Some Features of the Mossbauer Effect in Tellurium

A. A. OPALENKO, I. A. AVENARIUS, V. P. GOR'KOV, B. A. KOMISSAROVA, R. N. KUZ'MIN, AND P. N. ZAIKIN

Moscow State University

Submitted July 30, 1971

Zh. Eksp. Teor. Fiz. **62**, 1037–1042 (March, 1972)

An experimental and theoretical investigation of the integral asymmetry of doublet components of the polycrystalline tellurium Mossbauer spectrum is carried out. It is shown that despite the probability anisotropy of the Mossbauer effect in a tellurium single crystal, the Gol'danskiĭ-Karyagin effect is not observed because of peculiarities in the structure of tellurium. Formulas are obtained for the ratios of the peak intensities of the Mossbauer spectrum quadrupole splitting in polycrystals, $I_{3/2}/I_{1/2}$. The ratios are derived as functions of anisotropy $\epsilon = (f_{\parallel} - f_{\perp})/(f_{\parallel} + f_{\perp})$, orientation of the electric field gradient in the crystal, and the asymmetry parameter of the electric field gradient.

UNDER normal conditions, tellurium is a semiconductor having a chain structure of the type A8, belonging to a trigonal syngony with space group $P3_121$. The electric field gradient on the tellurium nucleus is due principally to the electrons that take part in the covalent bond. The electric field gradient in tellurium is described by a second-rank tensor with asymmetry parameter η, whose principal axis does not coincide with the c axis of the tellurium crystal. In addition, in one unit cell there exist three directions of the electric field gradient axes for the three crystallographically equivalent tellurium atoms. These features of the electric field gradient of tellurium should become manifest in the Mossbauer spectrum, which has a partly resolved hyperfine doublet structure characterizing quadrupole interaction.

The electric field gradient was calculated theoretically by Violet[1], who found that $V_{ZZ} = -8.4 \times 10^{18}$ V/cm^2 and $\eta = |(V_{XX} - V_{yy})/V_{ZZ}| = 0.654$. Figure 1 shows the position of the electric field gradient axes for each equivalent position of the atom in the crystal. The axes $z_{1,2,3}$ of the electric field gradient rotate along a helix around the c axis of the crystal with angle $\beta_{1,2,3} = 62°$. The electric field gradient was determined experimentally in[2,3] from an analysis of the intensity ratio of the doublet components of the Mossbauer spectra of tellurium single crystals. It was established that the quadrupole interaction constant is positive[3].

The experimental results of different investigations[3-7] of the asymmetry of the components of polycrystalline tellurium are listed in the table.

In view of the differences between the experimental results, we have carried out a theoretical and a second experimental investigation of the asymmetry of the doublet components for polycrystalline tellurium, for the purpose of establishing the existence of the Gol'danskiĭ-Karyagin effect in tellurium. We have measured the anisotropy of the probability of the Mossbauer effect in a tellurium single crystal in[7] at a temperature 80°K, and the more accurate ratio $f'_{\gamma \parallel c}/f'_{\gamma \perp c} = 1.5 \pm 0.2$.

Calculation by means of formula (4) of the Appendix for tellurium with allowance for $f_{\parallel}/f_{\perp} = 1.5 \pm 0.2$, $\eta = 0.654$, $\beta_1 = \beta_2 = \beta_3 = 62°$, $\alpha_1 = 270°$, $\alpha_2 = 30°$, $\alpha_3 = 150°$, yields for the intensity ratio

$$I_+/I_- = \sum_{i=1}^{3} (I_{3/2})_i \Big/ \sum_{i=1}^{3} (I_{1/2})_i = 0{,}99 \pm 0{,}01.$$

To observe such a small effect it is necessary to have high measurement accuracy and high spectrometer operating stability. The measurement of the spectrum shown in Fig. 2 lasted several days. The source was $\beta - Te^{125m}O_3$, which has the largest value of f among the known sources with Te^{125}, namely $f(\beta - TeO_3) \geq 0.54$ at T = 77°K, and the narrowest emission line, $\Gamma_S \leq 1.13\Gamma$[8]. The absorber was polycrystalline powder mixed with a carrier (beryllium oxide), with thickness of 1.1 mg/cm^2 relative to Te^{125}. The spectra were measured several times, and after each measurement the absorber was again mixed thoroughly, so as to prevent texture formation. The Mossbauer spectra were processed with a computer at the Computation Center of the Moscow State University, using the standard program of I. N. Silin[9]. The value obtained for the spectrum of Fig. 2 is $I_{3/2}/I_{1/2} = 1.00 \pm 0.01$.

Thus, the results of the theoretical calculations and of the experiments show that the Gol'danskiĭ-Karyagin

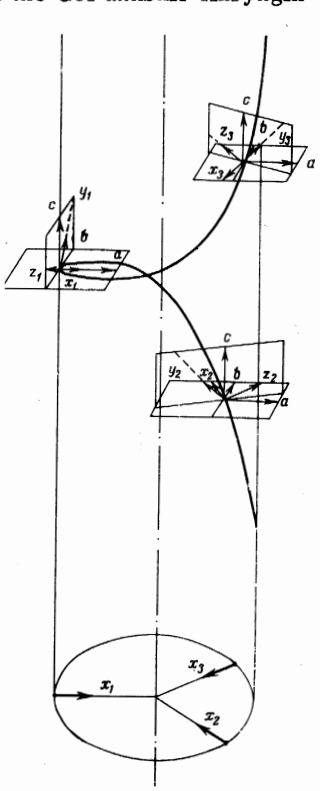

FIG. 1. Arrangement of the system of principal axes of the electric field gradient tensor for three equivalent positions of the atoms in the unit cell of tellurium.

Intensity ratio $I_{1/2}/I_{3/2}$	Temperature, °K	Reference	Intensity ratio $I_{1/2}/I_{3/2}$	Temperature, °K	Reference
1.17±0.04	77	[4]	1.05±0.03	80	[7]
1.16±0.05	77	[5]	$(1.04\pm0.01)^{-1}$	4	[3]
1.00±0.04	4; 77	[6]			

effect does not appear in tellurium, in spite of the large value of the anisotropy of the quantity f′ in the single crystal, owing to the special electric structure of tellurium.

APPENDIX

As shown by Karyagin[10], the ratio of the intensities of the hyperfine-structure components of the Mossbauer absorption spectrum of a polycrystalline sample depends noticeably on the anisotropy of the Debye-Waller factor relative to the crystallographic axes. In the case when the hyperfine structure is due to the interaction of the nucleus with the gradient of an extranuclear electrostatic field of arbitrary symmetry, the intensity of the spectrum component corresponding to the transition of the nucleus from the initial state $|J_0 n_0\rangle$ with spin J_0 and proper energy E_{n_0} into an excited state $|Jn\rangle$ is determined by the following expression (accurate to factors that are the same for all the hyperfine structure components):

$$I_{n_0\to n}=\sum(-1)^{2J-L'+m_0+m'}\langle n_0|m_0\rangle\langle n_0|m_0'\rangle \cdot\langle n|m\rangle^*\langle n|m'\rangle f_{lr}C_{l0}(LL')\begin{pmatrix} J & L & J_0\\ m & M & -m_0\end{pmatrix}\begin{pmatrix} J & L' & J_0\\ m' & M' & -m_0'\end{pmatrix} \cdot\begin{pmatrix} L & L' & l\\ M & -M' & S\end{pmatrix}D_{sr}^{l}(\alpha,\beta,\gamma)\langle J_0\|L\pi\|J\rangle^*\langle J_0\|L'\pi'\|J\rangle,$$

where the summation is carried out over m_0, m_0', m, m′, L, L′, l, s, r, M, and M′. Here m_0 and m are the projections of J_0 and J on the principal z axis of the electric field gradient tensor, L is the multiplicity of the Mossbauer transition, $\langle n_0|m_0\rangle$ and $\langle n|m\rangle$ are the nuclear eigenstates corresponding to the sublevels of the hyperfine structure of the ground and excited states in the m representation, $C_{l0}(LL')$ are the so-called radiation parameters of the γ transition[11], f_{lr} are the expansion coefficients (in the system of the principal axes of the electric field gradient tensor) of the Debye-Waller factor f(k) in spherical functions Y_{ls} whose arguments are the angles (θ, φ) defining the direction k of the propagation of the γ quantum relative to the system of principal axes of the electric field gradient tensor:

$$f(\mathbf{k})=\sum_{lsr}f_{lr}D_{sr}^{l}(\alpha,\beta,\gamma)Y_{ls}(\theta,\varphi),$$

and $\langle J_0\|L\pi\|J\rangle$ is the reduced nuclear matrix element.

The Euler angles α, β, and γ characterize the position of the system of the principal axes of the electric field gradient tensor at the nucleus relative to the system of the principal axes of f(k), the z axis of which coincides with the direction of a crystallographic axis of higher order, and D_{sr}^{l} are the elements of the unitary three-dimensional rotation matrix[12].

Thus, the presented form for $I_{n_0\to n}$ contains the dependence of the intensities of the quadrupole hyperfine structure components not only on the anisotropy f(k), but also on the orientation of the electric field gradient relative to the crystallographic axis.

We present below formulas for the relative intensities of the quadrupole doublet components $J_0 = 1/2$, $J = 3/2$, $L = L' = 1$ for several particular cases. All were obtained under the assumption that f(k) is axially symmetrical in its own system of principal axes.

A. If the electric field gradient at the nucleus is axially symmetrical and its symmetry axis coincides with that of f(k), then[10]

$$\frac{I_{3/2}}{I_{1/2}}=\frac{1+F_1}{1-F_1},\quad F_1=\frac{1}{2\sqrt{5}}\frac{f_2}{f_0}. \tag{1}$$

B. If the electric field gradient has an arbitrary symmetry and the z axis of its principal coordinate system coincides with the symmetry axis of f(k), then[10]

$$\frac{I_+}{I_-}=\frac{1+F_2}{1-F_2},\quad F_2=\frac{1-A^2}{1+A^2}\frac{1}{2\sqrt{5}}\frac{f_2}{f_0}, \tag{2}$$

where $A=\eta/\sqrt{3}(1+\sqrt{1+\eta^2/3})$ and η is the asym-

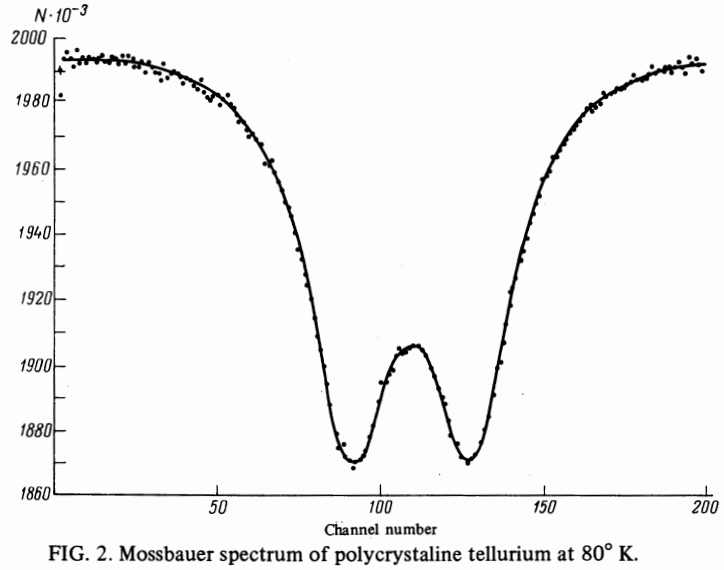

FIG. 2. Mossbauer spectrum of polycrystaline tellurium at 80° K.

metry parameter of the electric field gradient. The plus and minus signs correspond to the high- and low-energy components of the doublet, respectively.

C. If the electric field gradient is axially symmetrical and its symmetry axis does not coincide in direction with that of f(k), then

$$\frac{I_{3/2}}{I_{1/2}}=\frac{1+F_3}{1-F_3},\qquad F_3=\frac{P_2(\cos\beta)}{P_0(\cos\beta)}\frac{1}{2\sqrt{5}}\frac{f_2}{f_0}. \tag{3}$$

D. If the electric field gradient has an arbitrary symmetry and the direction of its z axis does not coincide with that of the symmetry axis of f(k), then

$$\frac{I_+}{I_-}\left(=\frac{I_{3/2}}{I_{1/2}}\right)=\frac{1+F_4}{1-F_4},$$

$$F_4=\left[\frac{1-A^2}{1+A^2}\frac{P_2(\cos\beta)}{P_0(\cos\beta)}+\frac{A\sqrt{3}}{1+A^2}\frac{\sin^2\beta\cos 2\alpha}{P_0(\cos\beta)}\right]\frac{1}{2\sqrt{5}}\frac{f_2}{f_0}. \tag{4}$$

The parameters f_2/f_0, which depend on the anisotropy f(k), can be calculated from the exact formulas given by Karyagin in[10]. For small values of the anisotropy, however, it is possible to use the following approximation. We limit the expansion of f(k) in spherical harmonics to second-order terms (i.e., in its own system, $f(k)=f_0P_0(\cos\theta)+\sqrt{5}f_2P_2(\cos\theta)$), and we introduce the characteristic of the anisotropy f(k):

$$\varepsilon=\frac{f_\parallel-f_\perp}{f_\parallel+f_\perp}=\frac{3\sqrt{5}f_2/f_0}{4+\sqrt{5}f_2/f_0},$$

where $f_\parallel$ and $f_\perp$ are the values of f in the directions parallel and perpendicular to the z axis of the f(k) system, i.e., $f_\parallel=f(\theta=0^\circ)$ and $f_\perp=f(\theta=90^\circ)$. It is clear that ϵ varies in the range $[-1,+1]$. Then formulas (1)–(4) are expressed in terms of ϵ as follows:

$$\frac{I_{3/2}}{I_{1/2}}=\frac{3-0{,}6\varepsilon}{3-1{,}4\varepsilon}, \tag{1'}$$

$$\frac{I_+}{I_-}=\frac{(3-\varepsilon)+F_2'}{(3-\varepsilon)-F_2'},\qquad F_2'=0{,}4\varepsilon\frac{1-A^2}{1+A^2}, \tag{2'}$$

$$\frac{I_{3/2}}{I_{1/2}}=\frac{(3-\varepsilon)+F_3'}{(3-\varepsilon)-F_3'},\qquad F_3'=0{,}4\varepsilon\frac{P_2(\cos\beta)}{P_0(\cos\beta)}, \tag{3'}$$

$$\frac{I_+}{I_-}\left(=\frac{I_{3/2}}{I_{1/2}}\right)=\frac{(3-\varepsilon)+F_4'}{(3-\varepsilon)-F_4'},$$

$$F_4'=0{,}4\varepsilon\left[\frac{1-A^2}{1+A^2}\frac{P_2(\cos\beta)}{P_0(\cos\beta)}+\frac{A\sqrt{3}}{1+A^2}\frac{\sin^2\beta\cos 2\alpha}{P_0(\cos\beta)}\right]. \tag{4'}$$

Our calculations have shown that the values of $I_{3/2}/I_{1/2}$ calculated from the approximate formulas (1′)–(4′) agree within 1% with the results of calculations in accordance with the exact formulas when ϵ lies in the range $[-0.5-0.7]$. This range corresponds to the most frequently encountered values of $f_\parallel/f_\perp$ $[0.3-5]$.

The authors are grateful to S. V. Karyagin for a discussion of the results.

[1]C. E. Violet, R. Booth, and F. Wooten, Phys. Lett. **5**, 230 (1963).
[2]R. N. Kuzmin, A. A. Opalenko, and V. S. Shpinel, Proc. of the Conf. on the Application of the Mossbauer Effect (Tihany, 1969), [Publ. by Hungarian Acad. Sci., 1971], p. 785.
[3]P. Boolchand, B. L. Robinson, and S. Jha, Phys. Rev. B **2**, 3463 (1970).
[4]E. P. Stepanov, K. P. Aleshin, R. A. Manapov, B. N. Sklyarevsky, and V. G. Stankevic, Phys. Lett. **6**, 155 (1963).
[5]G. Albanese, C. Lamborisio, and I. Ortalli, Nuovo Cimento B **50**, 65 (1967).
[6]C. E. Violet and R. Booth, Phys. Rev. **144**, 225 (1966).
[7]R. N. Kuz'min, A. A. Opalenko, V. S. Shpinel' and I. A. Avenarius, Zh. Eksp. Teor. Fiz. **56**, 167 (1969) [Sov. Phys.-JETP **29**, 94 (1969)].
[8]V. A. Lebedev, R. A. Lebedev, A. M. Babeshkin, and A. N. Nesmeyanov, Vestnik MGU, Seriya Khim. **3**, 128 (1969).
[9]I. N. Silin, JINR Preprint, 11-3362, Dubna, 1967.
[10]S. V. Karyagin, Dokl. Akad. Nauk SSSR **148**, 5 (1963); Dokl. Akad. Nauk SSSR **148**, 1102 (1963).
[11]G. Frauénfelder and R. Steffen, in Alpha, Beta, and Gamma Spectroscopy, ed. by K. Siegbahn, North Holland, 1966, Chap 19A, Sec. 4.
[12]A. Edmonds, CERN 55-26, Geneva, 1955.

Translated by J. G. Adashko
124