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Bondings on the TeI_4 Tetramer, as Studied by Means of NQR

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The ^{127}I NQR and its Zeeman effect on the TeI_4 single crystal were investigated. Ten nonequivalent iodine atoms were detected, in agreement with the X-ray analysis by Krebs and Paulat. Six of them were assigned to terminal atoms, two to bridge atoms, and the remaining two to pyramidal iodine atoms, on the basis of their quadrupole coupling constants and asymmetry parameters. One of the bridging iodine atoms takes an efg z-axis parallel to the shorter Te–I bond, but the other bridging iodine atom takes an efg z-axis perpendicular to the bridging plane. This difference can be explained by a simple model based on the Townes-Dailey treatment and is consistent with that difference to be expected from the bridging-bond length. The extremely small coupling constants for the pyramidal iodine atoms could be interpreted by covalency, assuming a hybridization of the s-orbital to the pure p-bond configuration.

According to Krebs and Paulat[1] the crystal of tellurium tetraiodide is orthorhombic (space group Pnma), with 16 TeI_4 in the unit cell. As is shown in Fig. 1, the structure is built of $(Tel_4)_4$ tetramers which are different from the $(TeCl_4)_4$ tetramer in molecular structure.[2] The $(Tel_4)_4$ tetramer has a reflection plane parallel to the ac plane. This tetramer is interesting in its structure and bonding, because it consists of three types of iodine atoms, that is, terminal, bridging, and pyramidal atoms. The last type of iodine atom was called "triply bridging iodine" by Krebs and Paulat. In the light of the NQR study, the following information has been obtained and may be discussed with the framework of the Townes-Dailey theory. (1) Angular bridging halogens are well known in dimeric compounds, M_2X_6 (M=Al, Ga, and In; X=Br and I). In these molecules, the bridging bonds are symmetrical, so that the orientations of the efg axes can be expected from the symmetry.[3,4] However, as the bridging iodine atoms in this tetramer form asymmetric bonds with two tellurium atoms, the orientations of the efg axes should depend upon the covalent character of the two Te–I bonds. In addition, it is valuable to examine the temperature dependence of the e^2Qq/h for the asymmetric bridging iodine with a definite efg axis orientation. (2) The quadrupole coupling constants for the pyramidal halogen in a normal oxidation state have been reported only for CdI_2 (X=Br and I),[5] as far as we know. The small e^2Qq/h values for the halogens in CdI_2 were interpreted in terms of covalency, assuming the hybridization of the s-orbital to the three-orthogonal-p-bonding configulation. The validity of this model was tested for the pyramidal iodine in the TeI_4 tetramer.

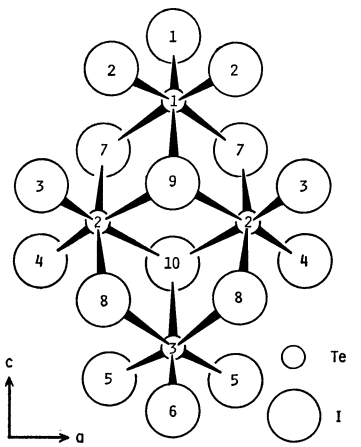

Fig. 1. Tetrameric molecular unit in the TeI_4 crystal.[1]

A part of this work has already reported elsewhere,[6] but there has been no precise discussion of the bridging iodine because of the lack of the crystal structure, which is now established.

Experimental

The TeI_4 single crystal was grown by the Bridgman-Stockbarger method in a Pyrex tube in which stoichiometric amounts of tellurium and iodine were sealed under reduced pressure. The NQR spectra and their Zeeman effect were observed according to a procedure similar to one described previously.[6,7] In the detection of the pyramidal iodine NQR signal, a Zeeman modulated Dean-type spectrometer was used. The Zeeman effect for the bridging iodine atom was observed at the temperature of liquid nitrogen in order to increase the S/N ratio of the NQR signal.

Results

The Zeeman effect on the terminal iodine was observed in order to obtaine the orientations of the crystal axes for the single crystal employed. As is to be expected from the Laue symmetry of the crystal, four zero-splitting cones were observed for the iodine in the general position. Table 1 shows the direction cosine of the efg z-axis with respect to the crystal axes, which were determined from the symmetry of the observed zero-splitting cones. As is evident from the last column of this table, the efg z-axis coincides with that of the Te–I bond within one degree.

On the other hand, in any discussion of the bridging iodine, not only the z-axis but also the x- and y-axes are necessary. In the case of an iodine atom with a pair of lines, $\nu_1(\pm 1/2 \leftrightarrow \pm 3/2)$ and $\nu_2(\pm 3/2 \leftrightarrow \pm 5/2)$, the behavior of their zero-splitting cones on η has been described elesewhere.[6] In general, efg x-, y-, and z-axes are determined only from the ν_1 cone except for $\eta \fallingdotseq 0$ and $\fallingdotseq 1$. Figure 2 shows the ν_1 patterns and the corresponding efg axes for the I(7) atom at 77 K, where the center of the pattern is pointed toward its y-axis ($\eta > 0.412$). When an η value approaches 1, such as in the case of I(8), the ν_1 and ν_2 lines both show axially symmetric cones around their y- and

Table 1. Direction cosines of the efg q_{zz}-axes and the corresponding terminal Te-I bonds (in parentheses) with respect to the crystal axes (296 K)

	e^2Qq/h / MHz	η	Direction cosine			$\angle q_{zz}$, Te-I / degree
			a	b	c	
I(1)	1522.3	0.032	−0.7035	0.001	0.7107	0.88
			(−0.6924)	(0)	(0.7215)	
I(2)	1680.9	0.029	0.5670	0.7361	0.3697	0.52
			(0.5597)	(0.7394)	(0.3741)	
I(3)	1672.0	0.014	0.6262	0.6498	0.4308	0.38
			(0.6225)	(0.6549)	(0.4285)	
I(4)	1612.8	0.056	−0.5791	0.6890	−0.4357	0.60
			(−0.5825)	(0.6921)	(−0.4262)	
I(5)	1560.1	0.056	−0.5479	0.7466	−0.3773	0.61
			(−0.5554)	(0.7404)	(−0.3786)	
I(6)	1621.8	0.012	0.6791	0.002	−0.7340	
			(0.6756)	(0)	(−0.7372)	0.32

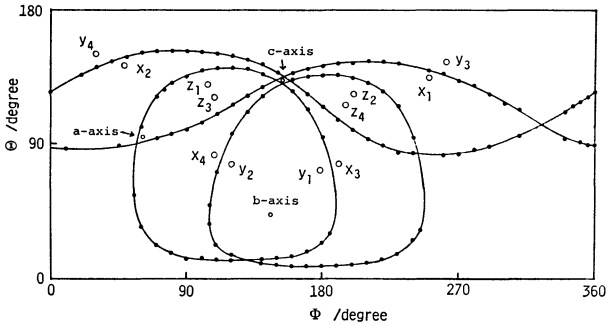

Fig. 2. Zero-splitting loci of the ν_1 line corresponding to the I(7) atom at 77 K.
○: Crystal axis, ○: efg axis.

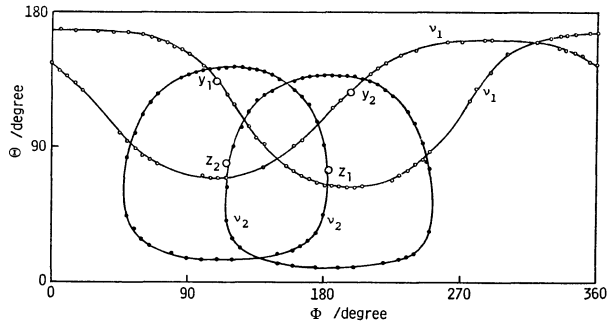

Fig. 3. Zero-splitting loci of the ν_1 and ν_2 lines corresponding to the I(8) atom.
–○–: ν_1, –●–: ν_2, ○: efg axis.

z-axes respectively. Therefore, the Zeeman effect on both ν_1 and ν_2 lines must be measured in the determination of the three orthogonal efg axes. Figure 3 shows the zero-splitting patterns corresponding to ν_1 and ν_2 for the I(8) atom. Because of the small S/N ratio, two patterns out of four were observed. The other two orientations of the patterns may be expected from the crystal symmetry. The resultant orientations of the efg axes with respect to their bridging bonds are illustrated in Fig. 4, while their angles are shown in

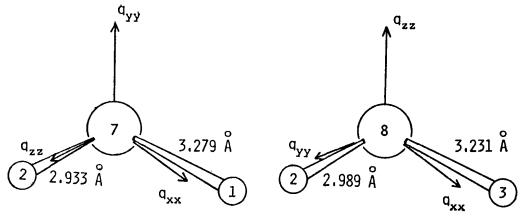

Fig. 4. Orientations of the efg axes with respect to its bridging plane.

Table 2. Bridging iodine NQR parameters (296 and 77 K) and angles between efg axes and Te-I bonds[a)]

	e^2Qq/h / MHz	η	Angles: efg axis	Bridging bond	
				Te(2)-I(7)	Te(1)-I(7)
I(7)	929.6	0.738	x	90.9°	6.4°
	(940.5)	(0.752)	y	89.4°	92.9°
			z	1.2°	95.9°
				Te(2)-I(7)	Te(3)-I(8)
I(8)	775.1	0.949	x	85.5°	10.4°
	(793.7)	(0.917)	y	4.5°	98.0°
			z	90.1°	88.5°

a) NQR parameters at 77 K in parentheses.

Table 2, also with the NQR parameters. In this calculation, we assumed that there is no significant change in the crystal structure from room temperature to 77 K because of the continuous temperature dependence of the e^2Qq/h.[6)]

Table 3 gives the NQR parameters of the pyramidal halogens in TeI_4 and $TeBr_4$. The crystal of tellurium tetrabromide consists of tetramers, containing terminal and pyramidal bromine atoms, and is isomorphous with tellurium tetrachloride.[8,9)]

Discussion

Quadrupole Coupling Constants for the Bridging Iodine. According to the X-ray data, the bridging bond lengths

Table 3. ^{127}I and ^{81}Br NQR parameters of the pyramidal halogens at 293 and 77 K (in parentheses)[a]

Compound	$\nu_1(\pm1/2\leftrightarrow\pm3/2)$ MHz	$\nu_2(\pm3/2\leftrightarrow\pm5/2)$ MHz	e^2Qq/h MHz	η
TeI_4	8.794 (7.984)	17.008 (15.529)	57.00 (51.99)	0.163 (0.148)
	8.982 (9.278)	16.472 (17.189)	55.68 (60.22)	0.268 (0.250)
$TeBr_4$	13.539 (12.513)[b]			
	12.626			

a) Estimated error in ν: 0.01 MHz. b) Doublet.

in the Te(1)–I(7)–Te(2) are 2.933 and 3.279 Å, while those in the Te(2)–I(8)–Te(3) are 2.989 and 3.231 Å. The former bridging is more asymmetric than the latter. As is obvious from Fig. 4, the bridging atoms take their efg x-axes in the direction of their longer bonds in both cases, but the z- and y-axes change in different directions. We will explain the large asymmetry parameter and the orientations of the efg axes using a simple model. We assume that the bonding of the iodine atom is composed of pure p-orbitals, because the bridging angle is close to 90° ($\angle$Te(1)I(7)Te(2)=95.3°; $\angle$Te(2)I(8)Te(3)=95.7°). Furthermore, the p_x, p_y, and p_z orbitals of the bridging iodine atom are chosen to lie along the efg x-, y-, and z-axes of the I(7) atom. Then, Te–I–Te bonds are formed by donations from the two lone-pair electrons on the I^- ion to the orbitals of the tellurium atoms. The p_y orbital, which is normal to the bridging plane, is assumed to be occupied by a lone pair. The quadrupole coupling constants are easily obtained as follows:[10]

$$\left.\begin{aligned} e^2Qq_{xx}/e^2Qq_p &= N_x - (2+N_z)/2 \\ e^2Qq_{yy}/e^2Qq_p &= 2 - (N_x+N_z)/2 \\ e^2Qq_{zz}/e^2Qq_p &= N_z - (2+N_x)/2 \end{aligned}\right\}, \quad (1)$$

where e^2Qq_p/h is a quadrupole coupling constant for one 5p electron of iodine, and where N_x and N_z are the occupation numbers for the p_x and p_z orbitals. Then, the electrons donated to the tellurium atom from the p_x and p_z orbitals are represented by $2-N_x$ and $2-N_z$ respectively. We here introduce the parameter, k, defined by the donating-electron ratio from the I^- ion, *i.e.*:

$$k = (2-N_x)/(2-N_z), \quad (2)$$

where $0\leq k\leq 1$.

Thus Eq. 1 becomes:

$$\left.\begin{aligned} e^2Qq_{xx}/e^2Qq_p &= (2-N_z)\{(1/2)-k\} \\ e^2Qq_{yy}/e^2Qq_p &= (2-N_z)\{(1/2)+(k/2)\} \\ e^2Qq_{zz}/e^2Qq_p &= (2-N_z)\{-1+(k/2)\} \end{aligned}\right\}. \quad (3)$$

This equation holds only for the case of $0\leq k\leq 1/2$ because of the $|e^2Qq_{zz}|\geq|e^2Qq_{yy}|\geq|e^2Qq_{xx}|$ condition. In such a case, the asymmetry parameter is given by:

$$\eta = 3k/(2-k). \quad (4)$$

When $1/2\leq k\leq 1$, the absolute quadrupole coupling constant along y-axis becomes larger than that of the z-axis. Therefore, the efg z- and y-axes change their orientations in relation to each other. In this case,

Table 4. Bond length, p-orbital population, and net charge for the three types of iodine atoms (296 K)

Bonding type	Bond length/Å	Population	Net charge
Terminal	2.769[a]	1.30, 2.00, 2.00	−0.30
Bridge	2.933, 3.279	1.49, 1.80, 2.00	−0.29
	2.989, 3.231	1.55, 1.77, 2.00	−0.32
Pyramid[b]	3.232[a]	1.77, 1.77, 1.77	−0.30

a) Mean values. b) sp^3 hydridization assumed.

e^2Qq_{zz}/h is given by:

$$e^2Qq_{zz}/e^2Qq_p = (2-N_z)\{(1/2)+(k/2)\}, \quad (5)$$

with the asymmetry parameter:

$$\eta = (3-3k)/(1+k). \quad (6)$$

Using Eqs. 2—6 and the observed efg-axes orientations, we obtained k=0.395 and 0.519 for the I(7) and I(8) atoms respectively. In this calculation, the e^2Qq/h values for the I(7) and I(8) atoms were regarded as opposite in sign because of the orientation of their z-axes. These k values are consistent with the expectation from the bond length. Table 4 shows the occupation numbers of the p-orbitals.

In a previous paper we reported the temperature dependence of the e^2Qq_{ii}/h values (ii=xx, yy, and zz) for the two bridging iodines, where quite different features were observed in each case. We explained it with a model in which the characteristic oscillation of the bridging atom leads to an anisotropic change in the quadrupole coupling tensor. Thus, the differnt orientations of the efg axes were predicted from the temperature dependence, although symmetrical bridging bonds were assumed at that time.

Quadrupole Coupling Constants for the Pyramidal Iodine. The mean Te–I bond length in the pyramidal iodine atoms is 3.232 Å, nearly equal to the longer bridging bond length, 3.231 Å, of Te(3)–I(8) or that of 3.279 Å of Te(1)–I(7). This fact suggests the small extent of the covalent character on the pyramidal iodine. Therefore, the extremely small e^2Qq/h value is explained by the fact that the three bonding orbitals are nearly orthogonal. We adopt an sp^3 hydridization with C_{3v} symmetry, according to Ref. 5. The quadrupole coupling constant for the pyramidal iodine is, then, given by:[11]

$$e^2Qq/e^2Qq_p = \{3\cos\theta/(\cos\theta-1)\}(N_s-N_p), \quad (7)$$

where θ is the $\angle$TeITe angle (92.08° on the average) and where N_s and N_p are the populations for the

lone pair and the Te–I bond respectively. From this equation, we get $N_p=1.766$, assuming $N_s=2.0$.

Bonding and Charge Distribution in the Tetramer. Table 4 lists the bond length, p-orbital population, and net charge on the iodine, where no s-oribtal of the terminal atom is assumed to participate in the hybridization, as was suggested by the Mössbauer parameters.[12] If we plot the p-orbital population against its bond length, a smooth line can be obtained containing all the Te–I bonds. Therefore, it seems reasonable to assume an sp^3 hybridization model on the pyramidal atom to account for its e^2Qq/h value. In addition, it is interesting that the net charges on the iodine atoms are all in the same range, in spite of their quite different bonding schemes.

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