^{129}I nuclear quadrupole interaction in trigonal Te and the role of oxygen contamination

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^{129}I Mössbauer spectra of trigonal Te are shown to be sensitive to the presence of oxygen contamination of the starting enriched ^{128}Te metal used in these measurements. The oxygen is shown to be chemically bonded as a TeO_2 phase. Results on pure Te taken with a thin ^{129}INa absorber (15 mg/cm^2) yield, at 4.2 K, $e^2qQ = -397.4(1.7)$ MHz, $\eta = 0.70(1)$, $\delta = +1.16(1)$ mm/s, and $\Gamma_{obs} = 1.13(1)$mm/s.

I. INTRODUCTION

Since the discovery of the Mossbauer effect in ^{129}I, the nuclear quadrupole interaction in Te metal has been measured by several authors.[1-4] The lack of agreement between results of different measurements is particularly striking (see Table I). Equally important is the fact that analysis of observed Te metal spectra in terms of a twelve-line pattern characteristic of a pure nuclear quadrupole interaction for the $\frac{5}{2}^+ \rightarrow \frac{7}{2}^+$, 27.8-keV gamma resonance exhibits, in general, significant intensity misfits of the absorption peaks. The deviation of observed intensities from expected theoretical ones for the polycrystalline case (i.e., a purely random orientation of Te crystallites) can arise either due to an anisotropy of recoil-free fraction or the presence of some texture. In this paper we show that the intensity misfits we observe in our Te metal spectra are not due to either of the two causes cited above, but in fact arise from a substantial oxygen contamination of enriched ^{128}Te metal used as a starting material. On purifying the enriched ^{128}Te metal, we have succeeded in completely removing the intensity misfits alluded to above. The ^{129}I quadrupole coupling constant for a pure Te sample has been measured at 78 and 4.2 K.

II. EXPERIMENTAL CONSIDERATIONS AND DATA ANALYSIS

Enriched ^{128}Te (99.19%) in its elemental form, purchased from Oak Ridge National Laboratory, Oak Ridge, Tennessee was used as a starting material for the present investigations, and will henceforth be denoted as the virgin sample. Oxygen content of the virgin sample was established by a nuclear analysis involving fast neutron activation of ^{16}O by the reaction ^{16}O$(n, p)^{16}$N. The γ's from the short-lived (7.2 s) ^{16}N can be used to quantitatively detect as little as 75 μg of oxygen. The analysis revealed $2.7 \pm 0.07\%$ by weight of oxygen in the virgin sample. The measurement was performed commercially by Union Carbide Corporation, Tuxedo, New York.

Purification of the virgin sample was performed by encapsulating it in a 24-cm long evacuated quartz ampoule and heating it to 675 °C for 24 h while keeping the ampoule vertical. Examination of the ampoule at room temperature after an air quench revealed a bead of Te and a white coating of, presumably, TeO_2 on the inner wall. The coating existed over a 1-cm length from the bottom of the ampoule. The ampoule was inverted and placed in the furnace at 525 °C allowing the Te bead to fall to the far end. The length of the evac-

TABLE I. ^{129}I Mossbauer parameters of crystalline Te reported by various authors. The isomer shift δ are quoted relative to ^{129}INa.

T (K)	e^2qQ (MHz)	η	δ	Authors
80	−373(6)	0.80(5)	+1.15(5)	Pasternak and Bukshpan (1967)
80	−349(11)	0.69(3)	+0.94(3)	Warren *et al.* (1971)
80	−406(6)	0.73(2)	+1.18(4)	Langouche *et al.* (1974)
4.2	−403(4)	0.73(2)	+1.19(3)	Langouche *et al.* (1974)
4.2	−396(3)	0.69(2)	+1.26(3)	Kim and Boolchand (1979)
78	−387.5(2.1)	0.74(2)	+1.17(1)	Present work
4.2	−397.4(1.7)	0.70(1)	+1.16(1)	Present work

uated ampule was shortened by 4 cm from the oxide coated end by resealing the Te bead in the clean segment of the ampule and heated again to 525 °C. This process was repeated twice on this same ampule, at the end of which a clear shiny bead of Te exhibiting metallic luster was obtained.

10-mg quantities of enriched ^{128}Te samples both of the virgin and purified materials were encapsulated in evacuated suprasil ampules. The encapsulated samples were neutron activated at the University of Missouri research reactor facility, to produce the 33-day ^{129m}Te Mossbauer parent nucleide. The irradiation was carried out for a 2-week period at a 2×10^{14} neutron flux. Low-temperature Mossbauer spectra of the ^{129m}Te sources were recorded at 78 and 4.2 K using an exchange gas Dewar.[4] Care was taken to finely powder the activated Te metal before mounting the source material in between masking tape. The constant acceleration drive was calibrated using the Zeeman splitting of ^{57}Co-Fe source against a metallic Fe foil absorber. The quadrupole coupling, asymmetry parameter, and isomer shift (e^2qQ, η, and δ) parameters were extracted from the spectra as follows. Spectra were analyzed[4] as a superposition of 12 resonance lines (one chemical site) or where appropriate in terms of 24 resonance lines (two chemically inequivalent sites) keeping the relative line positions and relative line intensities of a given chemical site constrained to a polynomial[5] in η. The ratio of the quadrupole moment Q^*/Q was kept fixed at 1.238 (Ref. 6). In the two-site analysis, as an option, the parameters of one of the sites could be constrained to a predetermined value.

III. RESULTS AND DISCUSSION

A. Quadrupole coupling in pure Te

The most striking feature of the ^{129}I spectra of Te metal observed (see Fig. 1) is the clear difference in intensity of the two prominent absorption peaks between the virgin [spectrum (a)] and pure sample [spectrum (c)]: The intensity asymmetry present in the virgin sample is found to completely disappear in the pure sample. Secondly, the intensity of the two less prominent outer absorption peaks observed in these spectra shows a more subtle difference between the virgin and pure sample: These peaks are noticeably narrower and smaller in intensity in the pure sample [compare spectrum (a) to (c)]. In fact, analysis of the pure Te sample spectrum (c) in terms of one chemical site provides an excellent fit to the data. An equally good fit to the data of the pure sample, taken at 78 K, is possible in terms of one site. The results of these mea-
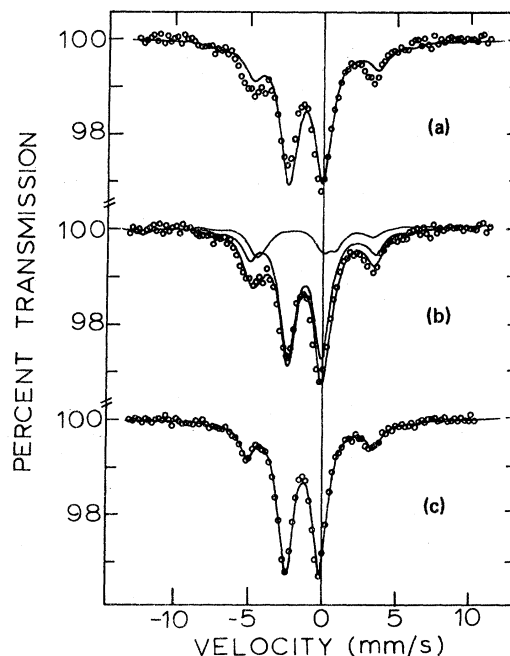

FIG. 1. ^{129}I Mossbauer spectra of ^{129m}Te sources in Te metal taken at 4.2 K: (a) virgin Te metal spectrum fit to one site, (b) virgin Te metal spectrum fit to two sites, (c) pure Te metal fit to one site. Results of spectral analysis appear in Table II.

surements summarized in Table II show that e^2qQ at 78 K is about 2% smaller than at 4.2 K. The observed linewidths for the pure Te sample are the narrowest observed to date and appear to be accountable in terms of the minimum observable linewidth $2\Gamma = 0.58(1)$ mm/s and the finite thickness of the anhydrous Na^{129}I absorber.

B. Virgin Te sample and the chemical state oxygen

The excellent fit of the pure Te spectrum [Fig. 1(c)] to one site clearly suggests that anisotropy of recoil-free fraction is not intrinsic to Te, and therefore such a mechanism is not responsible for the intensity misfits in the absorption peaks of the virgin sample; further, since both the virgin and pure Te samples were powdered and mounted in the same way, it is unlikely that texture of the two samples are any different. Clearly then, the intensity misfits in the virgin sample spectrum cannot be due to some degree of partial orientation of Te crystallites in the source. The possibility of an additional, chemically inequivalent ^{129}I site must be considered. We have analyzed the spectrum of the virgin sample [Fig. 1(a)], in terms of two chemically inequivalent ^{129}I sites in a number of ways. On constraining the e^2qQ, η, and δ values of one of

TABLE II. ^{129}I Mossbauer parameters of crystalline Te extracted from spectra of Fig. 1.

^{129m}Te (Te metal) source	T (K)	e^2qQ (MHz)	δ [a] (mm/s)	η	Γ_{obs} (mm/s)
Virgin sample (one-site fit)	4.2	−402.5(2.5)	1.14(1)	0.70(2)	1.36(2)
Virgin sample (two-site fit)	4.2	−397.4 [b]	1.16 [b]	0.70 [b]	1.24(3)
		+810.0(2)	2.50(4)	0.31(3)	1.24(3)
Purified sample	78	−387.5(2.1)	1.17(1)	0.74(2)	0.96(2)
Purified sample	4.2	−397.4(1.7)	1.16(1)	0.70(1)	1.13(2)

[a] Isomer shifts are quoted relative to anhydrous ^{129}INa.

[b] Parameters kept fixed in the fit.

these sites to the ones established for pure Te and permitting the second site to choose its best-fit value, we obtained the fit shown in Fig. 1(b). Both + and $-e^2qQ$ values for the second site were tried, and a decidedly superior fit to the data was possible under the assumption of a $+e^2qQ$. Interestingly, the e^2qQ value of the second site in the virgin Te sample falls quite close to the one known[7] for the tetragonal modification of TeO_2 (see Table III).

From the analysis of spectrum (b) in Fig. 1, we find that the intensity ratio $I_2(TeO_2)/I_1(Te)$ = 0.25(4). Site intensities observed in Mossbauer experiments are related to the site populations through the recoil-free fractions as follows:

$$\frac{I_2}{I_1} = \frac{N_2}{N_1}\frac{f_2}{f_1} .$$

There is good evidence that the "f" factor in TeO_2 is significantly larger than in Te metal (i.e., $f_2 > f_1$). A comparison[6] of tetragonal TeO_2 spectrum with Te metal spectrum, both taken at the same temperature of 80 K, with the same absorber, shows that the size of the effect in the former host is nearly twice as large as in the latter host, thus suggesting $f_2/f_1 \cong 2$. We therefore estimate N_2/N_1, the population of TeO_2 phase to Te phase in the virgin Te sample, to be 0.13(3). Indeed, if all the oxygen in the virgin Te sample is assumed to be chemically bonded as TeO_2, then based on the measured oxygen weight percent

TABLE III. ^{129}I Mossbauer parameters of indicated hosts. The isomer shifts are quoted relative to ^{129}INa. The parameters of the TeO_2 polymorphs are taken from Ref. 7.

Host	e^2qQ (MHz)	η	δ (mm/s)
2nd site in virgin Te sample	+810(10)	0.31(3)	2.50(4)
Tetragonal TeO_2	+812(21)	0.52(7)	3.21(14)
Orthorhombic TeO_2	+786(7)	0.55(5)	1.98(1)

of 2.74(7) one can calculate the amount of the TeO_2 phase present. This calculation gives TeO_2/Te to be 0.11(2) in reasonable agreement to the Mossbauer data.

The solubility of oxygen in liquid Te has been measured[8] and found to be 2.2×10^{-3} at. % at the melting point. Based on the present work, it appears to us that the solubility of oxygen in crystalline Te is actually quite small, as one would expect.

C. General implications

The present results bear directly on ^{129}I Mossbauer experiments that utilize alloying trace amounts of neutron activated enriched ^{128}Te metal in other hosts such as chalcogenide glasses, magnetic materials, etc. We have, during the course of our investigations on chalcogenide glasses, observed the contaminant TeO_2 phase of the starting material in spectra of the glasses.

The presence of oxygen contamination of other enriched Te isotopes such as ^{124}Te and ^{125}Te supplied by Oak Ridge National Laboratory cannot be ruled out. Unfortunately, it is difficult to infer the presence of the contaminant TeO_2 phase in enriched ^{125}Te metal since the isomer shift and quadrupole splitting of both the TeO_2 phases and Te metal are known[1,2] to be nearly the same. The lack of complete agreement on ^{125}Te isomer shifts and quadrupole splittings on a variety of Te compounds could be related to sample purity. Oxygen, isoelectronic to Te, has strong affinity for Te and is a natural and likely candidate for contamination of Te compounds.

ACKNOWLEDGMENTS

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