ANISOTROPY OF THE MÖSSBAUER EFFECT IN TELLURIUM SINGLE CRYSTALS

R. N. KUZ'MIN, A. A. OPALENKO, V. S. SHPINEL', and I. A. AVENARIUS

Moscow State University

Submitted August 19, 1968

Zh. Eksp. Teor. Fiz. 56, 167–174 (January, 1969)

The anisotropy of the probability of the Mössbauer effect of Te^{125} nuclei in tellurium single crystals was investigated experimentally at 80°K. The theoretical and experimental results on the asymmetry of the doublet components of the Mössbauer spectrum of polycrystalline tellurium were compared. The sign of the quadrupole interaction constant for tellurium was determined.

INTRODUCTION

THE anisotropy of the probability f′ of the resonant absorption (emission) of γ quanta in noncubic crystals has been investigated theoretically and experimentally by several workers.[1-6] The most interesting among the monatomic noncubic crystals, in which the Mössbauer effect is observed, are tin, tellurium, and antimony. The dependence of the probability of the recoilless resonant absorption of γ quanta on the orientation of a single crystal of white tin, β-Sn, which belongs to the tetragonal system, has been investigated experimentally[2, 3] and it has been found that the anisotropy decreases when the temperature is lowered. At 40°K, β-Sn exhibits an inversion of the anisotropy of f′.[4]

Tellurium is an equally interesting subject because of a strong anisotropy of its elastic properties: Young's modulus along the c axis is 4350 kg/mm^2, and at right-angles to this axis, is 2090 kg/mm^2. Moreover, the Mössbauer spectrum of tellurium has a well-resolved doublet, indicating a quadrupole interaction, which makes it possible to obtain a quantitative estimate of the asymmetry of the components in a polycrystalline sample due to the anisotropy in the probability f′ of the Mössbauer effect.[5]

EXPERIMENTAL PROCEDURE

The electrical properties of tellurium indicate that it is a semiconductor. Its hexagonal structure (shown in Fig. 1) consists of parallel helical chains of tellurium in which each tellurium atom is separated by 2.86 Å from an atom in the next chain. The valence angle in the chains is 102.6°. Tellurium atoms in these chains are bound by covalent bonds. The distance between the atoms within the chains is 3.74 Å. Tellerium belongs to the trigonal system, its space group is D_4^3 ($P3_121$), and its lattice parameters are:

$$a = 4{,}4570 \text{ Å}; \quad c = 5{,}9290 \text{ Å}; \quad c/a = 1{,}3301.$$

Tellurium single crystals, grown by the Czochralski method, were used in our investigations. These crystals were bounded by (1010) prismatic planes and elongated along the c axis. Plates with their planes perpendicular to the c axis were cut from a single crystal. A mosaic was made of 30 samples placed on a substrate and cemented by an epoxy resin. The area of sample No. 1, prepared in this way, was ~3 cm^2 but the useful area was 20% less; the gaps between the components of the sample were filled with powdered Wood's alloy. The sample was reduced to a thickness of 93 ± 4 μ by grinding. The finished absorber was investigated by the Laue x-ray diffraction method, which showed that the angles between blocks in each of the components of the sample were not greater than 0.5° and a deviation of a screw axis 3_1 relative to a beam of γ quanta did not exceed 5° for 25% of the components and not more than 1° for the rest of the components of the sample.

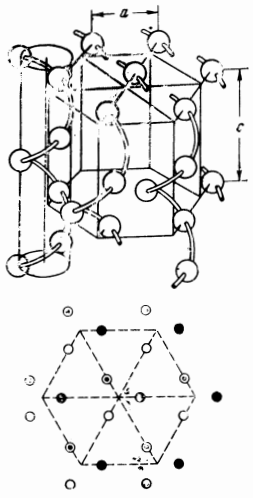

FIG. 1. Packing scheme of atoms in a tellurium crystal. Atoms lying in different planes are denoted by different symbols.

Sample No. 2 was a monolithic part of a single crystal, with an area of ~1 cm^2, cemented to a substrate so that the direction of the incidence of the γ rays was perpendicular to the natural (1010) face of the crystal. The thickness of the sample was reduced to 24 ± 1 μ by grinding. Next, the directions of the twofold symmetry axes were determined by x-ray diffraction, and the angles required for aligning these axes along the γ-beam direction were calculated; the error in the orientation of the sample was not more than 1°.

Sample No. 3 was an absorber made of polycrystalline tellurium enriched with Te^{125} to 56%. This sample was carefully ground in an agate mortar, mixed with berylium oxide (used as a filler), and compacted into tablets of 25 mm diameter and 1 mm thick; the thickness, in terms of Te^{125}, was 1.1 mg/cm^2.

The Mössbauer spectra of these samples are shown in Fig. 2. The spectra were recorded using an electrodynamic apparatus working under constant accelera-

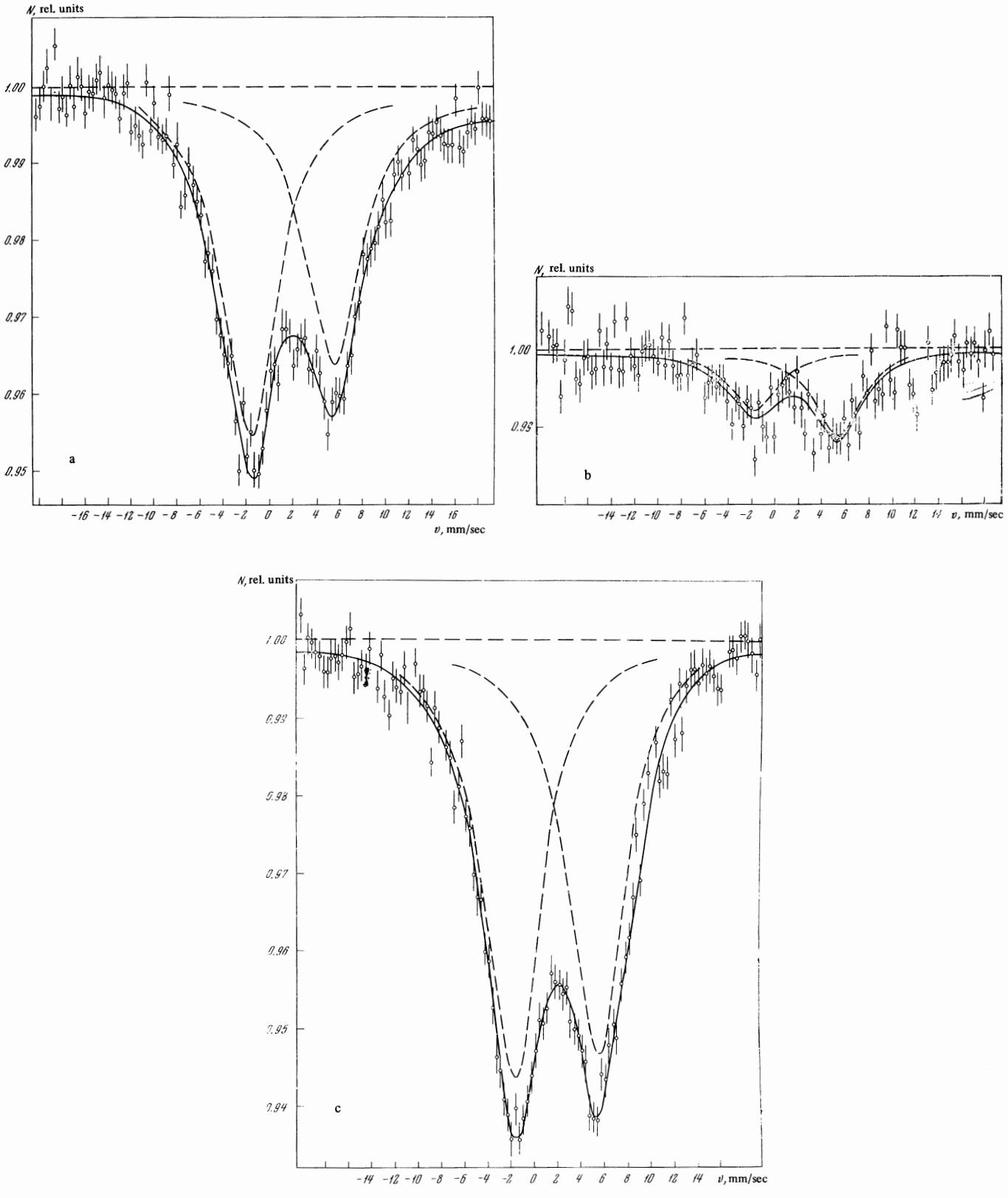

FIG. 2. Mössbauer spectra of single-crystal and polycrystalline tellurium: a) single-crystal sample No. 1, γ quanta incident parallel to the c axis; b) single-crystal sample No. 2, γ quanta incident at right-angles to the c axis; c) polycrystalline sample No. 3. The statistical error is indicated at each experimental point.

tion conditions. The measurements were carried out using a source in the form of $Te^{125m}O_3$; the source and the absorber were kept at 80°K; the absorber was set in motion. The resonant emission of the 35.6 keV γ rays of Te^{125m} was recorded using a scintillation counter with a NaI : Tl crystal 0.1 mm thick, employing an emission peak of 7 keV escape energy. Figure 3 shows parts of the amplitude spectra of Te^{125m} for single-crystal absorbers.

ANALYSIS OF EXPERIMENTAL DATA

To determine the anisotropy of the Mössbauer effect, it is necessary to estimate the probability f′ of the recoil-less absorption of γ quanta. Since the area under the resonance absorption curve is independent of the emission line profile and is governed solely by the absorption spectrum, we can determine f′ by the method of areas described by Bykov and Pham Zuy Hien:[7]

$$S_{exp} = \varkappa f n C_A e^{-C_A/2}[I_0(C_A/2) + I_1(C_A/2)], \quad (1)$$

where χ is the fraction of the resonant γ quanta in the emission spectrum; f is the probability of emission of the Mössbauer γ quanta; I_0 and I_1 are the Bessel functions of the zeroth and first orders with an imaginary argument. The dimensionless quantity $C_A = n_A f' \sigma_0$, where n_A is the number of resonating nuclei per 1 cm^2 of the absorber and $\sigma_0 = 3.1 \times 10^{-19}$ cm^2, is, in the case of thin absorbers ($C_A \lesssim 1$), proportional to the area of the spectrum under the resonance curve.[7] The value of C_A for our samples was considerably less than unity and therefore the relative values of f′ were determined from the formula

$$f'_{rel} = \text{const}\frac{S_{exp}}{\varkappa n_A} = \text{const}\frac{S_{exp}}{\varkappa x}, \quad (2)$$

where x is the thickness of the sample, in respect of Te^{125}, expressed in mg/cm^2. The areas of the experimentally determined spectra were measured with a planimeter and the value of κ was found by a geometrical analysis of the amplitude spectra (cf. Fig. 3). Table I gives the results of the measurements.

Using the experimental values of f'_{rel}, we determined the anisotropy of the Mössbauer effect in tellurium at 80°K, which was

$$f_{\parallel c}'/f_{\perp c}' = 1.45^{+0,55}_{-0,45}.$$

Assuming that in a tellurium single crystal the axis of the crystal field gradient coincides with the c crystallographic axis, we find that $f'(\theta)$ is given by[1]

$$f'(\theta) = \exp\{-T_1 + (T_3 - T_1)\cos^2\theta\} = \exp(-a + b\cos^2\theta), \quad (3)$$

where T_3 and T_1 are the components of the tensor of the electric field gradient, which are governed by the elastic properties of a crystal along and at right-angles to the c axis, respectively; T_3, $T_1 > 0$. Using Eq. (3) and the value of the anisotropy, we obtained

$$f_{\parallel c}'/f_{\perp c}' = e^{-a+b}/e^{-a} = e^b = 1.45,$$

and therefore $b = 0.37^{+0.3}_{-0.2}$, i.e., the average value of the square of the amplitude of vibrations along the c axis in tellurium was less than that at right-angles to this axis.

Examination of the areas of the Mössbauer spectra (cf. Fig. 2) showed directly that the sign of the quadrupole interaction constant of metallic tellurium was negative, i.e., $E_{\pm 3/2} < E_{\pm 1/2}$. Assuming $q < 0$[9] for the electric field gradient at the Te^{125} nuclei in crystalline tellurium, we found that the quadrupole moment of the Te^{125} nuclei is $Q > 0$.

Let us now consider the results obtained for the polycrystalline sample No. 3. Karyagin[5] showed that in the case of a polycrystalline isotropic absorber, the asymmetry of the quadrupole splitting doublet, due to the anisotropy of the values of f′, is given by the following expression:

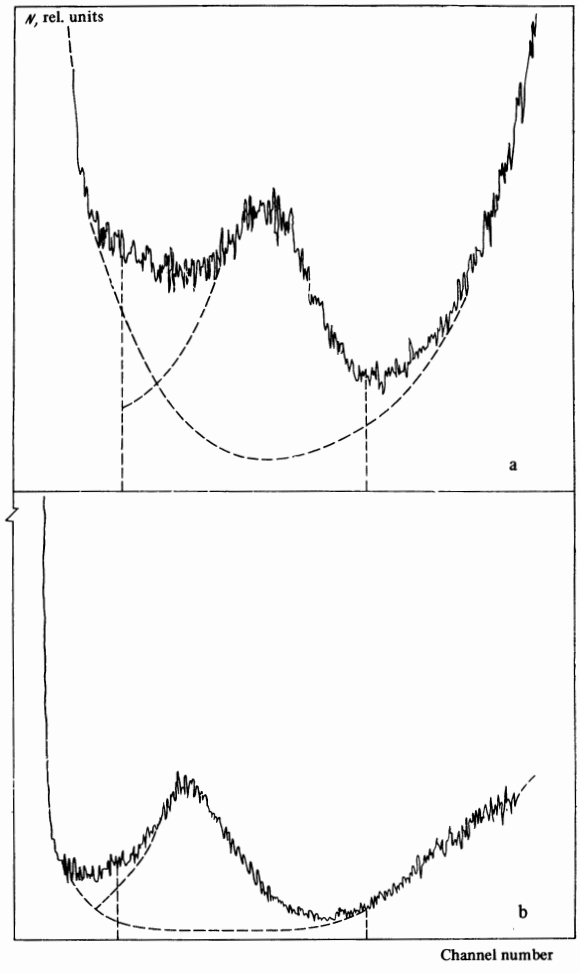

FIG. 3. Parts of the amplitude spectra of Te^{125m} : a) single-crystal sample No. 1; b) single-crystal sample No. 2.

Table I

Direction of γ quanta	S_{exp}, rel. units	$\varkappa$	x, mg/cm^2 for Te^{125}	f′, rel. units
$\parallel c$	363 (±2%)	0.66 ($^{+5}_{-10}$%)	4.05 (±5%)	136 ($^{+17\%}_{-12\%}$)
$\perp c$*	80 (±10%)	0.80 (±5%)	1.06 (±5%)	94.5 (±20%)

*The experimental values represent the averages of measurements of the Mössbauer absorption spectra for two directions parallel to the a axis and perpendicular to the (1010) plane of a tellurium single crystal.

$$i_\pi/i_\sigma = \int_0^\pi I_\pi f'(\theta)\sin\theta\, d\theta \Big/ \int_0^\pi I_\sigma f'(\theta)\sin\theta\, d\theta, \qquad (4)$$

where i_π and i_σ are, respectively, the intensities of the Mössbauer transitions $(\pm 3/2) \rightarrow (\pm 1/2)$ and $(\pm 1/2) \rightarrow (\pm 1/2)$; $I_\pi(\theta) = \text{const}\cdot(1 + \cos^2\theta)$ and $I_\sigma(\theta) = \text{const}\cdot(5/3 - \cos^2\theta)$, where θ is the angle between the axis of the electric field gradient and the direction of a beam of γ quanta. Using the relationship $f(\theta) = \exp(-a)\cdot\exp(0.37\cos^2\theta)$, we obtain $i_\pi/i_\sigma = 1.05$ after integration of Eq. (4).

By resolving the experimental spectra (cf. Fig. 2) into a sum of two Lorentz lines, and taking account of the value of the isomeric shift $\delta = 1.7 \pm 0.1$ mm/sec and of the quadrupole splitting $\Delta E = 7.5 \pm 0.1$ mm/sec, we obtained the values of the line half-widths and the ratio of the intensities of the components, which are given in Table II.

It is evident from Table II that the experimentally determined ratio of the intensities of the quadrupole splitting components for a polycrystalline sample is in good agreement with the value calculated from Eq. (4).

It must be mentioned that the existence of the asymmetry of the Mössbauer doublet of tellurium was pointed out by Stepanov et al.[10] as well as by Albanese et al.[11] but had not been noticed by Violet et al.[9] The value of the ratio $i_\pi/i_\sigma = 1.16$, reported in[10,11], gives ~2.5 for the anisotropy in single crystals, which does not agree with the results of our investigation. The absence of the asymmetry in tellurium spectra at 80°K, reported in[9], is probably due to the considerable thickness of the absorber (22 mg/cm^2 in respect of Te^{125}) used in that investigation, while at 4.2°K these authors may have failed to observe the asymmetry be-

Table II

Sample	Γ_A, mm/sec	(i_π/i_σ) exp
No. 1, γ quanta $\parallel$ c	6.0	1.25±0.05
No. 2, γ quanta $\perp$ c	5.0	0.67±0.13
No. 3, polycrystalline	6.0	1.05±0.03

cause of a reduction in the value of the anisotropy of f′, similar to that reported in experiments on tin.[2-4]

The value of the asymmetry parameter $\eta = 0.654$ for the electric field gradient in tellurium, reported in[9], makes it possible to compare the theoretical and experimental values (Table II) of the ratio of the intensities of the components of the quadrupole splitting doublet. Using the results of Pham Zuy Hien,[12] we obtain:

$$I_\pi(\theta) = \left(1 + \frac{a^2}{3}\right)(1 + \cos^2\theta) + \frac{4}{3}a^2\sin^2\theta + \frac{2a}{\sqrt{3}}\sin^2\theta\cos 2\varphi,$$

$$I_\sigma(\theta) = \left(\frac{1}{3} + a^2\right)(1 + \cos^2\theta) + \frac{4}{3}\sin^2\theta - \frac{2a}{\sqrt{3}}\sin^2\theta\cos 2\varphi,$$

where

$$a = \frac{\eta/\sqrt{3}}{1 + \sqrt{1 + \eta^2/3}}$$

and θ, φ are the spherical angles which give the direction of the γ quanta in the system of the principal axes of the tensor of the electric field gradient. In our case, we have

$$\text{for } \theta = 0°: \frac{I_\pi}{I_\sigma} = \frac{3 + a^2}{1 + 3a^2} = 2.72;$$

$$\text{for } \theta = 90°, \varphi = 45°: \frac{I_\pi}{I_\sigma} = \frac{3 + 5a^2}{5 + 3a^2} = 0.62.$$

The discrepancy between these values, which is particularly large for $\theta = 0°$, and the experimental values of the ratio of the intensities of the components suggests that the axis of the tensor of the electric field gradient does not coincide with the c axis in crystalline tellurium.

The authors are very grateful to A. M. Babeshkin for the supply of the $Te^{125m}O_3$ source which was used in the measurements.

[1] Yu. Kagan, Dokl. Akad. Nauk SSSR 140, 794 (1961) [Sov. Phys.-Dokl. 6, 881 (1962)].

[2] N. E. Alekseevskiĭ, Pham Zuy Hien, V. G. Shapiro, and V. S. Shpinel', Zh. Eksp. Teor. Fiz. 43, 790 (1962) [Sov. Phys.-JETP 16, 559 (1963)].

[3] V. G. Shapiro and V. S. Shpinel', Zh. Eksp. Teor. Fiz. 46, 1960 (1964) [Sov. Phys.-JETP 19, 1321 (1964)].

[4] N. E. Alekseevskiĭ, A. P. Kir'yanov, V. I. Nizhankovskiĭ, and Yu. A. Samarskiĭ, ZhETF Pis. Red. 2, 269 (1965) [JETP Lett. 2, 171 (1965)].

[5] S. V. Karyagin, Dokl. Akad. Nauk SSSR 148, 1102 (1963).

[6] V. I. Gol'danskiĭ, E. F. Makarov, I. P. Suzdalev, and I. A. Vinogradov, Zh. Eksp. Teor. Fiz. 54, 78 (1968) [Sov. Phys.-JETP 27, 44 (1968)].

[7] G. A. Bykov and Pham Zuy Hien, Zh. Eksp. Teor. Fiz. 43, 909 (1962) [Sov. Phys.-JETP 16, 646 (1963)].

[8] G. K. Wertheim, Mössbauer Effect: Principles and Applications, Academic Press, New York, 1964.

[9] C. E. Violet, R. Booth, and F. Wooten, Phys. Letters 5, 230 (1963).

[10] E. P. Stepanov, K. P. Aleshin, R. A. Manapov, B. N. Samoilov, V. V. Sklyarevskii, and V. G. Stankevich, Phys. Letters 6, 155 (1963).

[11] G. Albanese, C. Lamborizio, and I. Ortalli, Nuovo Cim. 50B, 65 (1967).

[12] Pham Zuy Hien, Zh. Eksp. Teor. Fiz. 49, 1576 (1965) [Sov. Phys.-JETP 22, 1080 (1966)].

Translated by A. Tybulewicz
24