Nuclear Quadrupole Resonances of Tellurium Tetrachloride and Tellurium Tetrabromide

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The nuclear quadrupole resonances (NQR) due to ^{35}Cl and ^{81}Br in $TeCl_4$ and $TeBr_4$ have been observed and their Zeeman effects have been examined. Each spectrum consists of six resonance lines with equal intensities, which are assigned to the two species of $TeCl_3^+$ ions or $TeBr_3^+$ ions. The asymmetry parameter of the electric-field gradient is, at most, 5% in each case. The relative orientation among the zero-splitting patterns of six resonance lines is consistent with the crystal structure of $TeCl_4$, which consists of the tetramers of $(TeCl_3^+Cl^-)_4$, as was recently determined by X-ray diffraction analysis. The zero-splitting patterns of the $TeBr_4$ crystal are so similar to those of $TeCl_4$ that the former crystal seems likely to consist of tetramers of $(TeBr_3^+Br^-)_4$ as well. The average ∠X–Te–X bond angles in TeX_3^+ ions were found to be 95.9° for the chloride and 96.7° for the bromide. The values for the chloride are in good agreement with those obtained by the X-ray analysis. On the other hand, the bond character of the TeX_3^+ ions in TeX_4AlX_3 (X=Cl, Br) was compared with that of TeX_4 from NQR.

It has been described that the molecular shape of $TeCl_4$[1] in the gaseous state is a trigonal bipyramid with lone-pair electrons on one of its equatorial orbitals. From the nuclear quadrupole resonance study,[2] the molecular shape in the solid state has been presumed to be a trigonal bipyramid, as in the gaseous state, though six resonance lines were observed at the temperature of liquid nitrogen.

On the other hand, the structural study of solid TeX_4 (X=Cl, Br) by means of infrared spectroscopy[3–6] has suggested that the crystal consists essentially of the ionic structure $TeX_3^+X^-$ because of the existence of four infrared-active vibrations similar to those of $SbCl_3$ and $SbBr_3$.

Recently, from a three dimensional X-ray analysis of $TeCl_4$[7] it has been concluded that this compound crystallizes in the space group C2/c of the monoclinic system with a=17.076 Å, b=10.404 Å, c=15.252 Å, and β=116.28 °. As is show in Fig. 1, the crystal consists of tetramers formed with an arrangement of alternate $TeCl_3^+$ and Cl^- ions at the apexes of the distorted cube. The unit cell contains four tetramers, all of which are equivalent and have two-fold axes. Every Te atom has three terminal Cl atoms and three bridging Cl atoms at average distances of 2.31 Å and 2.93 Å respectively. The X-ray diffraction studies of $SeCl_4$ and $TeBr_4$[8,9] have shown that these compounds are isomorphous with $TeCl_4$.

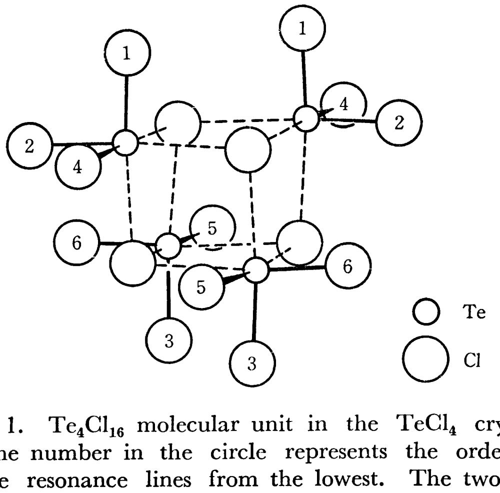

Fig. 1. Te_4Cl_{16} molecular unit in the $TeCl_4$ crystal. The number in the circle represents the order of the resonance lines from the lowest. The two-fold crystallographic axis passes vertically.

In the present experiment, the NQR spectra of $TeCl_4$ and $TeBr_4$ were observed in the temperature range from 77 K to 339 K, and the Zeeman effects on the spectra of the single crystals were examined at room temperature in order to clarify the bond character and molecular shape in the crystals. Furthermore, the bond characters were compared with those of TeX_3^+ ions in the TeX_4AlX_3 crystal.

Experimental

The single crystals of $TeCl_4$ and $TeBr_4$ were grown by the Bridgman-Stockbarger method. The NQR spectrometer used in this experiment was a super-regenerative oscillator with frequency modulation, and the absorption lines were observed on an oscilloscope. An LC–type super-regenerative oscillator was made to seach for the resonance lines of bromine isotopes in the region about 200 MHz. This oscillator was used only at room temperature and was put in the magnetic field for the study of the Zeeman effect. The resonance frequencies of the ^{81}Br nuclei were observed by the use of a super-regenerative oscillator consisting of Lecher-lines at various temperatures. The resonance frequencies were determined with a VHF signal generator and frequency counter of the Takeda Riken Co., TR–5578.

The Zeeman effect was examined by means of the zero-splitting cone method.[10] The orientation of the magnetic field for the zero-splitting was determined by means of polar coordinates (Φ, Θ), where Φ and Θ were the azimuthal and polar angles respectively, in the coordinate fixed to the sample. About forty experimental points were observed for each zero-splitting pattern. From these values, the best quadratic cone was obtained by the use of the least squares method, then the center of each zero-splitting pattern and the value of η were determined precisely.

Results and Discussion

The resonance frequencies of $TeCl_4$ and $TeBr_4$ are listed in Table 1. Powder samples of both $TeCl_4$ and $TeBr_4$ give rise to six resonance lines with equal intensities, although the ν_2' and ν_3' lines of $TeBr_4$ coincide at the temperature of liquid nitrogen. All the reso-

Table 1. ^{35}Cl and ^{81}Br NQR frequencies in TeX_4 (X=Cl, Br)

Compounds		Resonance frequencies (MHz) 26 °C	Resonance frequencies (MHz) −196 °C
$TeCl_4$	ν_1	26.782	27.304
	ν_2	26.947	27.370
	ν_3	27.024	27.471
	ν_4	27.471	27.926
	ν_5	27.685	28.110
	ν_6	27.968	28.461
$TeBr_4$	ν_1'	185.18	188.13
	ν_2'	187.68	190.42
	ν_3'	187.81	190.42
	ν_4'	190.91	193.56
	ν_5'	195.36	197.88
	ν_6'	197.34	200.06

nance frequencies decrease continuously with an increase in the temperature, and the temperature coefficients are nearly equal in each compound. This must result from the fact that the crystal consists of tetramers which have an approximately Td symmetry and that the terminal halogens therefore undergo nearly equal thermal vibrations.

The zero-splitting patterns of $TeCl_4$ are shown in Fig. 2, where Cl_1, Cl_2,···, Cl_6 indicate the direction of the z-axes of the field gradients at the chlorine atoms showing ν_1, ν_2,···, ν_6 resonance lines respectively. Two zero-splitting patterns were observed for each resonance line, and a two-fold axis was determined, as is shown in Fig. 2. The two zero-splitting patterns of all the resonance lines except ν_2 were well separated from one another. However, the ν_2 line gave partly overlapping zero-splitting patterns. Therefore, the evaluation of the asymmetry parameter for this line was less accurate. As the asymmetry parameters of field gradients are small, it can be assumed that the z-axis coincides with the bond direction. Therefore, the assignment of the z-axes to chlorine atoms in the tetramer is based on the two-fold symmetry axis determined from Zeeman experiments and on the various angles determined from X-ray analysis. In Fig. 3, the principal z-axes which are considered to arise from the same $TeCl_3^+$ ions are connected with solid or broken lines; triangles are thus formed. The triangles represented by solid or broken lines correspond to nonequivalent $TeCl_3^+$ ions in the crystal. Figure 3 supports the existence of the tetramers of $(TeCl_3^+Cl^-)_4$ for the $TeCl_4$ crystal, although these results are derived on the basis of the crystal structure from the X-ray analysis. The numbers in the circles in Fig. 1 show the chlorine species determined by the present experiment. In Fig. 4, the resonance frequencies of the terminal Cl atoms are plotted against the terminal bond length and the bond length of the bridging bonds which are located at the *trans* position to the terminal Cl atoms. This figure shows that each resonance frequency is affected by the bridging Cl atom which is located at the *trans* position to the terminal Cl atom. Therefore, the large spread in the resonance frequencies may be considered mainly due to the difference in the strength of the bonds between the bridging Cl atom and the Te atom.

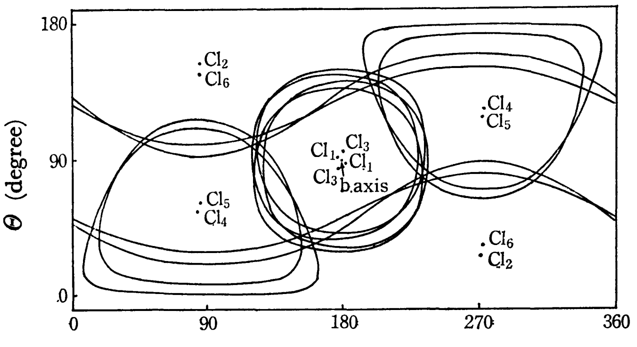

Fig. 2. Zero-splitting patterns of Zeeman lines of $TeCl_4$. The axis of $\Theta=0$ is taken as the rotation axis of the sample tube. The plane of $\Phi=0$ is arbitrarily chosen.

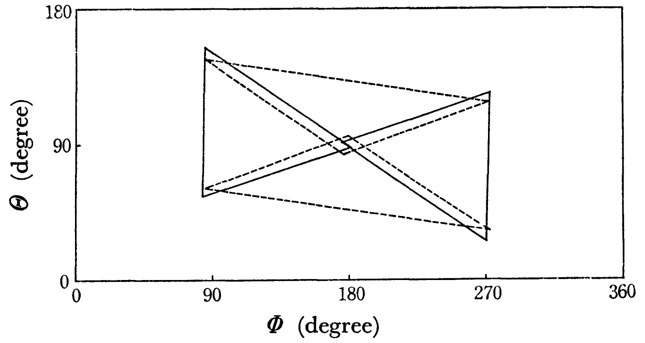

Fig. 3. Principal z-axes and its relationship in $TeCl_4$ crystal.

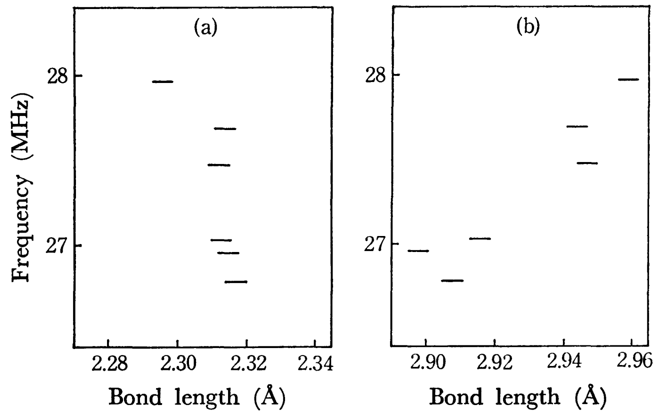

Fig. 4. The relationship between resonance frequencies and bond length in $TeCl_4$. a) resonance frequencies are plotted against their terminal bond length, b) resonance frequencies are plotted against the bond length of the bridging bond being located at the *trans* position to the terminal Cl atoms.

The zero-splitting patterns of $TeBr_4$ are quite similar to those of $TeCl_4$. From the similarity of the zero-splitting patterns of $TeBr_4$ to those of $TeCl_4$, and from the fact that they are isomorphous with each other,[8,9] it is evident that the former crystal consists of tetramers of $(TeBr_3^+Br^-)_4$. It may be considered on the basis

Table 2. The bond angles ∠XTeX in TeX_3^+ ions (X=Cl, Br)

Compounds		$\angle X_1Te_1X_2$	$\angle X_2Te_1X_4$	$\angle X_1Te_1Y_4$	$\angle X_3Te_2X_5$	$\angle X_5Te_2X_6$	$\angle X_6Te_2X_3$
$TeCl_4$	NQR	94.4°	98.2°	95.1°	96.2°	95.5°	96.3°
	X-ray	93.7°	95.7°	94.2°	94.9°	95.0°	95.1°
$TeBr_4$	NQR	94.6°	98.5°	95.6°	97.4°	96.8°	97.5°

Table 3. ^{35}Cl and ^{81}Br NQR parameters in TeX_4 (X=Cl, Br) (26 °C)

Compounds	η(%)	e^2Qq/h(MHz)	U_p	i(%)
$TeCl_4$	2.4±0.2	53.559	48.8	42.6
	up to 5.0	53.867	49.1	42.2
	3.0±0.2	54.040	49.2	42.1
	2.8±1.0	54.932	50.1	41.1
	1.9±0.2	55.362	50.4	40.7
	2.5±0.5	55.926	51.0	40.0
$TeBr_4$	4.5±0.3	370.22	57.6	32.2
	up to 5.0	375.34	58.4	31.3
	4.4±0.2	375.50	58.4	31.3
	3.6±0.3	381.74	59.4	30.1
	1.5±0.5	390.71	60.8	28 3
	2.7±0.2	394.63	61.4	27.8

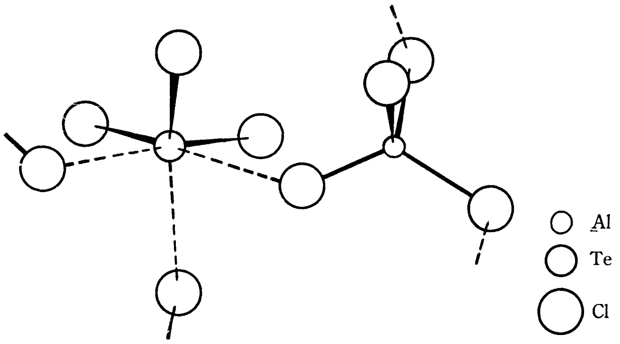

Fig. 5. The crystal structure of $TeCl_4AlCl_3$.

Table 4. NQR parameters of TeX_3^+ ions in TeX_4AlX_3 (X=Cl, Br) (25 °C)

Compounds	ν(MHz)	e^2Qq/h(MHz)[a]	Up(%)
$TeCl_4AlCl_3$	29.420	58.840	53.6
	29.574	59.149	53.9
	30.570	61.140	55.7
$TeBr_4AlBr_3$	207.33	414.66	64.5
	207.67	414.34	64.6
	208.12	416.24	64.7
	208.90	417.80	65.0
	212.45	424.90	66.1
	214.37	428.74	66.7

a) η is assumed to be zero, referring to the recent X-ray analysis.

of the orientation of the z-axes that this tetramer has a two-fold axis and contains two nonequivalent $TeBr_3^+$ ions. As the NQR spectra and their Zeeman patterns in $TeBr_4$ are similar to those in $TeCl_4$, one $TeBr_3^+$ ions contributes to the ν_1', ν_2', and ν_4' lines, and the other, to the ν_3', ν_5', and ν_6' lines. Table 2 shows the bond angles of the TeX_3^+ ions obtained from NQR, together with those obtained by X-ray analysis. The former values are slightly larger than the latter.

In the $TeCl_4$ crystal, π-bond character of the terminal Te-Cl bond may be neglected for three reasons: a) the terminal Te-Cl bond length is nearly equal to the corrected sum of the single covalent bond radii of 2.34 Å,[11] b) the resonance frequencies show negative temperature coefficients, and c) the asymmetry parameters are small. Table 3 lists the asymmetry parameter of the electric-field gradient (η), the quadrupole coupling constant (e^2Qq), the number of unbalanced p electrons (U_p), and ionic character (i) for the Te-X bond. These parameters are related by the following equations:

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

$$U_p = e^2Qq_{obs}/e^2Qq_{atom} = (1-s)(1-i), \qquad (2)$$

where e^2Qq_{obs}/h is the observed quadrupole coupling constant and e^2Qq_{atom}/h is 109.74 MHz for ^{35}Cl and 643.03 MHz for ^{81}Br.[12] s is the s-electron character in the bonding orbital of the halogen, which is assumed to be 0.15.[13] The ionic character of the terminal Te-X bond in $TeBr_4$ is smaller than that of $TeCl_4$, as is shown in Table 2. The same tendency is seen between chloride and bromide, which have the same structure, and may be attributed to the differences in the electronegativities of the relevant halogen atoms.

As is obvious from the crystal structure, $TeCl_4$ acts as a Cl^- donor and forms a compound with the Cl^- acceptor. An example is $TeCl_4AlCl_3$,[14] the crystal structure of which has recently been determined to be as is shown in Fig. 5. The $TeCl_3^+$ ion has a shape similar to that in $TeCl_4$, but the Te–Cl bonds in $TeCl_4$-$AlCl_3$ are shorter than those in $TeCl_4$. Table 4 shows the NQR parameters of $TeCl_4AlCl_3$ and $TeBr_4AlBr_3$. The resonance frequencies are assigned to those of halogens in TeX_3^+ ions, because those in AlX_4^- ions are expected to be much lower. The quadrupole coupling constants in the TeX_4AlX_3 crystal are larger than those in $TeCl_4$ and $TeBr_4$ by about 9.3% and 10.0% respectively. According to the X-ray analysis of the crystals of $TeCl_4AlCl_3$,[14] $TeCl_4$,[7] and $(NH_4)_2$-$TeCl_6$[15,16] all the tellurium atoms are octahedrally coordinated by six chlorine atoms. Although the $TeCl_6^{2-}$ ion in $(NH_4)_2TeCl_6$ is a regular octahedron, the $TeCl_3^+$ ion in $TeCl_4AlCl_3$ forms a distorted octahedron, as is shown in Fig. 5. There is a linear relationship between the quadrupole coupling constants and the bond lengths of the terminal Te–Cl bonds. From this relationship, it is obvious that the bond character of Te–Cl in the $TeCl_4$ crystal is intermediate between $TeCl_4AlCl_3$ and $(NH_4)_2TeCl_6$. The same tendency is seen in the bromine compounds.

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