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Quadrupole splitting and isomer shifts in Te oxides investigated using nuclear forward scattering

Benedikt Klobes · Nicolas Barrier ·
Benedicte Vertruyen · Christine Martin ·
Raphaël P. Hermann

Abstract Nuclear forward scattering by ^{125}Te is a viable alternative to conventional ^{125}Te Mössbauer spectroscopy avoiding all source related issues. Using reference compounds with known hyperfine parameters and Te oxides exhibiting stereochemically active lone pairs, we show that nuclear forward scattering by ^{125}Te can be reliably used to extract quadrupole splitting energy and relative isomer shift. The rough correlation between Te-O coordination and quadrupole splitting energy as put forward by Takeda and Greenwood (J. Chem. Soc. Dalton, 2207, 1975), is corroborated by the presented results.

Keywords Quadrupole splitting · Lone-pair · Nuclear forward scattering

1 Introduction

Valence and local coordination of Tellurium are archetypal objects of ^{125}Te Mössbauer spectroscopy and can be characterized using isomer shift and quadrupole splitting energy.

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B. Klobes (✉) · R. P. Hermann
Jülich Centre for Neutron Science JCNS and Peter Grünberg Institute PGI, JARA-FIT,
Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
e-mail: b.klobes@fz-juelich.de

N. Barrier · C. Martin
Laboratoire CRISMAT, UMR 6508 CNRS ENSICAEN,
6 bd Maréchal Juin, 14050 Caen Cedex 4, France

B. Vertruyen
Department of Chemistry, University of Liege, 4000 Liege, Belgium

R. P. Hermann
Faculté des Sciences, Université de Liège, 4000 Liège, Belgium

Questions related to both parameters are of particular importance for modern fields of solid state physics and inorganic chemistry related to tellurium such as phase change materials [1], thermoelectric compounds [2], catalysts [3] as well as Fe-Te based parent compounds of superconducting materials [4, 5]. Moreover, the formation of stereochemically active lone pairs in Te^{4+} containing compounds as well as their relation to superconductivity are interesting from a fundamental perspective [6, 7].

Due to source related issues, i.e. its rather short half-life and the necessity to cool the source [8], classical ^{125}Te Mössbauer spectroscopy is nowadays infrequently applied. However, the ^{125}Te Mössbauer resonance[1] has been accessed using synchrotron based nuclear resonance scattering (NRS) techniques [9, 11] including nuclear forward scattering (NFS) [10], which can be considered as time-domain Mössbauer spectroscopy though dynamic scattering effects can make it slightly more complicated than the Fourier transform of the classical Mössbauer spectrum [12]. In this way, the radioactive source is substituted by a not necessarily monochromatized synchrotron radiation beam and time-domain spectroscopy is facilitated by the bunched time structure of synchrotron radiation [13].

Since, up to now, merely NFS measurements of metallic Te were published [9], we herein present NFS measurements of Te oxides, which are mostly characterized by a pronounced quadrupole splitting due to electronic lone pair formation. Moreover, relative isomer shifts are determined.

2 Materials and methods

NFS measurements were carried out in 16-bunch mode at the nuclear resonance beamlines ID18 and ID22N [14] of the European Synchrotron Radiation Facility in Grenoble, France. Essential parts of the experimental setups are a high-resolution sapphire backscattering monochromator and a combination of fast discriminating electronics and fast detectors. While the former is necessary in order to achieve meV resolution required both for the prevention of detector overload and for maintaining sufficient flux for the excitation of the Mssbauer resonance, the latter allow for detecting nuclear fluorescence of the short-lived ^{125}Te isotope. A detailed description of the experimental setup is given in [9, 15]. All measurements were performed at about 14 K and NFS spectra were analyzed using MOTIF [16].

The samples $CaTeO_3$, $CaTe_2O_5$ and $CdTe_2O_5$ were synthesized by solid state reactions from stoichiometric mixtures of TeO_2 with $CaCO_3$ for the Ca base phases and CdO for the $CdTe_2O_5$ phase. The different reagents were intimately ground and placed in platinum crucibles. $CaTeO_3$ is obtained after heating the mixture at 1023 K for 72 h under N_2 flux. $CaTe_2O_5$ is obtained after heating the mixture under N_2 flux at 1023 K for 24 h and cooling down to 673 K in 24 h. For $CdTe_2O_5$ the mixture was fired under N_2 flux at 923 K for 24 h and also cooling down to 673 K in 24 h. The $SrTe_3O_8$ oxide was synthesized by solid state reaction using a stoichiometric mixture of SrO_2 (stored in a glove box under Ar atmosphere) and TeO_2 oxides. The samples were first intimately ground in an agate mortar,

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[1] The published natural lifetime and transition energy of the ^{125}Te Mössbauer resonance are 2.131(12) ns and 35493.12(39) keV, respectively [9]. This results in a natural linewidth $\Gamma_0 \approx 1.3$ mm/s. The natural abundance of ^{125}Te is 6.99 % [10].

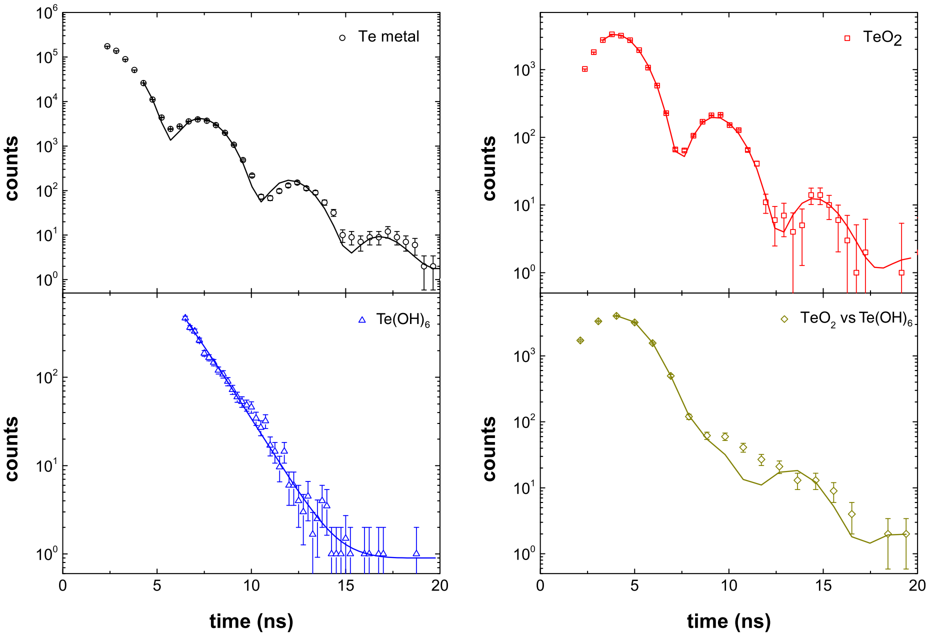

Fig. 1 Nuclear forward scattering spectra of reference samples exhibiting quantum beats due to quadrupole splitting in the case of Te metal and TeO_2 and an exponential decay in the case of $Te(OH)_6$ as expected for a single line absorber. The relative isomer shift between TeO_2 and $Te(OH)_6$ also agrees with literature [8, 18]

then pressed in the form of bars. Subsequently, they were placed in evacuated quartz tubes and heated up to 923 K with a heating rate of 100 K/h, held at this temperature for 12 h and cooled to room temperature in 6 h. The compositions of all samples were checked by powder X-ray diffraction with a PANalytical X'pertPro diffractometer equipped with an X'Celerator detector working with Cu-K_α radiation in the 2θ range of 8 to 90. Only the sample corresponding to the $CdTe_2O_5$ synthesis contains a negligible amount of TeO_2. The trirutile Mn_2TeO_6 [17] sample was prepared by a solid state reaction of $MnC_2O_4{\cdot}2H_2O$ and $Te(OH)_6$ at 893 K for 12 h in air.

3 Results and discussion

^{125}Te metal and natural isotopic abundance TeO_2 and $Te(OH)_6$ were used as reference samples and the corresponding NFS spectra are shown in Fig. 1. While Te metal and TeO_2 each exhibit a quadrupole splitting[2] ΔE_Q, which gives rise to the observed beating modulation of the decay of the Mössbauer level, so-called quantum beats, the NFS spectrum of $Te(OH)_6$ is essentially an exponential decay representing a single line absorber within the terminology

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[2] The quadrupole splitting ΔE_Q is given in terms of $\frac{1}{2}eQV_{zz}$ herein, where e is the elementary charge, Q is the nuclear quadrupole moment of the first excited state of ^{125}Te and V_{zz} is the absolute value of the main component of the electric field gradient.

Table 1 Quadrupole splitting energy ΔE_Q and relative isomer shift δ determined using nuclear forward scattering as well as the corresponding type of Te-O coordination geometry according to [29]

compound	site	ΔE_Q (mm/s)	δ (mm/s) , comment	Te^{4+}-O coordination
Te		7.49(3)		
TeO_2		6.68(2)		bipyramidal
$Te(OH)_6$		0	$\delta(TeO_2$ vs. $Te(OH)_6) = 2.08(8)$	
$CaTeO_3$	all	5.84(5)	only average ΔE_Q	tetrahedral
$CaTe_2O_5$	all	7.18(9)	only average ΔE_Q	modulated structure, see text
$CdTe_2O_5$	all	7.02(5)	only average ΔE_Q	modulated structure, see text
$SrTe_3O_8$	Te1	5.84(9)		octahedral
	Te2	< 0.4	δ(Te1 vs. Te2) = 1.78(3)	
Mn_2TeO_6		0	$\delta(Mn_2TeO_6$ vs. $TeO_2) = 2.4(3)$	

of conventional Mössbauer spectroscopy [18]. The determined values of ΔE_Q are summarized in Table 1 and are in good agreement with previous NFS measurements (in the case of Te metal) [9] and conventional Mössbauer spectroscopy [18–21]. In order to investigate isomer shifts using NFS, it is necessary to use (at least) two samples/absorbers at the same time, one of which then provides the reference system which is provided by the radioactive source in conventional Mössbauer spectroscopy. Notably, since NFS is basically an interference effect, such measurements only allow for determining the absolute values of isomer shifts. The common NFS spectrum of TeO_2 and $Te(OH)_6$ is also shown in Fig. 1. Using the sample parameters, in particular thicknesses and ΔE_Q in the case of TeO_2, as determined on the basis of the single sample NFS measurements, one can determine their relative isomer shift δ = 2.08(8) mm/s (see also Table 1), which is a typical isomer shift between Te^{4+} and Te^{6+} in agreement with literature [8, 18]. Thus, these reference measurements demonstrate the feasibility to measure hyperfine interactions and isomer shifts using NFS by ^{125}Te.

A notable advantage of NFS as compared to conventional Mössbauer spectroscopy, which is related to the absence of a radioactive source, is the possibility to reduce the measurement resolution to its natural limit, i.e. to the natural linewidth Γ_0. In Fig. 2 published, conventional Mössbauer spectra of TeO_2 [8] as well as of metallic Te [22] are compared to absorption spectra calculated from the corresponding NFS fits using MOTIF. Although the NFS samples turn out to be almost *dark* absorbers in classical Mössbauer terminology with very high absorption compared to the *thin* samples investigated with conventional Mössbauer spectroscopy, the calculated linewidth in the case of NFS is still well below the one in the conventional case. The effective thicknesses [23] of the samples discussed herein ranged between 0.5 in the case of $Te(OH)_6$ and 3.5 in the case of pure Te, which corresponds to sample quantities of 35 mg/cm^2 and 102 mg/cm^2 respectively considering natural isotopic abundance and assuming a Lamb-Mssbauer factor of about 0.4 at measurement temperature. The Lamb-Mössbauer factor at measurement temperature was estimated using the corresponding Debye model [24]. The other sample thicknesses were within the boundaries as set by $Te(OH)_6$ and pure Te.

NFS spectra[3] of Te oxides, each of which contains Te^{4+}, are shown in Fig. 3. The spectra for $CaTeO_3$, $CaTe_2O_5$ and $CdTe_2O_5$ are characterized by well resolved quantum beats due

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[3] Typical acquisition times of spectra presented herein were about 15 minutes.

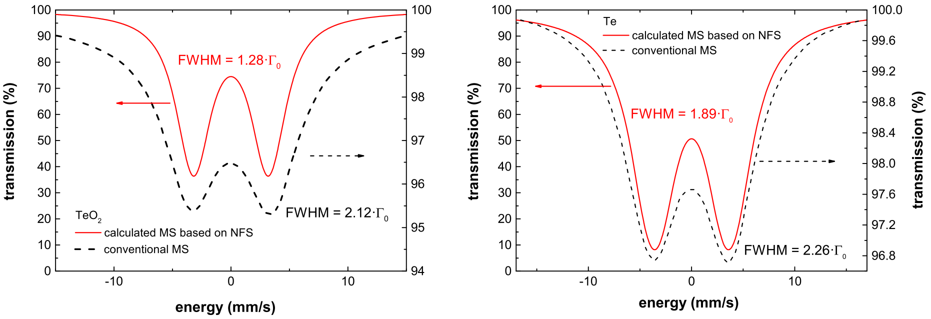

Fig. 2 Comparison of Mössbauer spectra calculated from NFS spectra using MOTIF [16] with spectra obtained using conventional Mössbauer spectroscopy. (*left*) TeO_2 data measured at 77 K is taken from [8]. (*right*) Te data measured at 4 K is taken from [22]. The full linewidth at half maximum (FWHM) is given for each case. Note the different scales for the calculated and measured Mössbauer spectra

to quadrupole splitting, which can be associated to the stereo-active lone pair in these compounds. Although all three compounds aforementioned exhibit different crystallographic Te sites [25, 26], each spectrum can be reasonably modeled using a single value describing the quadrupole splitting. These compounds exhibit different coordination environments for the Te^{4+} cations. In $CaTeO_3$ all Te atoms are in tetrahedral coordination TeO_3E (E corresponding to the electronic lone pair) [25] and $CaTe_2O_5$ as well as isostructural $CdTe_2O_5$ [26] exhibit incommensurable modulated structures . The positions of Te and surrounding O atoms as well as the occupancy of the crystallographic sites of these oxygen atoms are modulated unit-cell by unit-cell. In this way, the Te coordination environment is varied from tetrahedral (TeO_3E) to bipyramidal (TeO_4E) and to hexagonal (TeO_4E). However, NFS spectra of both $CaTe_2O_5$ and $CdTe_2O_5$ could be satisfactorily analyzed using a single quadrupole splitting energy, which indicates a rather gradual nature of the structural modulation.

Due to the mixed valency of Te in $SrTe_3O_8$, which contains both Te^{4+} and Te^{6+} [27], the corresponding NFS response is more complex as compared to the previously discussed ones, since this compound would yield a three line pattern in energy-domain Mössbauer spectroscopy. The quadrupole splitting energy associated to Te^{4+} as well as the relative isomer shift between Te^{4+} and Te^{6+} in $Sr(Te^{+4})_2(Te^{+6})O_8$ are summarized in Table 1.

Although there is no well defined relation between the value of the quadrupole splitting and the local environment around Te^{4+} in Te lone-pair oxides, a rough correlation could be established [28] showing that a bipyramidal configuration of oxygen coordination leads to rather high quadrupole splitting energies as compared to a tetrahedral configuration. In general, this is corroborated by the presented results (see Table 1). Moreover, a distorted octahedral environment [29] as in the case of $SrTe_3O_8$, which is not considered in [28], leads to a similar quadrupole splitting energy as in the case of tetrahedal coordination.

The relative isomer shift of Mn_2TeO_6 with respect to TeO_2 was also determined using NFS (see. Fig. 4). The NFS spectrum of the single compound exhibits a low frequency beating due to sample thickness [10], which is also shown in Fig. 4. Using known thicknesses of both compounds, the relative isomer shift for Mn_2TeO_6 with respect to TeO_2 can be accurately determined to be 2.4(3) mm/s as expected for a Te^{6+} species.

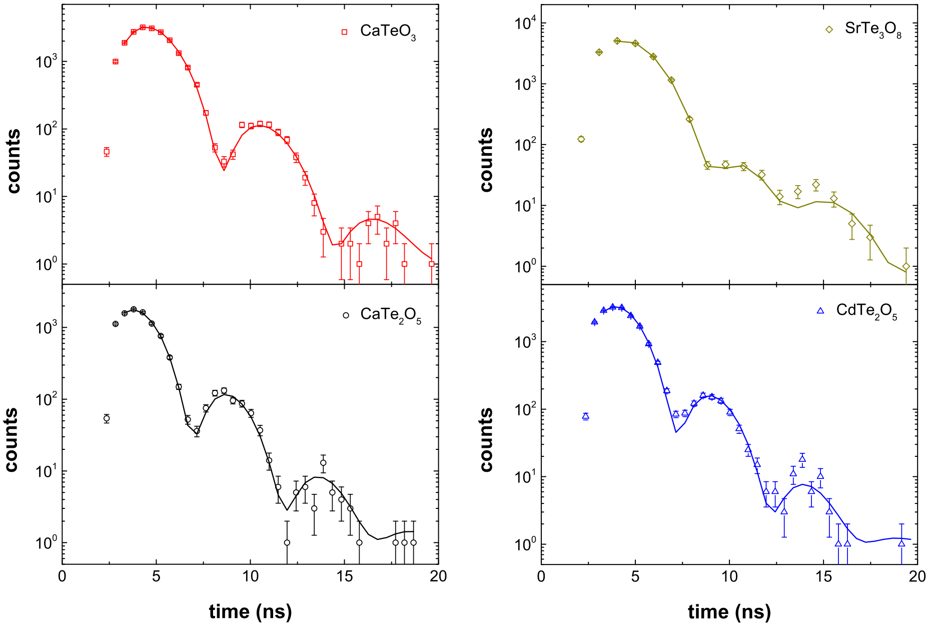

Fig. 3 Nuclear forward scattering spectra of lone-pair Te oxides. In each case the lone-pair associated to Te^{4+} gives rise to a pronounced quadrupole splitting

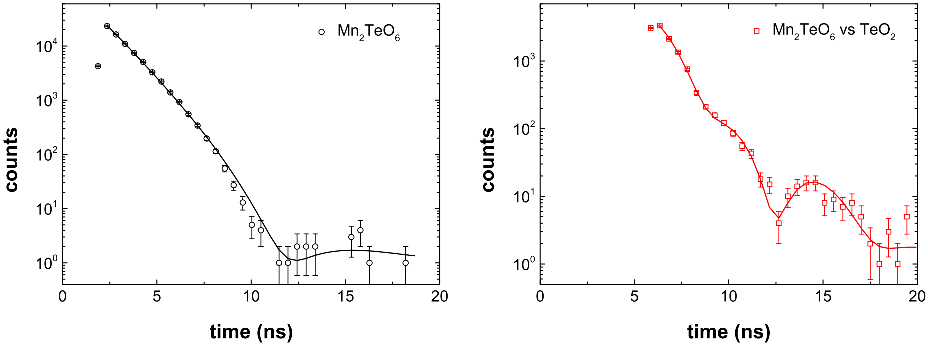

Fig. 4 Nuclear forward scattering spectra of Mn$_2$TeO$_6$ and of the combination of Mn$_2$TeO$_6$ and TeO$_2$

4 Conclusions

Quadrupole splitting energies in Te oxides as well as relative isomer shifts were determined using nuclear forward scattering. Good agreement with conventional Mössbauer spectroscopy results could be obtained for materials with published Mössbauer data. Even using highly absorbing samples, NFS was shown to outperform conventional Mössbauer spectroscopy in terms of linewidth/resolution. Stereochemically active lone pairs in Te^{4+} containing compounds give rise to pronounced quadrupole splitting energies, which appear to depend, to some extent, on the local coordination of Te [28]. Thus, NFS can be considered a valuable, more precise alternative to conventional Mössbauer spectroscopy. In particular, due to the high brilliance of third generation synchrotrons and the absence of any solid angle effect, NFS using the ^{125}Te Mössbauer resonance may be especially fruitful for investigations using more complex in-situ sample environments as required in catalysis.

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