

^{125}Te and ^{129}I Mössbauer Spectroscopic Studies of the Tetragonal and Orthorhombic Forms of Tellurium(IV) Oxide

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^{125}Te and ^{129}I Mössbauer spectra have been measured for the tetragonal (α) and orthorhombic (β) forms of TeO_2 . The Mössbauer data show that there are no significant differences between the two modifications in either the electronic structure or the chemical bonding of the tellurium atoms; this is consistent with the crystallographic data. From a comparison of the Mössbauer data for ^{125}Te with those for ^{129}I , we have concluded that the ^{129}I daughter nucleus, produced by the nuclear β^- decay of ^{129}Te , is present in the same lattice environment as the parent ^{129}Te nucleus in TeO_2 . A Cu^{125}I crystalline compound has been used as the Mössbauer source of ^{125}Te , which emits a single line of resonance γ -ray. The values of the isomer shift and line width for the source are found to be -0.13 mm s^{-1} relative to the ZnTe standard absorber and 6.53 mm s^{-1} respectively.

Tellurium(IV) oxide (TeO_2) is known to have two crystalline forms, a colorless tetragonal (α) form and a yellow orthorhombic (β) form.¹⁾ In both modifications the coordination about the tellurium atom is a slightly distorted trigonal bipyramid, with one corner of the equatorial triangle unoccupied. The four Te–O bond distances are 1.903 Å (equatorial) and 2.082 Å (axial) for the tetragonal form and from 1.88 to 2.19 Å for the orthorhombic form. These bond distances suggest a considerable covalent character of the Te–O bonds, since the sum of the covalent bond radius for each atom is 2.03 Å.²⁾ The surroundings of the Te sites (the bond distances and the bond angles) in the trigonal bipyramid are similar in the two modifications, although a weak Te–Te bond with the distance of 3.17 Å exists in the β -form. This fact suggests that there are no significant differences in the electronic structure and the chemical bonding of the Te atoms for the α - and β -forms. However, the results of ^{129}I Mössbauer emission investigations have exploded the expectations based on the coordination figures.^{3,4)} The isomer shift observed in the ^{129}I Mössbauer emission spectrum of the α -form is considerably larger than that in the β -form. Warren et al.⁴⁾ have concluded that the difference in the isomer shifts arises from differences in the s-character of the parent Te–O bonds in the two forms. If this conclusion is correct, a difference in the isomer shifts should be observed in the ^{125}Te Mössbauer absorption spectra for the two modifications.

In the present paper we wish to report our results on the ^{125}Te Mössbauer absorption spectra for the tetragonal (α) and orthorhombic (β) forms of TeO_2 . Further, the ^{129}I Mössbauer emission spectra were measured for these compounds in order to compare their values with the previous data. Thus, the specimens were investigated both as absorbers and as sources.

Experimental

Materials. The commercially available TeO_2 (Wako

Pure Chemical) was found by X-ray powder diffraction analysis using graphite monochromated $\text{Cu K}\alpha$ radiation to be the orthorhombic (β) phase. The tetragonal (α) form prepared by melt-quenching was also confirmed by X-ray diffraction. The diffraction patterns of the α - and β -forms are given in Fig. 1; they are in good agreement with the values in the literature (ASTM cards 1-0870, 1-0117).

Measurements. ^{125}Te Mössbauer Absorption Spectra: Cu^{125}I crystalline powder, prepared from the standard form of Na^{125}I in a 0.1 mol dm^{-3} NaOH solution (New England Nuclear Co.), was used as the Mössbauer source of ^{125}Te . The radioactive compound had first been used as the

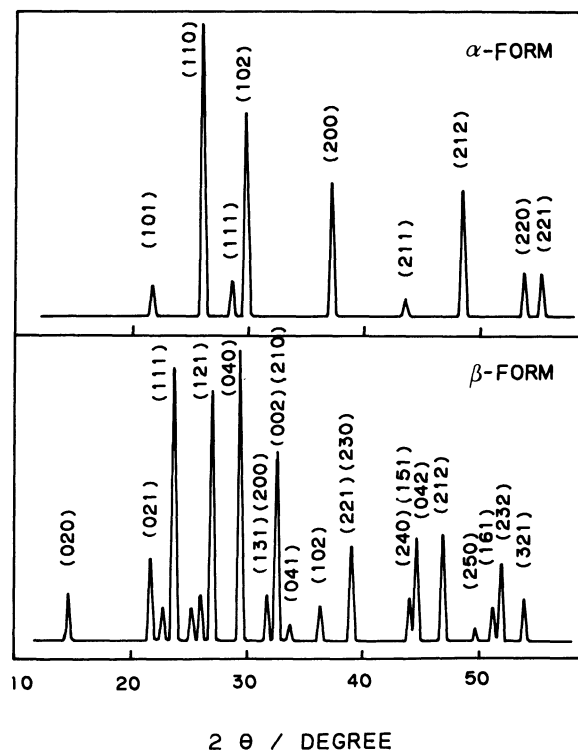


Fig. 1. X-Ray powder diffraction patterns of the tetragonal (α) and orthorhombic (β) forms of TeO_2 obtained by using graphite monochromated $\text{Cu K}\alpha$ radiation.

γ -ray source for the ^{125}Te Mössbauer spectroscopy by Ambe and Ambe.⁵⁾ They found that the source emitted a single line of resonance γ -ray. In the present investigation, the source was also verified to be a single line from the spectra against a ZnTe absorber ($2 \text{ mg cm}^{-2} \text{ }^{125}\text{Te}$) at 16 K and 77 K. The line width at half maximum was found to be 6.53 mm s^{-1} for the single absorption peak; this value was comparable to such other sources as ^{125}I or ^{125}Sb deposited on Cu foil and $\text{Zn}^{125}\text{mTe}$. The natural line width of ^{125}Te is calculated to be 5.20 mm s^{-1} from the lifetime of the 35.50 keV state. The Mössbauer spectra were measured in the transmission geometry by cooling the source and the absorber (each a modification of TeO_2 ; $3 \text{ mg cm}^{-2} \text{ }^{125}\text{Te}$) to 16 K by the use of a closed-cycle helium refrigerator. The 35.5 keV Mössbauer γ -ray was detected indirectly by counting the 5.8 keV escaped peak in a Xe-filled proportional counter. The velocity scale of the spectrometer was calibrated with a six-line spectrum of an Fe foil.

^{129}I Mössbauer Emission Spectra: About a 300-mg portion of each form of TeO_2 was used as a γ -ray source, irradiated at a thermal neutron-fluence rate of $2 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ for 1 h in the Kyoto University Reactor (KUR). The Mössbauer experiments were performed with ^{129}I daughters produced by this nuclear reaction: $^{128}\text{Te}(n, \gamma) ^{129}\text{Te} \xrightarrow{\beta^-} ^{129}\text{I}$. The ^{128}Te abundance in natural tellurium is 31.8%, enough for it to serve as the source. A single line Cu^{129}I ($10 \text{ mg cm}^{-2} \text{ }^{129}\text{I}$), used as a Mössbauer absorber, was prepared from Na^{129}I in a Na_2SO_3 solution in a manner similar to that used for Cu^{125}I . The absorber was checked, by means of a spectrum, against the standard ZnTe source at 16 K, in which the isomer shift and the line width were found to be -0.42 mm s^{-1} and 1.42 mm s^{-1} respectively. Furthermore, the ^{129}I emission spectrum of the tellurium metal was measured at 16 K in order to calibrate the velocity scale of the spectrometer under the same experimental conditions; this was in addition to the measurement of the six-line spectrum of an Fe foil at room temperature. The Mössbauer measurements were carried out in the same way as those of ^{125}Te . The 27.8 keV γ -ray was detected by the use of a 1 mm-thick NaI(Tl) scintillation counter.

Results and Discussion

A. ^{125}Te Mössbauer Absorption Spectra. The ^{125}Te Mössbauer absorption spectra at 16 K of (a) ZnTe, (b) $\alpha\text{-TeO}_2$, and (c) $\beta\text{-TeO}_2$ are shown in Fig. 2. The spectra were analyzed with Lorentzian curves by means of the least-squares method. The Mössbauer parameters, such as the isomer shift (δ) relative to the ZnTe standard absorber, the quadrupole splitting (2ε), and the full width at half maximum (2Γ), are summarized in Table 1. Various δ values have been reported by different laboratories for the same Te compound, for example, TeO_2 .⁶⁾ These discrepancies, as has been pointed out by Dobud and Jones,⁷⁾ seem to arise from the difficulties inherent in calibrating the spectrometer, for the ^{125}Te Mössbauer study requires a relatively high velocity region. Therefore, the standard Te compounds, such as Te metal and $\beta\text{-TeO}_3$, in addition to ZnTe, were measured under the same experimental conditions. The results are also given in

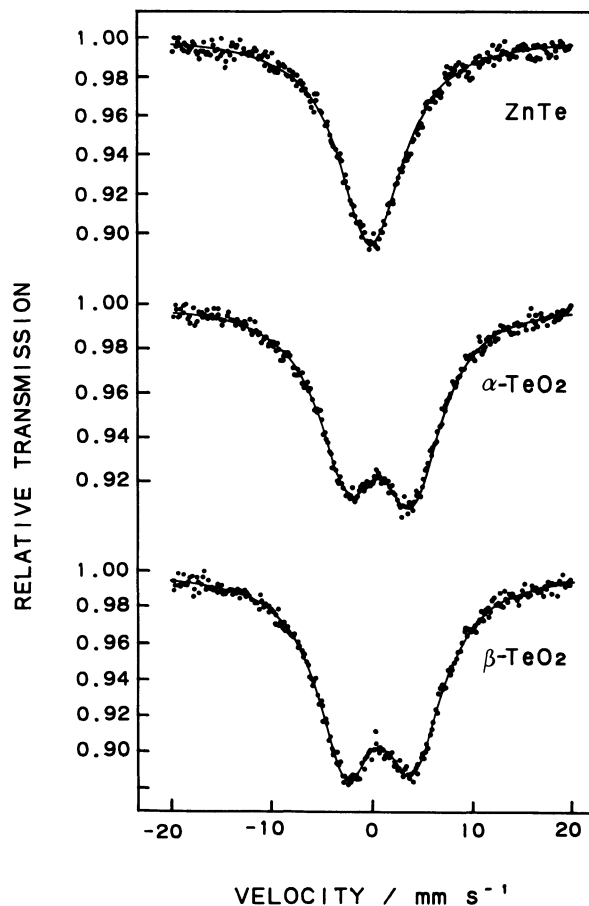


Fig. 2. ^{125}Te Mössbauer absorption spectra at 16 K of the ZnTe standard absorber, $\alpha\text{-TeO}_2$, and $\beta\text{-TeO}_2$ against the Cu^{125}I source.

Table 1. ^{125}Te Mössbauer Parameters of α - and $\beta\text{-TeO}_2$, Te Metal, and $\beta\text{-TeO}_3$

	T	δ	2ε	2Γ
	K	mm s^{-1} ± 0.08	mm s^{-1} ± 0.08	mm s^{-1} ± 0.10
$\alpha\text{-TeO}_2$	16	0.73	6.48	7.25
$\beta\text{-TeO}_2$	16	0.70	6.80	7.10
Te metal	16	0.57 (0.66)	7.30	6.28
$\beta\text{-TeO}_3$	16	-1.11 (-1.11)	0	7.79
ZnTe	16	0	0	6.53

The δ values are relative to the ZnTe absorber. The δ values in parentheses are taken from Ref. 8.

Table 1, together with the δ values recommended by Stevens and Gettys.⁸⁾

The δ value of ZnTe against the Cu^{125}I source has been found to be $+0.13 \text{ mm s}^{-1}$; this value is different from the recommended value (-0.02 mm s^{-1}) against the ^{125}I source deposited on a Cu foil.⁸⁾ The difference implies that the electronic structure of iodine in the CuI crystal is different from that in the Cu metal. As

will be shown below, the result we have obtained from the Cu¹²⁵I source is reasonable, since the δ value of the Cu¹²⁹I absorber against the Zn¹²⁹Te source is about -0.4 mm s^{-1} in the ¹²⁹I Mössbauer study. It is of interest that the Cu¹²⁵I source has given a single resonance line; that is, no anomalous charge state of ¹²⁵Te following the electron capture (EC) decay of ¹²⁵I has been observed for the spectrum. Violet and Booth⁹ and Jung and Triftshäuser¹⁰ observed four-line spectra for an NaIO₃ source. The latter authors concluded from the δ and 2ε values of two pairs of lines that the spectrum indicated the coexistence of Na₂TeO₃ and TeO₃, resulting from the K-capture decay of ¹²⁵I in NaIO₃ and the subsequent electron-rearrangements.

The ¹²⁵Te Mössbauer absorption spectra for the α - and β -forms of the TeO₂ crystal are similar to each other. The asymmetry in the spectrum of the α -form may be due to the preferred orientation of the specimen. The δ value of the α -form is in good agreement with that of the β -form, within the limits of experimental error. This result is apparently not in accord with that obtained from the ¹²⁹I Mössbauer emission spectra for both modifications. Warren et al.⁴ have determined the isomer shift ratio, $\delta(^{125}\text{Te})/\delta(^{129}\text{I})$, for the ¹²⁵Te and ¹²⁹I nuclei in precisely the same lattices. They found this ratio to be $+0.29 \pm 0.03$ for several tellurium compounds. Therefore, if the ¹²⁹I resulting from the β^- decay of ¹²⁹Te finds itself in the same lattice environment as the parent TeO₂, the δ values relative to the ZnTe of the ¹²⁹I Mössbauer emission spectra should be observed to be about $+2.5 \text{ mm s}^{-1}$ for both modifications of the TeO₂ crystal, dividing the averaged δ value of ¹²⁵Te by 0.29. However, the δ values of ¹²⁹I for the α - and β -forms have been experimentally measured to be $+2.74 \pm 0.14 \text{ mm s}^{-1}$ and $+1.52 \pm 0.01 \text{ mm s}^{-1}$ respectively.^{3,4} The deviation, in particular for the β -form, between the expected and measured δ values indicates that the resulting ¹²⁹I is no longer in the same lattice environment.

It is interesting to examine the δ value of the Cu¹²⁵I source, for it is little used for ¹²⁵Te Mössbauer spectroscopy. The Cu¹²⁹I absorber is often used for source experiments in the ¹²⁹I Mössbauer spectroscopy, and the δ value relative to the ZnTe source has been established as -0.41 mm s^{-1} .¹¹ Therefore, the δ value of the Cu¹²⁵I source against the ZnTe absorber is estimated to be -0.12 mm s^{-1} from the isomer shift ratio for the ¹²⁵Te and ¹²⁹I nuclei; this value is in good agreement with the measured δ value (-0.13 mm s^{-1}). This implies that the ¹²⁵Te daughter nucleus, produced by the EC decay of ¹²⁵I, is present in the same lattice environment as the parent ¹²⁵I nucleus in the CuI crystal.

In the ¹²⁵Te Mössbauer absorption spectra, the quadrupole splitting $\{2\varepsilon = \frac{1}{2}e^2Qq(1 + \frac{1}{3}\eta^2)^{1/2}\}$ of the α -

form is slightly smaller than that of the β -form. This result also disagrees with that of the ¹²⁹I Mössbauer emission spectra, indicating that the quadrupole coupling constants (e^2Qq) for the α - and β -forms are $+812 \pm 21 \text{ MHz}$ and $+786 \pm 7 \text{ MHz}$ respectively.^{3,4} Warren et al.⁴ have determined the ratio of the quadrupole coupling constants for ¹²⁵Te and ¹²⁹I nuclei, as well as the isomer shift ratio, in equivalent lattice sites as follows:

$$\frac{e^2Qq(^{125}\text{Te})}{e^2Qq(^{129}\text{I})} \left(1 + \frac{1}{3}\eta^2\right)^{1/2} = 0.45. \quad (1)$$

Langouche et al.¹² have also determined this ratio to be -0.48 ± 0.02 by means of a detailed examination of the ¹²⁹I and ¹²⁵Te Mössbauer spectra for several Te-thiourea compounds. Using this ratio and our result for 2ε of ¹²⁵Te, we can derive the e^2Qq values of ¹²⁹I for the α - and β -forms to be 773 MHz and 810 MHz respectively. The agreement between the measured and estimated e^2Qq values is insufficient.

It is important to note that in the ¹²⁹I Mössbauer emission measurements discrepancies in the values of δ and e^2Qq are often observed for an identical compound. For example, the δ and e^2Qq values for the tellurium metal have been reported to be $+0.71 \pm 0.03 \text{ mm s}^{-1}$ and $-373 \pm 6 \text{ MHz}$ respectively by Pasternak and Bukshpan,³ whereas they have been reported to be $+0.52 \pm 0.13 \text{ mm s}^{-1}$ and $-349 \pm 11 \text{ MHz}$ respectively by Warren et al.⁴ The values of δ and e^2Qq obtained in the present work are $+0.69 \pm 0.05 \text{ mm s}^{-1}$ and $-403 \pm 10 \text{ MHz}$ respectively, values which are in good agreement with those of the more recent works of Langouche et al.¹³ ($\delta = +0.77 \pm 0.04 \text{ mm s}^{-1}$, $e^2Qq = -404 \pm 4 \text{ MHz}$) and Kim and Boolchand¹⁴ ($\delta = +0.80 \pm 0.03 \text{ mm s}^{-1}$, $e^2Qq = -396 \pm 3 \text{ MHz}$). Therefore, it is dangerous to conclude that the minor discrepancies in the reported and estimated δ and e^2Qq values for the two modifications of TeO₂ are to be attributed to the chemical effects accompanying the nuclear reaction and the β^- decay of the ¹²⁹Te nucleus.

B. ¹²⁹I Mössbauer Emission Spectra. ¹²⁹I Mössbauer emission spectra have been reinvestigated for both modifications of TeO₂ at 16 K, in order to examine in detail the chemical effects on the ¹²⁸Te (n, γ) ¹²⁹Te nuclear reaction and the β^- decay of the ¹²⁹Te and, furthermore, to clarify the origin of the large difference in the δ values of ¹²⁹I between the α - and β -forms previously reported. The spectra against the Cu¹²⁹I standard absorber are shown in Fig. 3 (b) and (c); no anomalous peak is observed. These spectra were analyzed by the least-squares method using a single set of fitting parameters, δ , e^2Qq , the asymmetry parameter (η), the full width at half maximum (2Γ), each peak intensity, and the base line. The solid lines in the figures represent the best-fitting Lorentzian curves. The Mössbauer parameters obtained are given in Table

Table 2. ^{129}I Mössbauer Parameters of α - and β - TeO_2 and of Te Metal

	T	δ	e^2Qq	η	Ref.
	K	mm s^{-1}	MHz	%	
α - TeO_2	16	$+2.44 \pm 0.12$	$+800 \pm 10$	58 ± 7	This work 4
	80	$+2.74 \pm 0.14$	$+812 \pm 21$	52 ± 7	
β - TeO_2	16	$+2.36 \pm 0.12$	$+780 \pm 10$	50 ± 7	This work
	16	$+2.40 \pm 0.12$	$+793 \pm 10$	46 ± 7	This work
	80	$+1.52 \pm 0.01$	$+786 \pm 7$	55 ± 5	3
Te metal	16	$+0.69 \pm 0.05$	$+403 \pm 10$	70 ± 7	This work
ZnTe	16	-0.42 ± 0.05	0	0	This work

a) The δ values are relative to the ZnTe source.

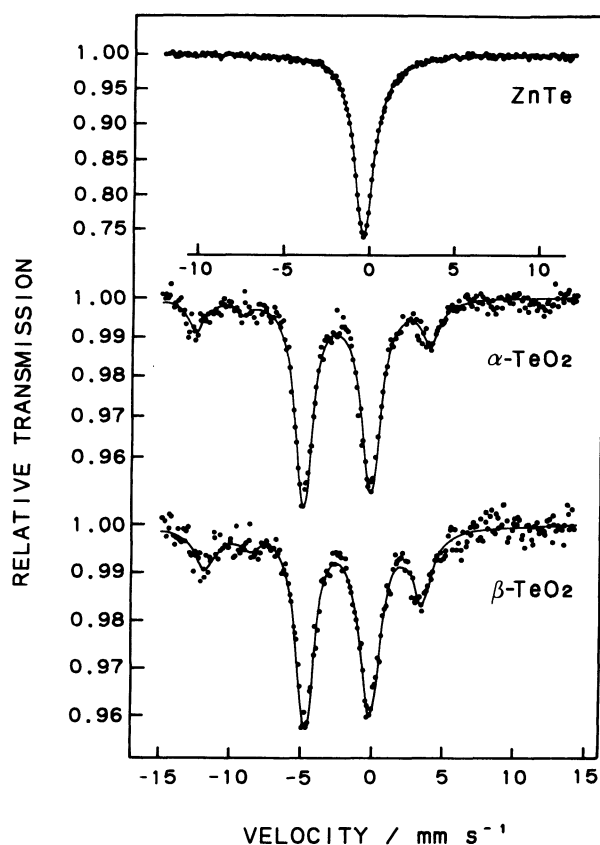


Fig. 3. ^{129}I Mössbauer emission spectra at 16 K of the ZnTe standard source, α - TeO_2 , and β - TeO_2 against the Cu^{129}I absorber.

2, together with the data of the previous works.^{3,4)} For the β -form of TeO_2 , the measurements were independently carried out twice because of the large difference in the δ value between the previous data³⁾ and our data. The δ values are relative to a Zn^{129}Te source, subtracting 0.42 mm s^{-1} (δ value for Cu^{129}I) from the actual δ values observed for the emission spectra.

The spectra observed in the present work are similar to the previously reported spectra independently mea-

sured by Pasternak and Bukshpan³⁾ and by Warren et al.⁴⁾ The values of e^2Qq and η for both modifications of TeO_2 are in good agreement with those reported by them, as may be seen in Table 2. However, the δ values, being close to each other for both modifications in this work, are different, especially for the β -form, from the previous data. The origin of the differences in the δ values is not clear. The differences might be attributable to the deviations between the ^{129}I spectra and ^{57}Fe calibrating spectra, since, in the ^{129}I Mössbauer measurements, the driving γ -ray source must be cooled in the cryostat, while the measurements of the ^{57}Fe calibrations are not accompanied by any such difficulty. One of the results obtained in the present investigation is that there are almost no differences in the δ values of ^{129}I for the α - and β -forms of TeO_2 ; this finding is consistent with that of the ^{125}Te absorption spectra. The isomer shift ratios of the ^{125}Te and ^{129}I nuclei are found to be 0.30 for both modifications of TeO_2 . This value is very close to that to be expected when the ^{129}I daughter nucleus is present in the lattice site equivalent to the parent ^{129}Te site. On the other hand, the ratios of the quadrupole coupling constants of the ^{125}Te and ^{129}I nuclei are observed to be 0.46 for the α -form and 0.49 for the β -form. These values are in agreement with the value reported by Langouche et al.,¹²⁾ within the limits of experimental error of the ^{125}Te and ^{129}I Mössbauer measurements. Therefore, we have concluded, from a comparison of the values of δ and e^2Qq for ^{129}I with those for ^{125}Te , that the ^{129}I daughter nuclei, produced as a consequence of the nuclear β^- decay of ^{129}Te , are present in the same lattice environment as the parent ^{129}Te nuclei in both modifications of TeO_2 .

C. Electronic Structures and Chemical Bondings. It is also of interest to consider the electronic structure and the chemical bonding of the tellurium atoms in the two forms of TeO_2 . The tellurium atoms are present in a slightly distorted trigonal bipyramidal environment, and the Te-O bonds are predominantly covalent in character, judging from a consideration of the bond lengths. These crystallographic results

suggest that the bonding of the tellurium is characterized by sp^2 hybridization in the equatorial plane and by pd hybridization in the axial direction. Since, however, the $\angle O-Te-O$ angles in the equatorial plane are $101^\circ-102^\circ$ for both modifications, the lone pair occupying one corner of the equatorial triangle may have significantly more s -character than that required in pure sp^2 hybridization. The contribution of the s -character to the bonding can be evaluated from the isomer shift (δ). The δ value reflects the s -electron density at the nucleus, $|\Psi_s(0)|^2$. Since the nuclear radius term $\Delta R/R$ is positive in sign for ^{125}Te , an increase in the s -electron density should lead to a more positive δ value. The $5s$ -electron density is shielded by outer $5p$ -electrons, therefore, δ is also dependent on the $5p$ -electron density. The removal of $5p$ -electrons of the tellurium atom in bonding will lead to an increase in the δ value, while the contribution of the $5s$ -electron to the bonding orbitals will directly decrease the δ value. These effects may be expressed quantitatively as follows:¹⁵⁾

$$\delta = -2.6 h_s + 0.44 h_p - 0.16 \quad (2)$$

(mm s⁻¹ for ZnTe reference material),

where h_s and h_p are the numbers of $5s$ - and $5p$ -electron holes respectively in the closed Te^{2-} configuration. The equation is obtained by multiplying the empirical formula of the ^{129}I Mössbauer isomer shift by 0.29, the isomer shift ratio, $\delta(^{125}Te)/\delta(^{129}I)$, described above.

The δ values observed for the two forms of TeO₂, smaller than those of the other Te(IV) compounds,⁶⁾ suggest that the s -electrons of the Te atoms take part in the bonding to some extent and that the Te-O bonds have a highly covalent character. Unfortunately, it is impossible to estimate independently the contribution of $5s$ -electrons to the bonding and the extent of the covalent character of the Te-O bonds. Dobud and Jones⁷⁾ have estimated the s -character in the bond to be about 9% for α -TeO₂, assuming that, in the absence of a $5s$ character, TeO₂ would have the same δ value as $TeCl_6^{2-}$ (+1.7 mm s⁻¹). The estimation has led to $5s^{1.6}5p^{1.9}$ for the electronic configuration of the Te atom, i.e., an effective charge of +2.5 on the Te atom. It is thought that this estimated charge of +2.5 is the upper limit of the effective charge localized on the Te atom in the α -TeO₂, because the Te-O bonds would be expected, considering the Te-O and Te-Cl bond distances, to have a more covalent character than the Te-Cl bonds in $TeCl_6^{2-}$. The covalent character of the Te-Cl bond in $(NH_4)_2TeCl_6$ has been estimated to be 0.32 from the ^{35}Cl NQR measurements.¹⁶⁾ For the Te-O bonds in TeO₂ the covalent character would be larger.

It is important to assign the configuration of the iodine produced in α - and β -TeO₂ in order to examine the influence of the nuclear β^- decay of ^{129}Te . Since

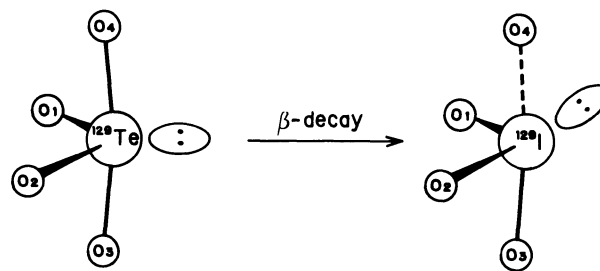


Fig. 4. Bonding configuration of the ^{129}I daughter atom produced by nuclear β^- decay of the ^{129}Te parent atom in TeO₂.

there are almost no differences in the values of δ , e^2Qq , and η between the two modifications, as has been described above, the resulting iodine species may be regarded to be identical. The values of δ , e^2Qq , and η observed for the iodine species in TeO₂ are very close to those for one iodine site (IO_3^-) in the I_2O_4 compound, consisting of two inequivalent iodine sites, IO^+ and IO_3^- .^{17,18)} The crystal structure of the I_2O_4 compound has not yet been established, but the IO_3^- part is believed to be similar to the configuration of HIO_3 , judging from the similarity in the values of e^2Qq and η .¹⁷⁾ Therefore, we may infer that the iodine formed in TeO₂ is situated at a vertex of a distorted trigonal pyramid and that it has three nearest oxygen neighbors at an average distance of about 1.9 Å. The mean interbond angle O-I-O would be close to that of HIO_3 (98°). The formation of such an iodine species in the TeO₂ crystal can be understood as follows: one of the two axial Te-O bonds is severed by the β^- decay of ^{129}Te and subsequent electron rearrangements [see Fig. 4]. Such a process was also observed for the tellurium metal and tellurium atoms doped in the other elemental chalcogen hosts, in which the twofold coordination of tellurium involving π -bonding orbitals with two chalcogens-near-neighbors transforms into a nearly onefold coordination of iodine involving σ -bonding orbitals with a chalcogen-neighbor.¹⁴⁾

In conclusion, the similarities between the Mössbauer spectra of the tetragonal (α) and orthorhombic (β) forms of TeO₂ indicate that there are no significant differences in the electronic structure and the chemical bonding of the tellurium atoms in the two modifications. In addition, the comparison of the Mössbauer data for ^{125}Te with those for ^{129}I indicates that the ^{129}I daughter nucleus, produced by the nuclear β^- decay of ^{129}Te , is present in the same lattice environment as the parent ^{129}Te nucleus in TeO₂.

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