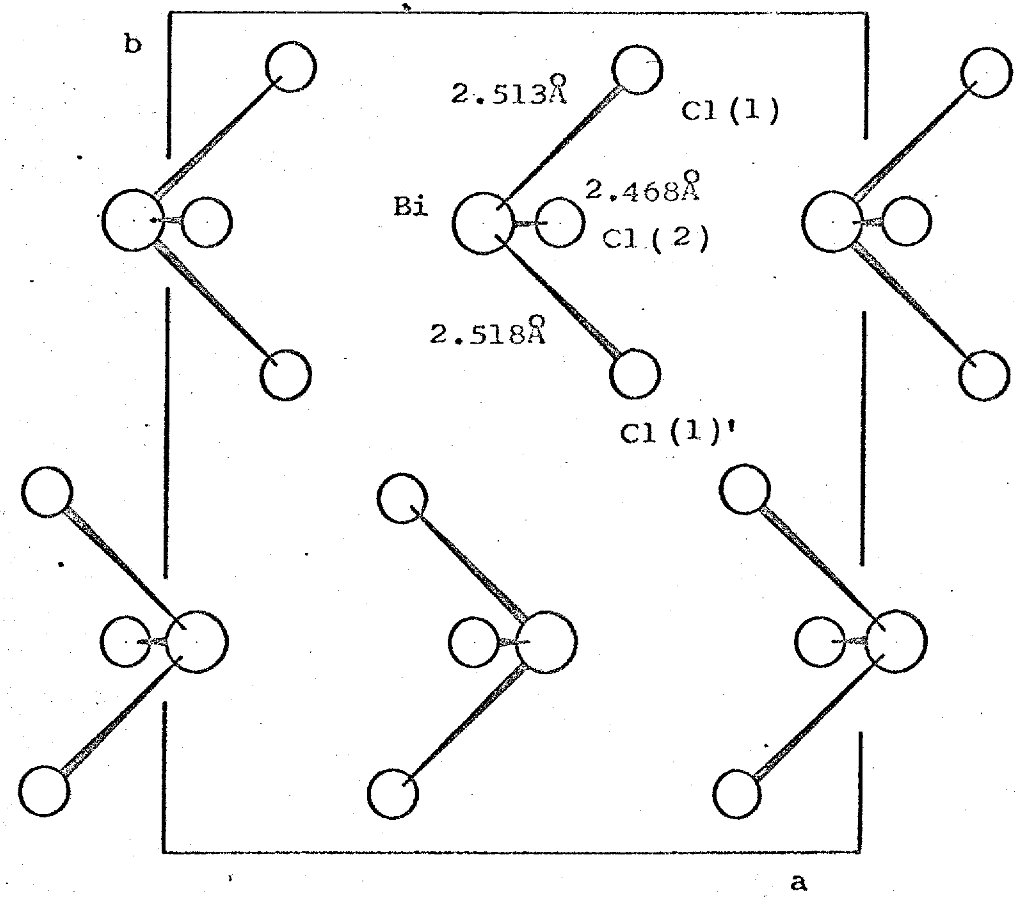

Fig. 1.

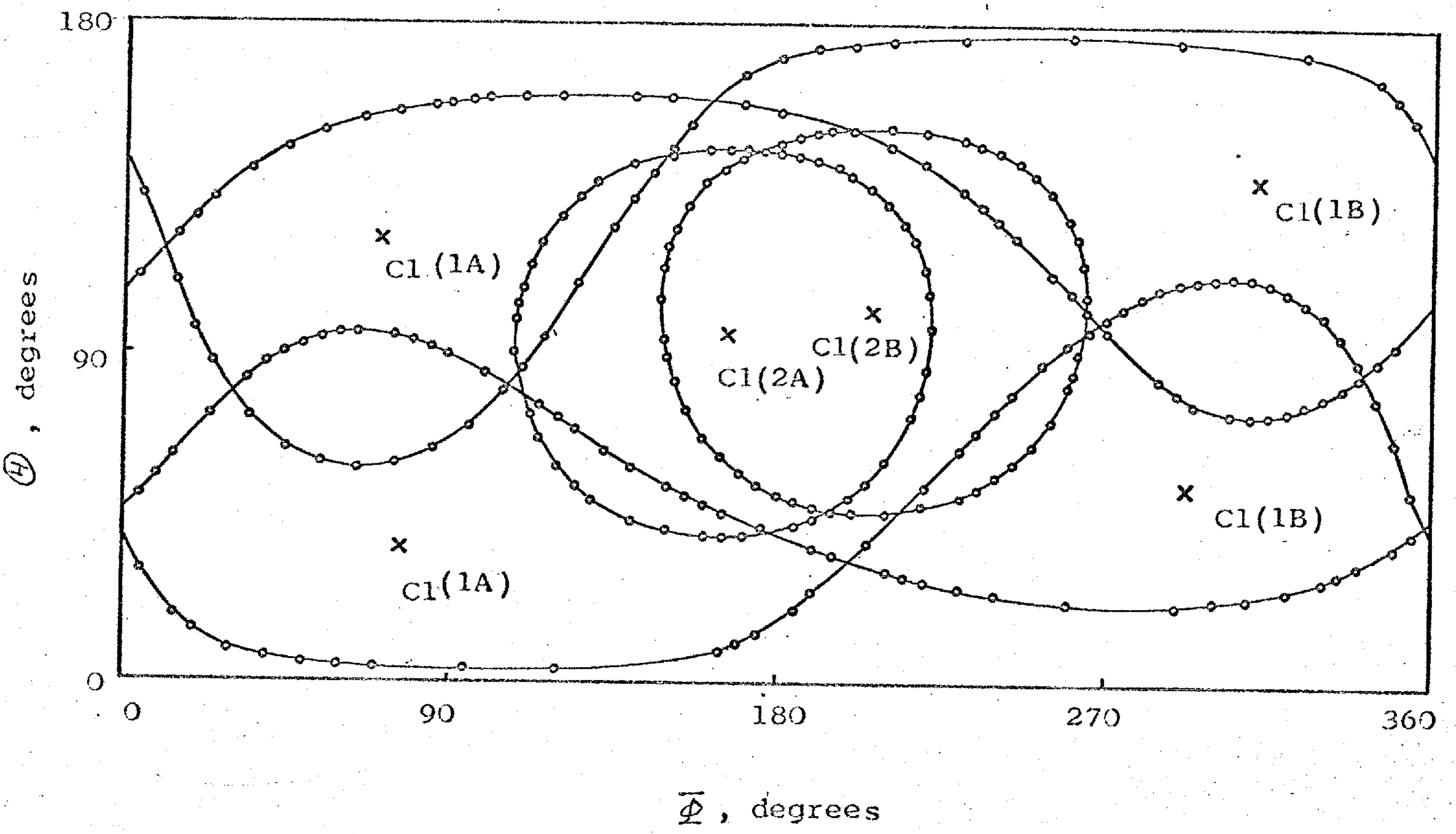
180
90
0
Ⓗ, degrees
0
90
180
270
360
Φ̄, degrees
Cl(1A)
Cl(1A)
Cl(2A)
Cl(2B)
Cl(1B)
Cl(1B)

Fig. 2.

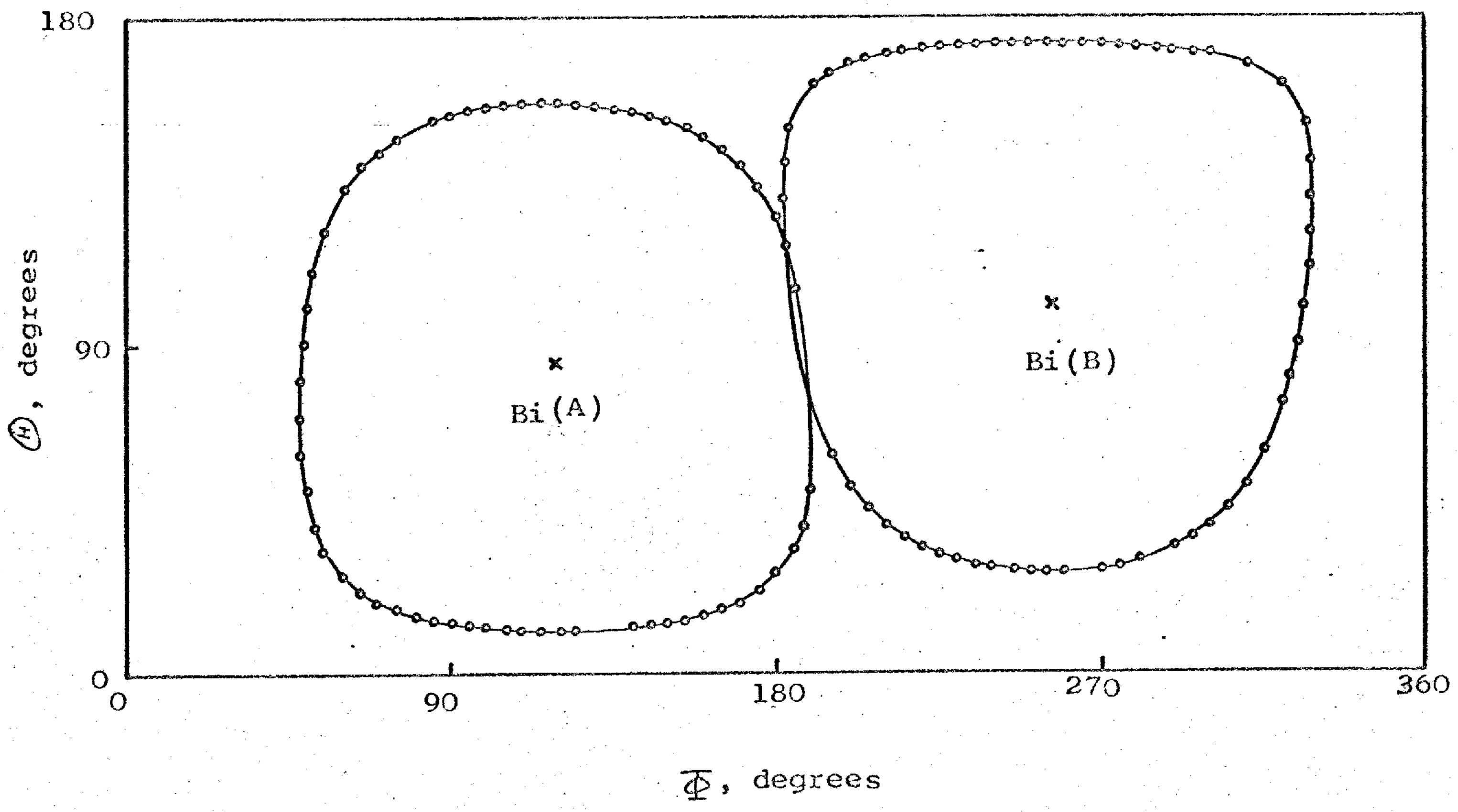

Fig. 3.

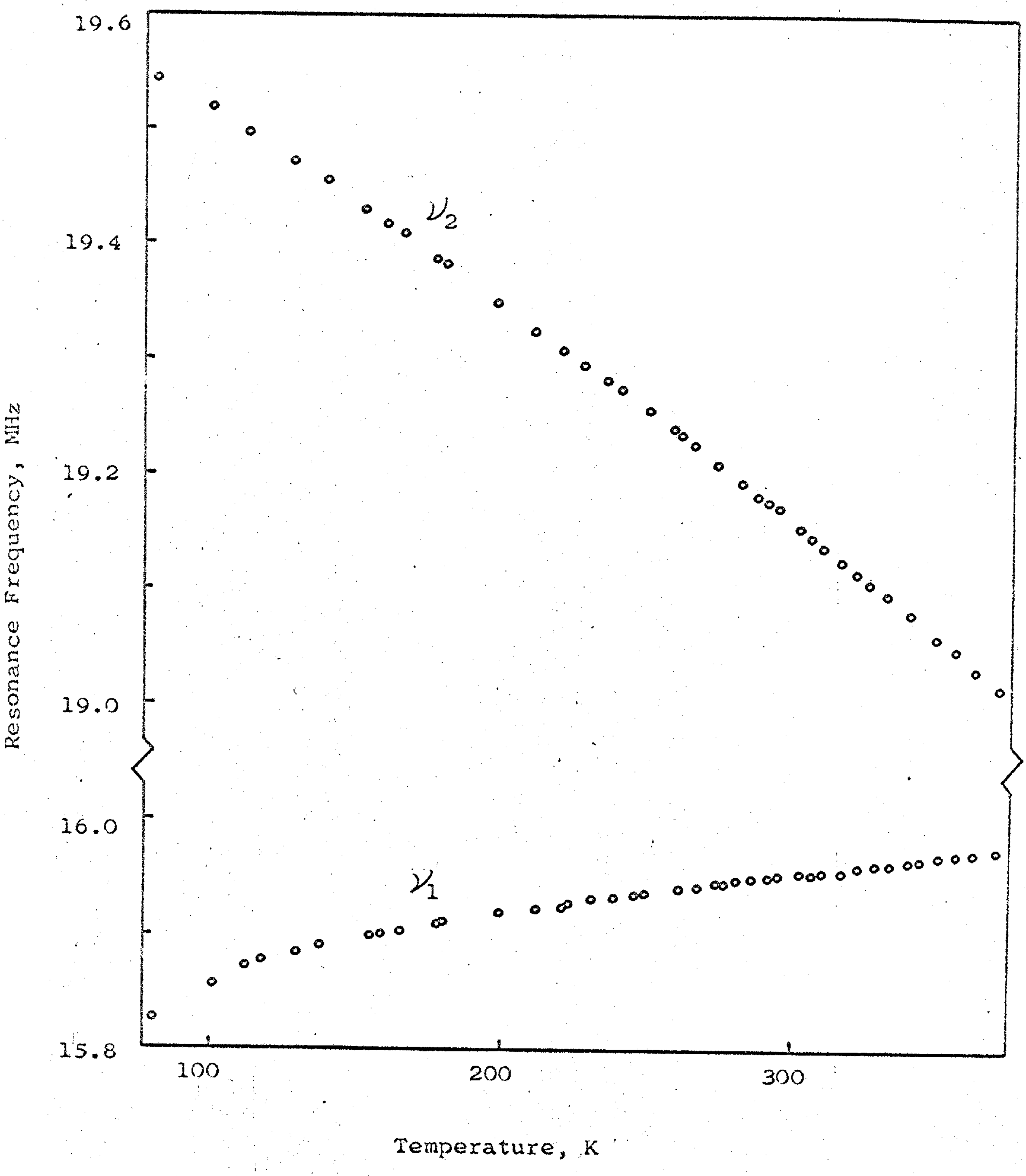
19.6
19.4
19.2
19.0
16.0
15.8
Resonance Frequency, MHz
ν_2
ν_1
100
200
300
Temperature, K

Fig. 4.

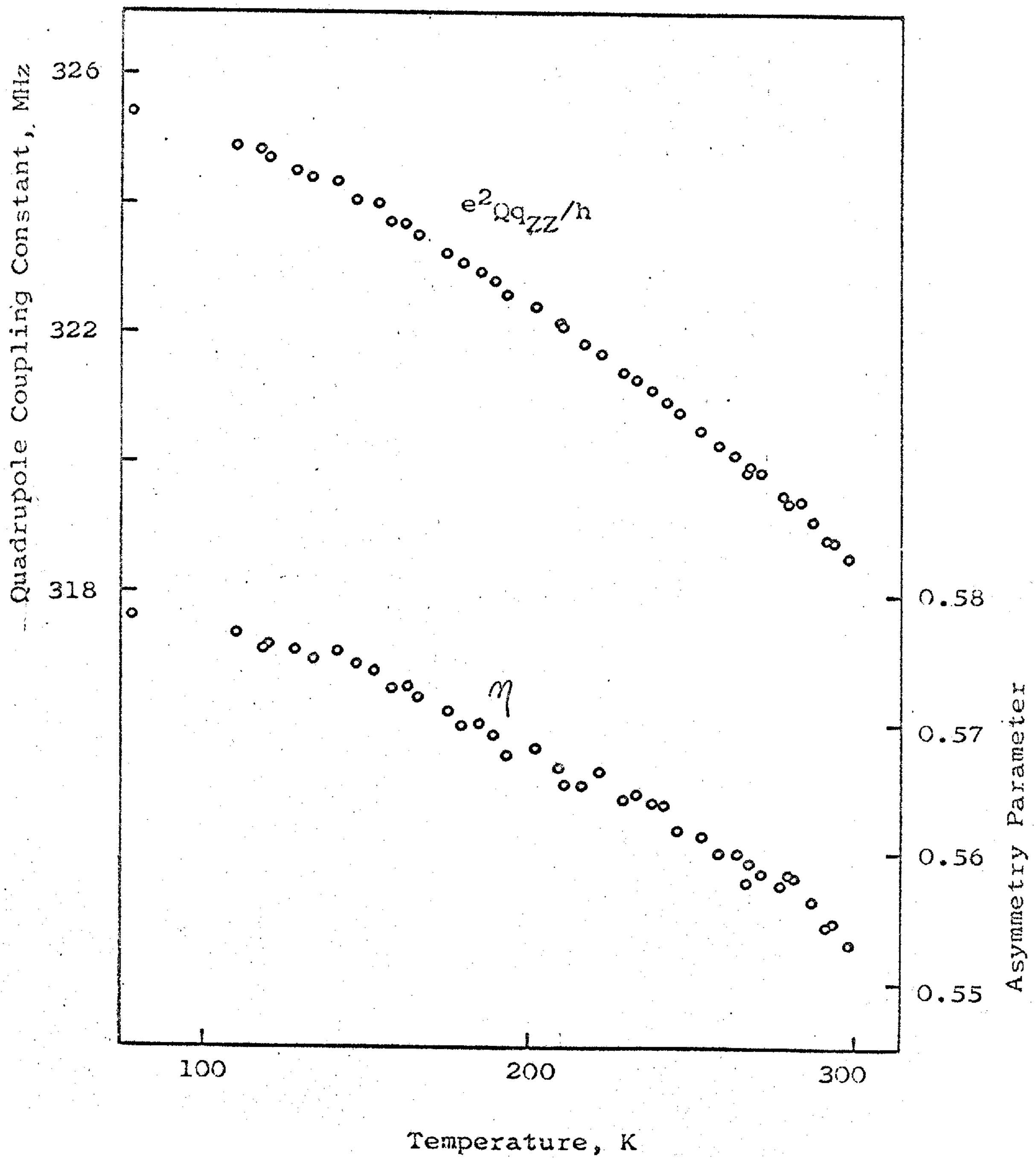
326
322
318
Quadrupole Coupling Constant, MHz
e^2Qq_{ZZ}/h
η
0.58
0.57
0.56
0.55
Asymmetry Parameter
100
200
300
Temperature, K

Fig. 5.

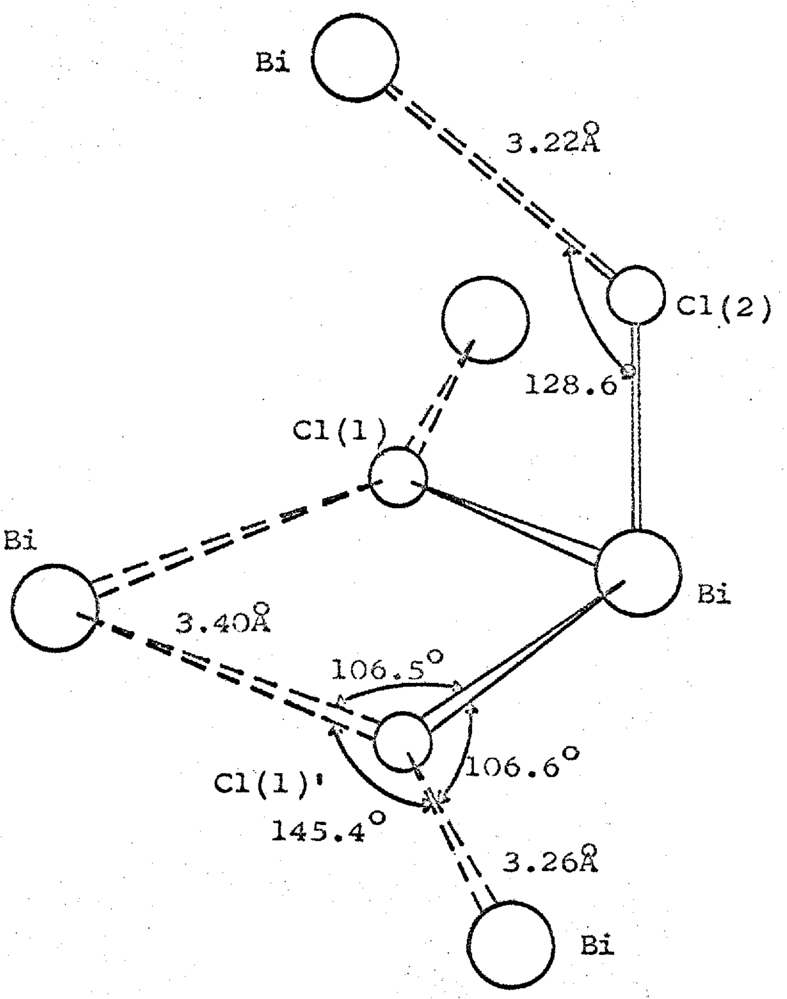

Fig. 6.

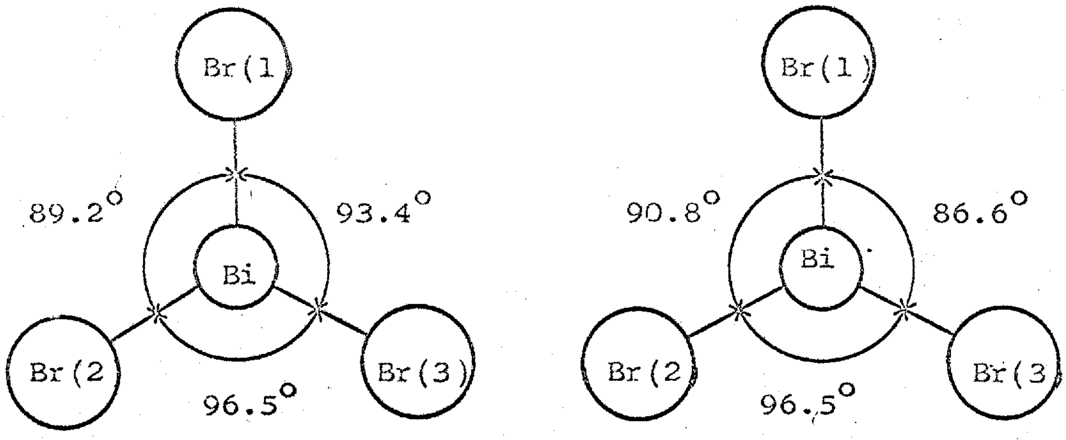

Fig. 7.

Captions of Figures

Fig. 1. Crystal structure of bismuth trichloride projected along c axis.[1)]

Fig. 2. Zero-splitting patterns of Zeeman effect on ^{35}Cl in bismuth trichloride.

Fig. 3. Zero-splitting patterns of Zeeman effect on the 5/2↔7/2 transition of ^{209}Bi in bismuth trichloride.

Fig. 4. Temperature dependences of the resonance frequencies due to ^{35}Cl in bismuth trichloride.

Fig. 5. Temperature dependences of the quadrupole coupling constant and asymmetry parameter of ^{209}Bi in bismuth trichloride.

Fig. 6. Intermolecular arrangement around the chlorine atoms in bismuth trichloride.[1)]

Fig. 7. Two possible molecular shapes of bismuth tribromide by means of the NQR Zeeman effect.

参考論文

参考論文

1. T. Okuda, Y. Furukawa, and H. Negita; ^{81}Br Nuclear Quadrupole Resonance of Modifications of Titanium Tetrabromide.
   Bull. Chem. Soc. Jap., 44, 2083 (1971).
2. T. Okuda, Y. Furukawa, and H. Negita; The Bromine Nuclear Quadrupole Resonance of the Molecular Complex of Aluminum Tribromide with Benzene.
   Bull. Chem. Soc. Jap., 45, 2245 (1972).
3. T. Okuda, Y. Furukawa, and H. Negita; Nuclear Quadrupole Resonance of the 1:1 Molecular Complex between Antimony Trichloride and Ethylbenzene.
   Bull. Chem. Soc. Jap., 45, 2940 (1972).
4. T. Okuda, Y. Furukawa, H. Shigemoto, and H. Negita; The Bromine Nuclear Quadrupole Resonance of Two Modifications of Indium Tribromide.
   Bull. Chem. Soc. Jap., 46, 741 (1973).
5. T. Okuda, Y. Furukawa, K. Yamada, and H. Negita; The Chlorine Nuclear Quadrupole Resonance of Several Oxygen-chlorine Bonds.
   Bull. Chem. Soc. Jap., 46, No. 9 (1973), in press.
6. H. Negita, K. Shibata, Y. Furukawa, and K. Yamada; Charge Transfer in Acetonitrile-halogen Complex.
   Bull. Chem. Soc. Jap., 46, No. 9 (1973), in press.