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Interpretation of ^{125}Te Mössbauer isomer shift data[1]

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Abstract

A simple interpretation of ^{125}Te Mössbauer data of solids based on a chemical bonding analysis is presented. From new measurements of the Mössbauer spectra for different compounds a scale of the isomer shifts is obtained. A qualitative analysis of this scale is proposed.

A semi-quantitative approach based on a tight-binding calculation provides information on the electronic configuration of Te in the solids. The results of this calculation are correlated with the values of the isomer shift and the oxidation states for tellurium oxides.

Keywords: Neutron diffraction; Site occupancies; Isomer shifts

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1. Introduction

Mössbauer spectroscopy is a powerful technique for the characterization of the local electronic structure of particular atoms (which will be referred to as the Mössbauer atom throughout this paper) in solids [1–3]. The resonant recoil-less absorption or emission of γ-rays (Mössbauer effect) is usually characterized by the isomer shift (δ), the quadrupole splitting (Δ) and the half (or full) width at the half maximum resonance (Γ).

A simple expression of the isomer shift is given by

$$\delta = \frac{Ze^2cR^2}{5\varepsilon_0 E_0}\frac{\Delta R}{R}\left(|\Psi_a^0|^2 - |\Psi_s^0|^2\right) \tag{1}$$

where e is the electronic charge, c is the velocity of light, ε_0 is the permittivity of vacuum, Z is the electron number and R the effective nuclear radius of the Mössbauer atom, $|\Psi^0|^2$ is the relativistic electron density at the nucleus (the subscripts a and s are relative to absorber and source, respectively), E_0 is the energy of the nuclear transition and $\Delta R/R$ is the variation of the nuclear radius. Eq. (1) shows that the isomer shift is related to the electron density at the nucleus of the Mössbauer atom in the absorbing material. This electron density is mainly of s-type because of the symmetry of the wavefunction. For different compounds containing the same Mössbauer element the isomer shift is sensitive to changes in the number of valence electrons of this element. Thus the values of the isomer shift provide some information on the oxidation states and the chemical bonding involved by the Mössbauer atom.

For a 3/2→1/2 transition, the quadrupole splitting is given by the expression

$$\Delta = \frac{1}{2} eQV_{ZZ}\left(1 + \frac{\eta^2}{3}\right)^{1/2} \tag{2}$$

The quadrupole splitting is related to the shape of the absorption (or emission) spectra and depends on a nuclear term eQ (electric quadrupole moment) and the electric field gradient: V_{ZZ} is the principal component of the diagonalized tensor of the electric field gradient and η is the asymmetry parameter. Eq. (2) shows that Δ provides information on the charge distribution

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around the Mössbauer atom, and therefore to the coordination pattern and the chemical bonding.

Among the different Mössbauer isotopes, ^{125}Te is of great interest because it is a constituent of a great number of compounds with particular properties [4], and it is used as a local active or passive Mössbauer probe in substitution of other chalcogens (S, Se) [5–8].

In this paper we want to give a simple interpretation of the ^{125}Te Mössbauer data. In Section 2 we give the main features of ^{125}Te and draw up an isomer shift scale from some reference compounds. Section 3 concerns a qualitative interpretation of this scale in terms of chemical bonding. In Section 4 we show a correlation between the experimental values of the Mössbauer isomer shift and the number of valence electrons of the Mössbauer atom evaluated from a tight-binding calculation.

2. ^{125}Te isomer shifts scale

Nuclear characteristics of the ^{125}Te isotope are given in Table 1. Experimental measurements are carried out with a $Mg_3^{125m}TeO_6$ source, instead of the classical sources like $Zn^{125m}Te$, $Sn^{125m}Te$, $Pb^{125m}Te$ or $^{125}Sb(Cu)$, because of its high recoil-less fraction factor (0.68 at 4.2 K).

2.1. Source preparation

$Mg_3^{124}TeO_6$ is prepared by a solid state reaction between 20.0 mg of ^{124}Te and 19.5 mg of MgO heated under air at 1173 K. The compound obtained by this chemical reaction is characterized by X-ray diffraction and corresponds to the rhombohedral (pseudo-cubic) form of Mg_3TeO_6 (space group R_3, $a = 6.05$ Å, $\alpha = 90.83°$ [9]).

$Mg_3^{124}TeO_6$ was irradiated under a flux of about 3.10^{14} n cm^{-2} s^{-1}, to $Mg_3^{125m}TeO_6$ (high flux reactor, Petten, Netherlands) for 2 months.

Table 1
^{125}Te nuclear parameters

Natural abundance (%)	6.99
Radioactive parent	^{125m}Te
Half-life period (days)	58
Mössbauer transition energy (keV)	35.5
Full width at half maximum natural emission (mm s^{-1})	5.21
Excitation nuclear radius variation	$+6.10^{-5}$ to $+1.3.10^{-4}$
Ground state spin	1/2
Excited state spin	3/2
Quadrupole moment (barns)	−0.19

Table 2
Structural data of the compounds used for the measurements of the Mössbauer spectra

Phase	Te coordination	Bond length (Å)	Reference
Mg_3TeO_6	6 O	1.91	[9]
ZnTe	4 Zn	2.64	[10]
SnTe	6 Sn	3.16	[10]
PbTe	6 Pb	3.23	[10]
Sb_2Te_3	3 Sb + 3 Te and 6 Sb	2.98–3.74 and 3.17	[11]
FeTe	4 Fe	2.62	[12]
Te	2 Te	2.83	[13,14]
TeO_2	4 O	1.88–2.07	[15]

2.2. Selection of a reference compound

The isomer shift scale is derived from well-known compounds; their structural specifications are shown in Table 2. They cover the oxidation state domain from Te^{VI} to Te^{IV} and display various tellurium coordinations (octahedral, tetrahedral, trigonal bi-pyramid, and coordination 2) with different kinds of Te–ligand bondings.

2.3. Absorber preparation and data collection

Absorbers were prepared by mixing and pressing at 50°C the powdered samples with polyethylene to 25 mm diameter pellets. Samples were weighted to obtain 1 mg cm^{-2} ^{125}Te concentration.

All the measurements were carried out at the Nuclear and Radiation Physics Institute (IKS, Leuven, Belgium). Spectra were recorded using an Xe/CO_2 detector, attached to a low-noise photomultiplier, with the escape peaks of the 35 keV radiation. Both source and absorber were held at liquid helium temperature. The source was moved, by a drive system designed at IKS, in the constant acceleration mode. Velocity calibration was obtained by a ^{57}Co(Cu) source and a 1 mg cm^{-2} enriched ^{57}Fe absorber.

The origin of the ^{125}Te isomer shift scale was determined from the $Mg_3^{125}TeO_6$ spectrum recorded under the same experimental conditions. The values of the Mössbauer isomer shift, the quadrupole splitting and the half-width height of the peak are given in Table 3. Some published results are also given.

Two typical spectra are shown in Fig. 1 for SnTe (single line) and polycrystalline Te (doublet with a high quadrupole splitting corresponding to the ±1/2 to ±1/2 and ±1/2 to ±3/2 transitions).

3. Data analysis

The electronic configuration of the neutral Te atom is [Kr] $4d^{10}$ $5s^2$ $5p^4$. In this configuration the valence

Table 3
^{125}Te Mössbauer data obtained for the compounds used for the scale of isomer shifts (δ is the isomer shift, Δ the quadrupole splitting, Γ the full width at half maximum resonance

Phase	δ (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})	References
Mg_3TeO_6	0	0	6.30(7)	
ZnTe	1.12(4)	0	6.23(6)	
SnTe	1.23(4)	0	6.83(6)	
PbTe	1.31(4)	0	6.49(7)	
Sb_2Te_3	1.38(4)	0	6.86(4)	
As_2Te_3	1.39(4)	3.46(4)	6.83(9)	
FeTe	1.40(4)	2.1(1)	7.9(1)	
Te	1.73(4)	7.74(3)	6.00(6)	
TeO_2	1.82(4)	6.18(2)	5.70(5)	
$TeCl_2$^{a}	1.98(8)	6.2(1)	5.8(2)	[16]
$TeBr_2$^{a}	2.27(5)	4.4(2)	9.4(2)	[16]
$TeCl_4$^{a}	2.34(1)	4.70(8)	6.5(2)	[16]
TeO_3^{b}	−0.06(1)	0	7.8	[17]
Te_2O_5^{b}	1.57(2)	6.90(5)	6.4	[17]
	0.22(2)	0	7.0	
Te_4O_9^{b}	1.68(7)	6.91(7)	6.7	[17]
	0.12(14)	0	6.7	

^{a} Isomer shifts are obtained by addition of 1.34 mm s^{-1} to the recorded values relative to ^{125}Sb(Cu)
^{b} Isomer shifts are obtained by addition of 1.12 mm s^{-1} to the recorded values relative to Zn^{125m}Te

shell is formed by two lone pairs (5s and 5p) and two single electrons (5p). This configuration provides a great number of possible oxidation states (Te^{6+}, Te^{VI}, Te^{-II}, Te^{II}, Te^{IV}, Te^{2+}, Te^{4+}) which can be described from the behaviour of the valence electrons. Two 5p electrons form ionic (Te^{2+}, Te^{2-}) or covalent (Te^{II}) bondings, four 5p electrons form ionic (Te^{4+}) or covalent (Te^{IV}) bondings, and finally two 5s electrons and four 5p electrons are involved in the formation of ionic (Te^{6+}) or covalent (Te^{VI}) bondings.

In fact, the situation is more complicated than with this simple description because of the behaviour of the lone pair electrons [18]. For example, the local geometry around Te(IV) is not limited to the classical tetrahedral environment, but includes other geometries: trigonal pyramid (threefold coordinated), trigonal bi-pyramid (fourfold coordinated) or square-based pyramid (fivefold coordinated). Similar variations in the coordination number of other elements are observed, for instance, with antimony [19].

A simplified classification of the Te oxidation states can be established from the electronic configurations and the local geometry (Table 4). It is then possible to give a simple interpretation of the tellurium Mössbauer isomer shifts (Fig. 2). Since the $\Delta R/R$ term is positive for Te [20], decreasing values of the isomer shift are mainly related to a decrease of the number of 5s electrons and to a lesser extent to an increase of the p (and/or d) shielding effect. Thus, the values at the two boundaries of the scale (Fig. 2) are characteristic of the oxidation states 6+ (δ close to 0 mm s^{-1}) and 4+ (δ greater than 2.30 mm s^{-1}) corresponding to the minimum s-density (5s^0 configuration) and the maximum s-density (5s^2 configuration), respectively. Between 1 mm s^{-1} (Te^{2-}) and 2 mm s^{-1} (Te^{2+}) two situations can be depicted:

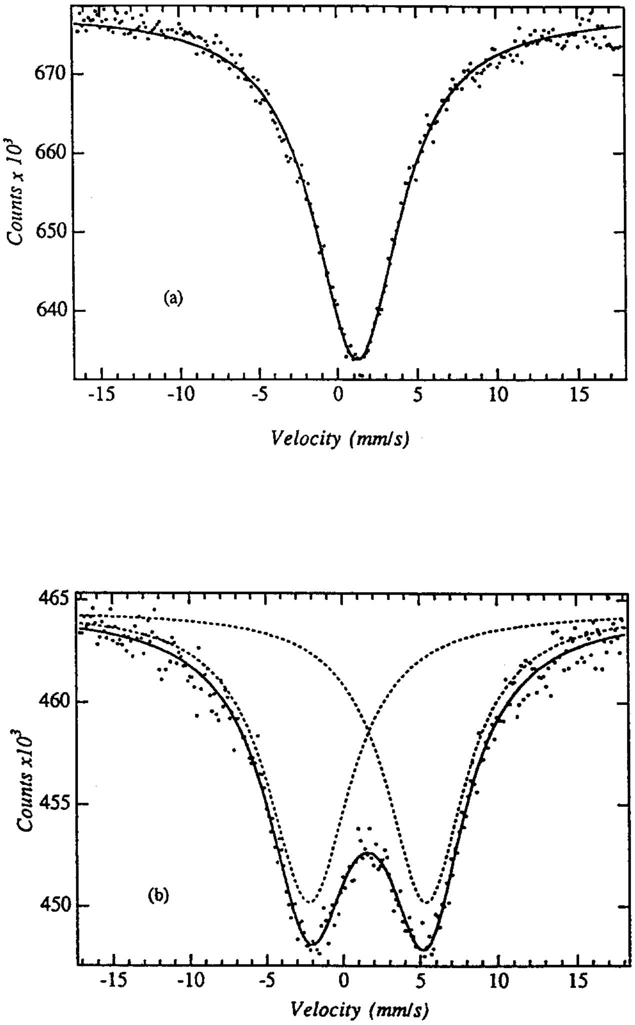

Fig. 1. ^{125}Te Mössbauer spectra of (a) SnTe and (b) Te at 4 K.

- Between the oxidation states Te^{2+} and Te^{II}, including the domain relative to Te^{IV}, the covalency increases (a non-bonding p-electron pair for TeBr$_2$, a non-bonding p-electron pair and two bonding p-electron pairs for Te) which leads to an increase of the shielding effect and of the stereochemical activity of the non-bonding s-pair [19]. These two effects give rise to a decrease of the isomer shift and to an increase of the quadrupole interaction (see Fig. 2 and Table 3).
- From Te^{2-} to Te^{II}, the increase of the covalency leads to a decrease of the shielding effect (three non-bonding p-pairs in ZnTe, one non-bonding p-

Table 4
Electronic configurations and local geometry of Te. The type of chemical bonding (NB: non-bonding, B: Bonding) is also indicated

	s-pairs		p-pairs		d-pairs	Geometry	Example
	NB	B	NB	B	B		
Te^{6+}	0	0	0	0	0	Octahedron	
Te^{VI}	0	1	0	3	2	Octahedron	Mg_3TeO_6
Te^{2-}	1	0	3	0	0	Tetrahedron	ZnTe
Te^{II}	1	0	1[a]	2	0	Angular	Te
Te^{IV}	1***[b]	0	0	3	0	Trigonal pyramid	
	1**[b]	0	0	3	1	Trigonal bi-pyramid	TeO_2
	1*[b]	0	0	3	2	Square-based pyramid	
	1	0	0	3	3	Octahedron	
Te^{2+}	1	0	1	0	0	Angular	$TeBr_2$
Te^{4+}	1	0	0	0	0	Octahedron	$TeCl_4$

[a] Contribute to long range interactions (between chains)
[b] The number of asterisk symbols is related to the stereochemical activity of the 5s electron pair of Te

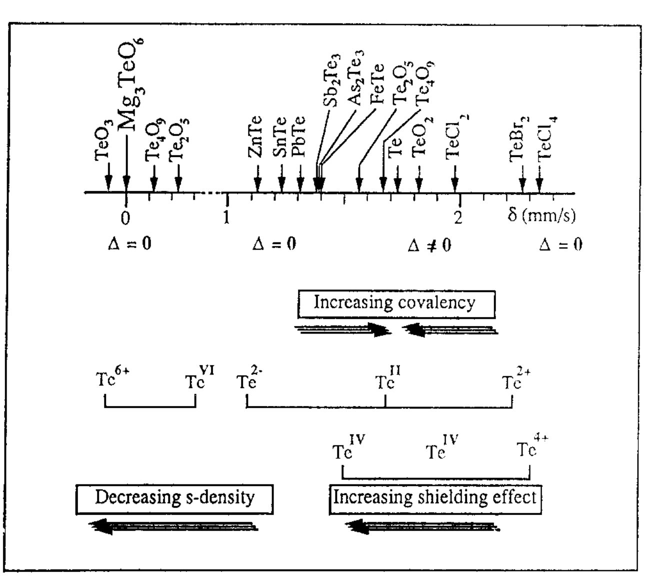

Fig. 2. Isomer shifts scale with reference to Mg_3TeO_6 for ^{125}Te.

pair and two bonding p-pairs in Te) and thus to an increase of the isomer shift and the quadrupole splitting.

4. Correlation between the isomer shift and the number of valence electrons

The isomer shift varies linearly with the electron density $\rho(0)$ at the nucleus according to Eq. (1), which can be written in a simple form:

$$\delta = \alpha \frac{\Delta R}{R} \Delta\rho(0) \tag{3}$$

The two first terms of this expression are related to the nucleus of the Mössbauer atom. The third term is the difference between the electron densities at the nucleus in the absorber and in the source: $\Delta\rho(0) = \rho_a(0) - \rho_s(0)$. This term is rather difficult to evaluate, since it requires the evaluation of the relativistic wavefunctions in the nucleus. We have followed the approach of Ruby and Shenoy [20], but a simpler form of the electronic charge density at the nucleus as a function of the numbers of s electrons n_s and p electrons n_p is used:

$$\rho(0) = \rho_c(0) + an_s + bn_p + c \tag{4}$$

where $\rho_c(0)$ is the contribution of the inner core electrons. The constants a, b and c are obtained by fitting $\rho(0) - \rho_c(0)$ to the values of the electronic density at the nucleus of the Te atom with different electronic configurations. In this case the numbers of s and p electrons are integer numbers when they are real for the atom in the solid. The values of the relativistic electronic density calculated by Ellis are considered [20], which give $a \sim 61$, $b \sim -8.5$ and $c \sim 23$. It is worth noticing that the signs of a and b are consistent with an increase of $\rho(0)$ with n_s and a decrease with n_p. From Eqs. (3) and (4) we obtain a simple expression for the isomer shift as a function of the numbers of valence electrons:

$$\delta = 8\alpha \frac{\Delta R}{R} (7.2\Delta n_s - \Delta n_p) \tag{5}$$

where Δn_s (Δn_p) is the difference between the numbers of 5s electrons (5p electrons) in the absorber and the source.

The numbers of valence electrons were evaluated by a semi-empirical tight-binding calculation [21] for the tellurium oxides (TeO_3, Te_2O_5, Te_4O_9, TeO_2). The electronic density is obtained from Eq. (4). Comparison of the experimental values of the isomer shift with the values of the charge density are shown in Fig. 3. The slope of the line obtained by a least squares fit to the points is 3.36×10^{-2} mm s^{-1}, which gives $\Delta R/R \sim 8.8 \times 10^{-5}$. This value is in good agreement with the

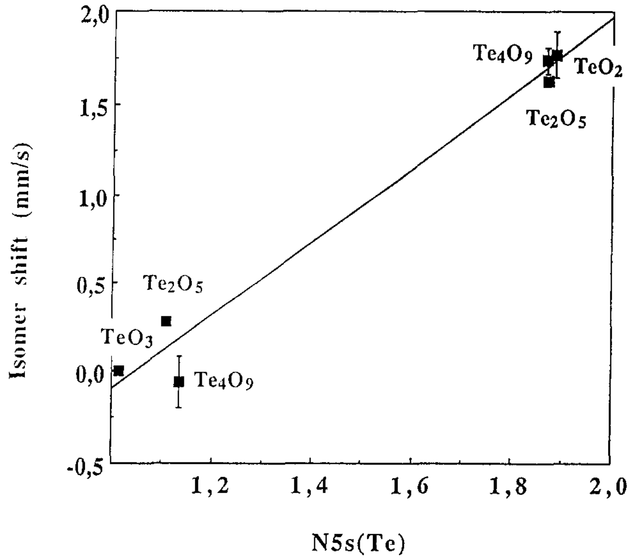

Fig. 3. Correlation between the experimental values of the isomer shift and the charge density.

published values (between 6×10^{-5} and 1.3×10^{-4}) [20].

In Fig. 4 are shown the experimental values of the isomer shift as a function of the number of 5s electrons on Te. Because the evaluated number of 5p electrons does not vary noticeably for the different compounds the distribution of the points is similar to that of Fig. 3. Fig. 4 shows that two groups of compounds can be distinguished from the values of the isomer shift: around 0 mm s^{-1} (I) and around 1.7 mm s^{-1} (II). These differences in the values of the isomer shift are correlated with the differences in the number of 5s electrons: around 1.1 (I) and around 1.9 (II). These can be related to the formal oxidation number Te^{VI} (I) and Te^{IV} (II) as noticed previously for tin compounds [22].

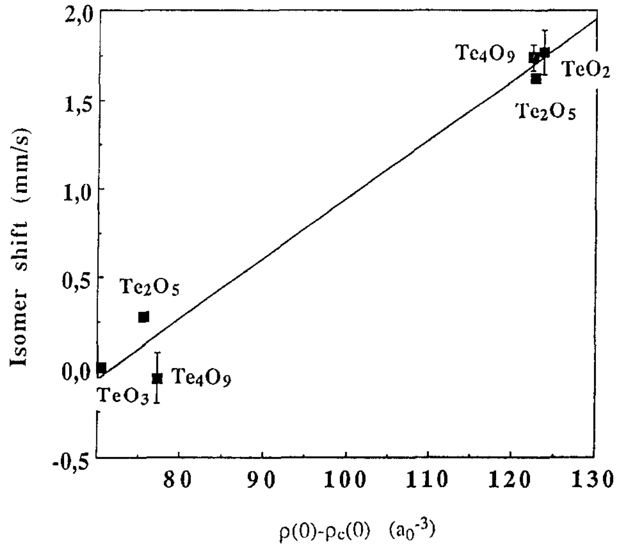

Fig. 4. Correlation between the experimental values of the isomer shift and the number of 5s electrons on Te.

5. Conclusion

The interpretation of the ^{125}Te Mössbauer data is rather difficult because of the large linewidth (5–6 mm s^{-1}). Thus it is important to draw up a scale for the values of the Te Mössbauer isomer shift from reference compounds. The values of the Te isomer shift vary in a small range (0–2 mm s^{-1}) for the observed Te oxidation states.

Some empirical rules have been established:

- Te^{6+} and Te^{4+} form the boundaries of the scale of the isomer shift values with a zero quadrupole splitting.
- From Te^{2+} to Te^{II} the decreasing values of the isomer shift and increasing values of the quadrupole splitting are related to an increase of the covalency, which leads to an increase of the p and d electron shielding effect. In this interval the data relative to Te^{IV} are found.
- From Te^{2-} to Te^{II} the increase of the isomer shift and the quadrupole splitting can be related to a combined effect of an increase of the covalency and a decrease of the shielding effect.

The variations of the Te isomer shift in different compounds are caused by the variations of the electronic density at the nucleus of the Te atom. A simple approach based on a tight-binding calculation is proposed for the evaluation of this electronic density. The first results are given for tellurium oxides, which explain the differences in the Te oxidation states for these compounds and the correlation with the values of the isomer shift. A study concerning other tellurium compounds is under investigation.

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