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Nuclear forward and inelastic spectroscopy on ^{125}Te and Sb$_2^{125}$Te$_3$

H.-C. Wille[1(a)], R. P. Hermann[2,3], I. Sergueev[4], U. Pelzer[4], A. Möchel[2,3], T. Claudio[2,3], J. Perßon[2],
R. Rüffer[4], A. Said[5] and Yu. V. Shvyd'ko[5]

[1] *Deutsches Elektronen-Synchrotron - D-22607 Hamburg, Germany, EU*
[2] *Institut für Festkörperforschung, JCNS und JARA-FIT, Forschungszentrum Jülich GmbH*
D-52425 Jülich, Germany, EU
[3] *Faculté des Sciences, Université de Liège - B-4000 Liège, Belgium, EU*
[4] *European Synchrotron Radiation Facility - F-38043 Grenoble Cedex, France, EU*
[5] *Argonne National Laboratory, Advanced Photon Source - Argonne, IL 60439, USA*

Abstract – We report on the observation of nuclear forward and nuclear inelastic scattering of synchrotron radiation by ^{125}Te and the application of both spectroscopic methods to tellurium compounds by using a high-resolution backscattering sapphire monochromator in combination with fast detection electronics. The lifetime of the nuclear resonance and the energy of the transition were determined to be 2.131(12) ns and 35493.12(30) eV, respectively. As applications, the nuclear inelastic spectrum in Sb$_2$Te$_3$ and the nuclear forward scattering by Te metal were measured. These measurements open the field of nuclear resonance spectroscopy on tellurium compounds such as thermoelectric and superconducting materials.

Introduction. – Tellurium is a constituent of several type of compounds that are currently attracting attention, notably many phase change materials used for rewriteable data storage devices [1], many thermoelectric materials [2], and more recently, iron-tellurium–based parent compounds of superconducting materials [3,4].

Mössbauer spectral studies on Te compounds have been performed since the early days of Mössbauer spectroscopy [5–7]. This transition occurs between the ground state with spin parity $I_g = 1/2+$ and the first excited state with spin parity $I_e = 3/2+$ and the published [8] energy $E_0 = 35492.2(5)$ eV. The reported half life is $t_{1/2} = 1.48(1)$ ns corresponding to a lifetime of $\tau = 2.14(1)$ ns [9], and the recoil energy is $E_R = E_\gamma/2m_{\text{Te}}c^2 = 5.41$ meV. The natural abundance of ^{125}Te is 6.99%. The major limitations for Mössbauer spectroscopy comes from the narrow range of isomer shifts for the different oxidation states as compared to the natural linewidth of 5 mm/s, the significant source broadening, and a rather limited source half-life of $\sim$60 days [7]. ^{125}Te is thus an appealing isotope for attempting measurements using synchrotron radiation nuclear resonance scattering. Since the first nuclear

resonant scattering experiment [10] on ^{57}Fe reported in 1985 and the first phonon measurements [11,12] reported in 1995, this field of research has been expanded to many Mössbauer isotopes [13] and most recently [14–16] to ^{121}Sb, an isotope with a resonance energy and lifetime similar to ^{125}Te. The different nuclear resonant scattering techniques are applied for a wide variety of topics in natural sciences including magnetism, solid-state dynamics, phase transitions, geophysics, as well as biological and chemical studies [17,18]. Due to the high brilliance of third generation synchrotron radiation sources these techniques offer unique opportunities in application to nanomagnetism [19], dynamical studies on nano systems [20] and high pressure physics where a high flux of photons matching the resonance energy through a very small sample volume is mandatory [17].

The nuclear scattering techniques put stringent requirements on the X-ray optics, and in particular, high-resolution monochromators (HRMs) are essential in order to achieve good resolution for phonon spectroscopy using nuclear inelastic scattering and, with some exceptions [21,22], to avoid the detector overload for nuclear forward scattering. In order to reach the $\sim$meV resolution needed for the study of phonon excitations in a solid, a
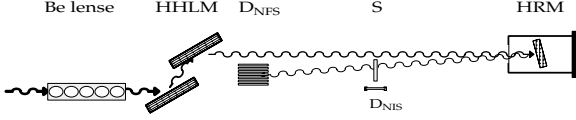
Fig. 1: Experimental arrangement of the Be lense, the double-crystal Si(111) high-heat-load monochromator, HHLM, the high-resolution monochromator, HRM, that consists of a temperature-controlled sapphire single crystal, the ^{125}Te-containing sample, S, and the Si APD X-ray detectors, D_{NIS} and D_{NFS}, see text.
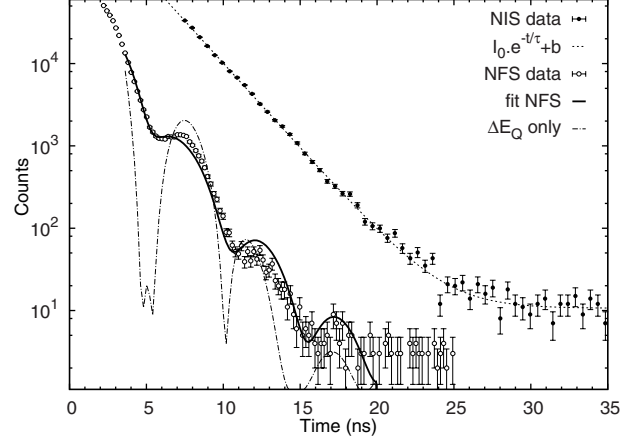

Fig. 2: Elemental Te time spectrum in the NIS channel, filled symbols, and fitted using an exponential decay plus background, dashed line. Elemental Te NFS time spectrum, at $T = 25$ K, open symbols, the fit with quadrupole interaction and thickness broadening starting at 4 ns, solid line, and the quadrupole interaction only model, dot-dashed line, see text.

resolution of the monochromator $\Delta E/E$ of 10^{-7} or better is thus required for nuclear resonances with energy of a few tens of keV. Further, whereas for resonance energies < 30 keV, efficient multiple bounce Si HRMs have been developed and are widely used (see reviews [23,24]). In this energy range single bounce sapphire Bragg backscattering monochromators are at least equally efficient and above 30 keV backscattering provides a more efficient alternative with sufficient angular acceptance, higher reflectivity, and a free choice of X-ray energy due to a larger choice of reflections [24,25]. Bragg backscattering monochromatization from sapphire has first been used for nuclear resonant scattering on ^{161}Dy at 25.61 keV [26] and recently a single-crystal Bragg backscattering sapphire, Al_2O_3 monochromator for ^{121}Sb antimony at 37.13 keV has been developed [14,16].

Herein, we report on nuclear forward scattering measurements (NFS) on ^{125}Te in Te metal and nuclear inelastic scattering measurements (NIS) on Sb_2Te_3 using the same monochromator at the $(20\,6\,\overline{26}\,2)$ reflection in Al_2O_3. The 6.6 meV resolution achieved herein allows for studies of phonon properties with relaxed resolution, and opens the way for nuclear resonance spectroscopy on many interesting Te bearing compounds.

Experimental. – The experiments were performed in 16-bunch mode at the nuclear resonance station [27] ID22N of the European Synchrotron Radiation Facility in Grenoble, France. In the experimental setup, see fig. 1, the beam is first collimated by a Be compound refractive lense [28] in order to reduce the vertical beam divergence to slightly less than $3\,\mu$rad and the vertical beam spot size on the sapphire to about $400\,\mu$m. A double-crystal Si (111) high-heat-load monochromator then filters out a 7 eV bandwidth at 35.49 keV with a typical integrated flux of $3 \cdot 10^{11}$ photons per second. The beam passes in the vicinity of the sample before reaching the high-resolution monochromator [14], a sapphire crystal located in a temperature-controlled nitrogen gas flow cryostat mounted on a 2-circle goniometer. The beam that is backscattered towards the sample has a narrow bandwidth of a few meV.

The beam transmitted through and scattered in forward direction by the sample is collected by the forward detector array D_{NFS}. The nuclear fluorescence products from the phonon-assisted nuclear absorption and the electronically scattered radiation are collected in the detector D_{NIS} located in transverse direction. The detectors are comprised of avalanche photodiode X-ray detectors [29] with a time resolution of 0.2 ns (NFS) and 1 ns (NIS) respectively. This permits the discrimination of the delayed nuclear resonant photons from the prompt electronically scattered photons impinging on the sample. The 0.2 ns time resolution of the NFS detector combined with fast discriminators allows signal collection as soon as 2 ns after the prompt synchrotron radiation, whereas signal collection can start only after about 6 ns in the NIS channel, see fig. 2.

The same sapphire-based monochromator has been succesfully introduced [14,16] for nuclear resonant scattering on ^{121}Sb. In the present experiment the monochromatisation [24] is obtained via diffraction by the planes $(20\,6\,\overline{26}\,2)$ of a sapphire crystal that fulfill the Bragg backscattering condition in the desired energy region around the ^{125}Te resonance energy, E_0. In order to separate the direct and backscattered beam, a glancing angle of $89.90(5)°$ was used, sufficiently large to retain an angular acceptance $\geqslant 6.5\,\mu$rad matching the full beam divergence [24]. The energy of the backscattered beam is tuned by scanning the sapphire temperature around the estimated temperature of 214 K corresponding to E_0 for this reflection. The sapphire thermal-expansion coefficient at T_0 yields [30] a linear energy variation of -114 meV/K. A temperature controller with a mK relative accuracy is used. The absolute accuracy of the crystal temperature is however limited by the X-ray heat load and by the temperature gradient between the sapphire and the sensor, a platinum resistor located in the nitrogen gas flowing around the sapphire.

The polycristalline Te metal and Sb$_2$Te$_3$ samples were enriched in ^{125}Te to 95%. In order to maximize the Lamb-Mössbauer factor for NFS and to minimize multiphonon scattering for NIS, the measurements were carried out with the samples at 25 K. Data evaluation of the NFS and NIS data was carried out using the programs MOTIF [31] and DOS [32], respectively. We also measured the ^{121}Sb NIS in Sb$_2$Te$_3$ using the $(15\,13\,\overline{28}\,14)$ reflection, similarly as in ref. [16], and extracted the Sb specific DOS; the resolution of the latter measurement is $\sim$3 meV.

Results and discussion. – The energy of the $(20\,6\,\overline{26}\,2)$ sapphire reflection matches the ^{125}Te nuclear resonant energy at $T_0 = 206(3)$ K, *i.e.* 8 K lower than expected. The corresponding ^{125}Te nuclear resonance energy of 35.49312(30) keV is obtained from the sapphire lattice constants [30], *i.e.* 0.9 eV larger than previously published [8].

The time spectra in D$_{\text{NFS}}$ and D$_{\text{NIS}}$ correspond to the coherent scattering that reveals the hyperfine interactions and the simple incoherent exponential decay of the ^{125}Te excited state, respectively, see fig. 2. From the incoherent decay measured by D$_{\text{NIS}}$, the natural lifetime $\tau = 2.131(12)$ ns of the nuclear transition is obtained, in excellent agreement with ref. [9]. The fitting of the intensity is done between $t = 8$ and 30 ns with the function $I(t) = I(0) \cdot \exp(t/\tau) + b$, where b is the background. The measured τ yields a natural linewidth of the excited state $\gamma_0 = \hbar/\tau = 309(2)$ neV.

The coherent nuclear forward scattering by elemental ^{125}Te reveals a quadrupole interaction of 2.96(10) γ_0, or 7.7(2) mm/s in Mössbauer velocity units in good agreement with early reports of 7.60(5) mm/s from Mössbauer spectroscopy [33,34]. The sample was chosen to have a maximum integrated intensity and had a large thickness along the beam. As a result, hybrid beats [35] appear in the spectrum of the nuclear forward scattering due to the interference of beats due to hyperfine interactions and due to multiple scattering. Further, thickness distribution smoothing out these beats resulted in this rather simple shape of the spectrum which nevertheless, requires taking into account the hybrid beats for the fit. In case measurements of the coherent nuclear scattering is desired, thin samples can be used which allow one to measure the hyperfine interactions with better precision. Note that carrying out NFS measurements might be especially useful for Te compounds as source broadening, a frequent problem for Mössbauer sources for ^{125}Te spectroscopy [7], is eliminated in this method. In contrast to Mössbauer spectral measurements for which the best possible resolution is $\geqslant 2\gamma_0$ it is γ_0 for NFS.

The time-integrated energy dependence of the intensities in D$_{\text{NFS}}$ and D$_{\text{NIS}}$ reveals the instrumental resolution function and the phonon-assisted nuclear inelastic scattering, respectively. The dependence of the nuclear forward and nuclear inelastic scattering intensities of Sb$_2$Te$_3$ upon the difference $E - E_0$ between the photon energy, E, and
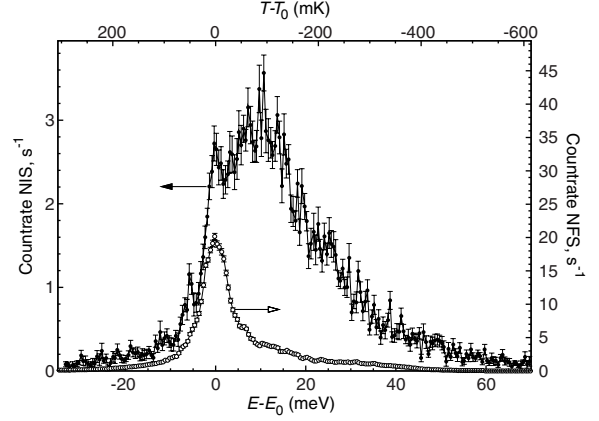

Fig. 3: The count rates in nuclear forward, filled symbols, and nuclear inelastic scattering, open symbols, for Sb$_2$Te$_3$ at 25 K as a function of the relative energy. The corresponding change in the sapphire crystal temperature relative to T_0 is indicated in the upper scale.

the nuclear resonant energy, E_0, is shown in fig. 3. The width of the instrumental functions was 6.6 meV, corresponding to a relative energy resolution of $2.1 \cdot 10^{-7}$, somewhat larger than the 4.5 meV bandwidth for earlier ^{121}Sb measurements [16]. This resolution is much larger than the theoretical value of 0.2 meV. The first reason could be related to the crystal quality. A resolution of 0.2 meV at 35.4 keV requires $2 \cdot 10^8$ perfectly parallel reflecting planes which corresponds to about 3 mm thickness of a dislocation free crystal. As reported from topography studies [36], the quality of available sapphire crystals is in general nowadays much worse than this requirement. The second reason could be the temperature gradient in the crystal over the sapphire thickness due to heat load from the impinging X-ray beam. A temperature gradient of 10 mK would lead to a broadening of 1 meV. The high flux, even after the high-heat-load monochromator, in combination with the good but finite thermal conductivity of sapphire at about 206 K could therefore result in a broadening in the meV energy range. Further studies for the reasons of the broadening and the developement of measures to improve the energy resolution are ongoing.

Because the ^{125}Te resonance recoil energy of 5.41 meV is rather large compared to the Debye energy of Te of 13.8 meV [37], the multiphonon contribution to the NIS, which is proportional to the ratio of the recoil and the Debye energy, is also rather large compared to other Mössbauer isotopes like ^{57}Fe or ^{119}Sn. This holds also for low sample temperatures. As a consequence, the elastic peak in the NIS spectrum can be smaller than the strongest phonon contributions, and special care must be taken in order to extract the density of phonon states (DOS). In Sb$_2$Te$_3$ the Lamb-Mössbauer factors are $f_{^{125}\text{Te}} = 0.52(5)$ and $f_{^{121}\text{Sb}} = 0.45(5)$ at 25 K. Consequently, $\sim$50% of the spectrum corresponds to multiphonon contributions. The extracted DOS, after
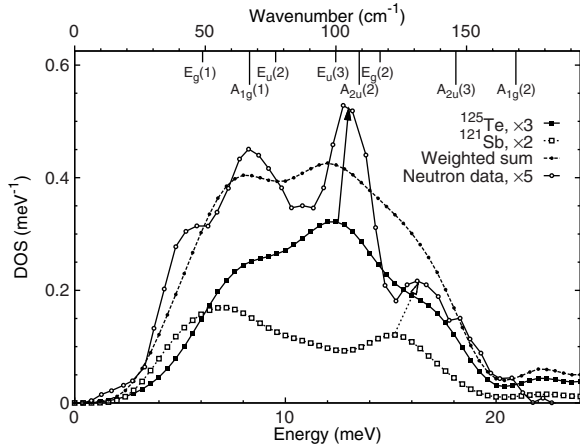
Fig. 4: Comparison of the partial DOS of Te and Sb in $Sb_2^{125}Te_3$ obtained from NIS, normalized to 3 and 2, filled and open squares respectively, and their sum weighted by the neutron scattering cross-sections, filled circles, with the DOS obtained from inelastic neutron scattering [42], normalized to 5, open circles. Calculated [43] Γ-point phonon mode energies and symmetries are indicated by the labeled tics.

elimination of the multiphonons and background [32,38], are shown in fig. 4.

The large recoil energy prevents direct measurements of the phonon DOS at higher temperatures, because broad multiphonon contributions start to wash out the one-phonon term when the sample temperature is similar to the Debye temperature. However, using the sum rules as outlined by Lipkin [39,40] it is in principle still possible to obtain a limited set of information, such as force constants, even at higher temperature. Nuclear inelastic scattering appears thus as a promising complementary technique to inelastic neutron scattering for force constant measurements, which have recently attracted interest in several tellurides [41].

By comparing the Te element specific DOS obtained herein with the by inelastic neutron scattering DOS [42], we can identify the peaks in the neutron data at 12.8 meV to be essentially related to Te vibrational modes, whereas the peak at 16.5 meV has a large Sb contribution. This attribution is in agreement with a recent report [43], which indicates that at $\sim 100\,cm^{-1}$, the $E_u(3)$ and $A_{2u}(2)$ modes are essentially Te modes, and $E_g(2)$ involves equally Sb and Te, whereas above $130\,cm^{-1}$ the $A_{2u}(3)$ $A_{1g}(2)$ modes have large Sb contributions.

Conclusion. – Nuclear forward and nuclear inelastic scattering measurements on ^{125}Te have been demonstrated utilizing a high-resolution sapphire Bragg backscattering monochromator. The resonace energy has been determined to be 35.49312(30) keV. From the inelastic spectrum the natural lifetime and linewidth of the nuclear transition were determined to be 2.131(12) ns and 309(2) neV, respectively. From the forward spectrum the quadrupole splitting in elemental Te was determined

to be 2.96(10) γ_0. Nuclear inelastic scattering spectra of Te and Sb in Sb_2Te_3 have been measured and the density of phonon states has been derived. Although these measurements still have a relaxed 6.6 meV resolution, they demonstrated the feasibility of nuclear scattering techniques on ^{125}Te. This opens the field for studies on the electronical, magnetic and dynamical properties of Te compounds like thermoelectrics or superconductors. Next steps include improvement of the resolution and application to other materials, such as $GeSb_2Te_4$ phase change materials.

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