Decay of Tc^{97} Ground State*

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The half-life of the ground state of Tc^{97} was found to be $(2.6\pm0.4)\times10^6$ years by comparison of its K x-ray intensity with that from the 90-day Tc^{97m} isomeric state. The L/K-capture ratio of Tc^{97} was compared with that of Tc^{96}; a somewhat larger ratio is indicated for the former. No γ rays were observed that could be attributed to Tc^{97}. The relation of these results to the occurrence of technetium in certain stars and to its possible occurrence in the earth's crust is discussed. Improved measurements of the Tc^{98} γ-ray energies yielded values of 669 ± 5 kev and 769 ± 6 kev.

INTRODUCTION

THE discovery of the optical spectrum of technetium in S-type stars by Merrill[1] in 1952 stimulated new interest and new research in several different directions. First, the question arose as to whether the technetium spectrum observed in the stars might be from an isotope whose half-life is long enough ($>2\times10^8$ years) to have existed since primordial element formation about 5×10^9 years ago. In 1952 the longest lived Tc isotope known was the 2.1×10^5-year Tc^{99}. The ground states of Tc^{97} and Tc^{98} were unknown, but it was suspected that these might be very long-lived. Efforts were intensified to produce these two isotopes by cyclotron and pile irradiations and to measure their nuclear properties.[2–4] Second, if one or both of these isotopes were very long-lived ($>2\times10^8$ yr), it should be possible to find some terrestrial and meteoritic technetium. Therefore efforts in this direction also were intensified.[5–9] Finally, if no very long-lived Tc isotope should exist, then the observed stellar technetium must be an indicator of recent element formation in certain types of stars. Several astrophysical theories have been proposed[10–14] which describe nucleogenesis of medium and heavy elements in these stars. The current status of these problems will be reviewed below in the Discussion.

The present investigation, which was begun in 1952, is mainly concerned with a measurement of the half-life of the Tc^{97} ground state.

HALF-LIFE MEASUREMENT

The two isomeric states of Tc^{97} were prepared by neutron irradiation of 2 g of natural ruthenium metal in the Materials Testing Reactor in Idaho ($\sim2\times10^{21}$ neutrons/cm^2). The method of chemical separation and purification was similar to that described elsewhere.[15] The 2.88-day Ru^{97} formed from Ru^{96} by neutron capture decays to both Tc isomers according to the scheme shown in Fig. 1. The upper limit of 3% on the fraction of 90-day Tc^{97m} which might decay by orbital electron capture was established by critical absorption measurements (Fig. 2). Molybdenum K x-rays were observed from the Tc^{97} ground state decay, but the 90-day isomer showed only Tc K x-rays. No γ rays were observed from Tc^{97}.

The half-life of the ground state was found by comparing its activity with that of the 90-day metastable state at the end of irradiation. The following equation was used:

$$\lambda_2=0.00041A_2(1-e^{-\lambda_1\tau})/(A_1{}^0\tau), \qquad (1)$$

where A_2 is the activity of the Tc^{97} ground state after decay of the 90-day Tc^{97m}; $A_1{}^0$ is the activity of the latter at the end of a bombardment of duration τ; 0.00041 is the fraction of 2.88-day Ru^{97} which decays to 90-day Tc^{97m}; and λ_1 and λ_2 are the disintegration constants of Tc^{97m} and Tc^{97}, respectively. It was assumed that the ratio of Tc^{97m} to Tc^{97} was not appreciably affected by their capture of neutrons during the irradiation. This assumption is valid if the (n,γ) cross sections of both isomers are less than 100 barns, or if these cross sections are approximately equal.

Both activities, $A_1{}^0$ and A_2 were measured by means of the K x-rays. The 90-day isomer decays by a highly

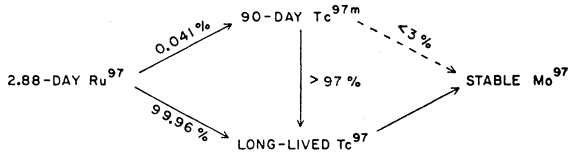

FIG. 1. Decay scheme of Ru^{97}.

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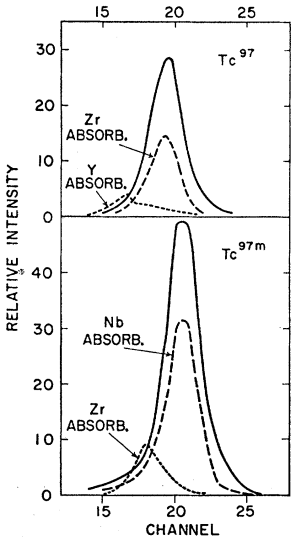

FIG. 2. The K x-rays of Tc^{97} and Tc^{97m} observed without absorbers and with ~27 mg/cm² of Y, Zr, and Nb. Zirconium is a critical absorber for Tc K x-rays and Y is critical for Mo K x-rays.

converted (>99%) isomeric transition[2] to the ground state; corrections were applied for L and M shell conversion, for the Tc K x-ray fluorescence yield, and for the fraction of the 18.4-kev K x-rays absorbed in the counter gas (see Table I). The Mo K x-ray intensity observed from the decay of Tc^{97} was corrected for L-capture (see below), Mo K x-ray fluorescence yield, and for the fraction of the 17.5-kev K x-rays absorbed in the counter gas (Table I). The decay of the K x-ray activity was measured with a 4-in. diameter, 2-atmosphere argon filled, thin beryllium window proportional counter connected to a single-channel analyzer. The first count was taken 11 months after the end of the irradiation; decay of the 90-day period was observed during the following 3 years; and then no further decay could be detected in the course of another year. A similar result was obtained when the total activity was followed with a small end-window proportional counter. From Eq. (1) and the data of Table I a value of $(2.6\pm0.4)\times10^6$ years was calculated for the half-life of the Tc^{97} ground state. The error results mainly from uncertainty in the Ru^{97} branching ratio and in the fraction of Tc^{97} decaying by K capture. The only previous determination[2] of this half-life gave an estimate of 10^4–10^5 years, but this was based on an estimate of considerable uncertainty in the relative yields of Tc^{97m} and Tc^{97} produced by deuteron irradiation of molybdenum.

L/K-CAPTURE RATIO

For allowed transitions the ratio of L capture to K capture is given by

$$P_L/P_K=(\psi_L/\psi_K)^2[(W-W_L)/(W-W_K)]^2, \quad (2)$$

where P_L and P_K are the probabilities of L and K capture, respectively; $(\psi_L/\psi_K)^2$ is the ratio of electron densities for the L and K shells at the nuclear radius;

TABLE I. Data for calculating half-life of Tc^{97}.

Irradiation time, τ	134 days
Obs. K x-rays of Tc^{97m} adjusted to end of bombardment	3.84×10^5 counts/min
Correction factor[a] for $L+M$ conversion in Tc^{97m}	1.61
K fluorescence yield,[b] Tc	0.78
Fraction of incident Tc K x-rays absorbed by counter gas	0.300
Corrected 90-day Tc^{97m} activity, $A_1{}^0$	2.64×10^6 counts/min
Obs. Mo K x-rays of Tc^{97} 1700 days after end of bombardment	212 counts/min
Correction factor[c] for L capture	1.205
K fluorescence yield,[b] Mo	0.77
Fraction of incident Mo K x-rays absorbed by counter gas	0.335
Corrected Tc^{97} activity, A_2	990 counts/min
Half-life of Tc^{97}, $0.693/\lambda_2$	$(2.6\pm0.4)\times10^6$ yr

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[b] Broyles, Thomas, and Haynes, Phys. Rev. **89**, 715 (1953).
[c] See section below on L/K-capture ratio.

W is the disintegration energy; W_L and W_K are the binding energies of the L and K electrons, respectively. When $W\gg W_K$, which is usually the case, the factor in square brackets is very nearly unity and Eq. (2) holds even for forbidden transitions. The ratio of electron densities as a function of atomic number is given by Rose and Jackson.[16]

For Tc^{97} the transition is second forbidden $(g_{9/2}-d_{5/2})$ and the disintegration energy is unknown. Estimates based on nuclear systematics[17,18] indicate that W may not be large compared with the K-shell binding energy of 20 kev. Therefore, an experimental determination of the L/K-capture ratio was made by comparison with the corresponding ratio from 4.2-day Tc^{96}. For this isotope it is expected that the ratio will be given by $(\psi_L/\psi_K)^2$, 0.107 according to Rose and Jackson,[16] since[19] $W\gg W_K$.

The measurements are complicated by the fact that L-shell vacancies are produced by the filling of K-shell vacancies as well as by L capture; and usually the former effect is about ten times the latter.[20] An added difficulty results from possible self absorption of the low-energy (2.3-kev) L x-rays. These complications were minimized by use of a mixed source of 4.2-day Tc^{96} and long-lived Tc^{97}. The Tc^{96} was made by an (α,n) reaction from Nb which was irradiated with 14-Mev α particles. It was chemically separated and purified, and then mixed with[21] some Tc^{97}. The isotopes were precipitated together as the sulfide with 150 μg of CuS, mounted on a stainless steel disk, and covered with ~15 μg/cm² of plastic plus ~10 μg/cm² of gold. The

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[21] The sample also contained some Tc^{98} and Tc^{99}. These interfered somewhat with the measurements as described below.

TABLE II. Intensity of K and L x-rays from Tc^{96} and Tc^{97}. % Tc^{97} = 100 − % Tc^{96}. I_K and I_L are given in counts per minute.

% Tc^{96}	I_K	I_L	I_K/I_L	% Tc^{96}	I_K	I_L	I_K/I_L	% Tc^{96}	I_K	I_L	I_K/I_L
97	2520	527	4.79	51	149	35.6	4.20	10	90.0	19.5	4.61
96	2190	471	4.65	37	99	27.3	3.64	4	72.8	17.8	4.09
96	1924	406	4.74					0	79.4	17.1	4.63
91	741	188	3.94					0	63.0	16.8	3.75
								0	65.7	18.3	3.59
								0	64.8	16.5	3.93
		Average	4.5±0.2							Average	4.1±0.3

source was placed inside a 3-in. diameter proportional counter filled with one atmosphere P-10 gas. Initially, the 4.2-day Tc^{96} intensity was 97% of the total. The relative intensities of the K and L peaks were measured with a PENCO 100-channel analyzer as a function of time. After decay of the Tc^{96}, the 0.3-Mev β rays from the Tc^{98} and Tc^{99} present in the source[21] produced a significant background (about $\frac{1}{3}$ of the K peak height) in the energy region of interest. This background was simulated with some Co^{60} (0.31-Mev β's) mounted in the same way as the Tc. Appropriate subtractions were made from the Tc activities in each channel, but this correction introduced another source of error. Table II gives the ratios of K x-ray intensity to L x-ray intensity derived from the corrected data.

The observed K/L ratio from the first four measurements, when the activity was nearly all Tc^{96}, is 4.5±0.2. The ratio from the last six measurements, when the x-ray activity was nearly all Tc^{97}, is 4.1±0.3. A smaller ratio is indicated for Tc^{97} than for Tc^{96} but the difference is not outside of experimental error. From these observed ratios of peak intensities it is possible to calculate P_L and P_K for Tc^{97}. For the observed intensity, I_K, of K x-rays we have

$$I_K = DP_K\omega_K\epsilon_K, \tag{3}$$

where D is the disintegration rate, ω_K is the K fluorescence yield, and ϵ_K is the detection efficiency of the counter for K x-rays. The observed intensity of L x-rays is given by

$$I_L = D\omega_L\epsilon_L(P_L + 0.9\times 0.99P_K), \tag{4}$$

where the first term arises from L capture and the second term is for L x-rays which follow K capture. The factor 0.99 gives the number of L vacancies produced[20] in the filling of a K vacancy in Mo; the factor 0.9 corrects for the L x-rays lost from the L peak by addition to K radiation which may be absorbed simultaneously in the counter gas. By substituting $P_L \approx 1 - P_K$ and dividing (3) by (4), we obtain

$$\frac{I_K}{I_L} = \frac{P_K\epsilon_K\omega_K}{(1-0.109P_K)\epsilon_L\omega_L}. \tag{5}$$

In the limit, when $W \gg W_K$, $P_K = 0.903$, and

$$\left(\frac{I_K}{I_L}\right)_{\text{lim}} = \frac{\epsilon_K\omega_K}{\epsilon_L\omega_L}. \tag{6}$$

Substituting (6) into (5) and solving for P_K, we have

$$P_K = \frac{(I_K/I_L)}{(I_K/I_L)_{\text{lim}} + 0.109(I_K/I_L)}. \tag{7}$$

For $(I_K/I_L)_{\text{lim}}$ we use the observed ratio for Tc^{96}, 4.5±0.2; for (I_K/I_L) we use the observed ratio for Tc^{97}, 4.1±0.3. Thus, for Tc^{97},

$$P_K = 0.83_{-0.09}{}^{+0.07}; \quad P_L = 0.17_{-0.07}{}^{+0.09};$$
$$P_L/P_K = 0.21_{-0.10}{}^{+0.14}.$$

It should be noted that Eq. (7) is independent of the L fluorescence yield, and that it is not very sensitive to the uncertainties in the numerical factors introduced in Eq. (4). Although Tc^{97} decays by a second forbidden transition and Eq. (2) cannot be applied, there is an indication that W may not greatly exceed W_K (=20 kev) since it is indicated that P_L/P_K is greater than the limiting value of 0.107.

GAMMA RAYS FROM Tc^{98}

While searching for possible Tc^{97} γ rays, improved measurements[4] were made on the γ spectrum from Tc^{98}. The radiation was detected with a 3-in.×3-in. NaI crystal and the pulse-height distribution was recorded with a PENCO 100-channel analyzer. The sample was placed close to the crystal so that an addition peak from the two coincident γ rays[4] would be observed as well as the two individual photopeaks. By comparison with the Co^{60} γ ray at 1.332 Mev the addition peak was found to be at 1.438±0.010 Mev. Since the energy ratio of the individual photopeaks was measured as 1.148±0.003, the two γ-ray energies are 669±5 kev and 769±6 kev. The lower energy γ ray was also observed to have the same energy as the 662-kev γ ray from Cs^{137}, within the experimental error of ±8 kev. These data were all taken at low counting rates (<200 counts/sec) to minimize any possible dependence of peak position on counting rate.

DISCUSSION

The ground state of Tc^{97} has the longest half-life of any technetium isotope. The half-lives of Tc^{98} and Tc^{99} are 1.5×10^6 years[22] and 2.1×10^5 years,[19] respectively. However, even the Tc^{97} period, 2.6×10^6 years, is at least 100 times too short to account for survival of "primordial" technetium in the earth's crust. The most recent geochemical investigations[9,23] do not support earlier reports[5–8] of terrestrial technetium. Thus both the nuclear physical and geochemical evidence indicate that the technetium observed[1,24] in late-type stars must have been formed within the last few million years.[25] Evidently conditions must exist in these stars for the synthesis of medium weight elements and for bringing them to the surface in a time comparable with the longest half-lives of the Tc produced.

In a recent elaboration[14] of a theory of nucleogenesis an attempt has been made to explain the abundance distribution of the elements. It is suggested that all of the elements have been synthesized in stars by a series of eight different processes starting with hydrogen as the only primeval element. One of these eight, called the "*s* process" (neutron capture at a *slow* rate compared to the beta lifetimes), accounts for the production of a considerable proportion of the isotopes of elements from Cu to Bi. This process occurs during the red giant stage of stellar evolution when the hydrogen in the core has already been exhausted, when the central temperature has reached $\sim10^8$ degrees, and when much of the helium has been converted to C^{12} by $3He^4\rightarrow C^{12}$. Considerable C^{13} and Ne^{21} are also present, having been produced by (p,γ) and (α,γ) reactions. The exothermic reactions $C^{13}(\alpha,n)O^{16}$ and $Ne^{21}(\alpha,n)Mg^{24}$ then provide an intense source of neutrons. These are captured by the iron group elements to produce heavier elements. Abundance peaks are produced at mass numbers 90, 138, and 208 because the neutron cross sections are low at the neutron magic numbers 50, 82, and 126. Three groups of stars (S, Ba II, and carbon) show direct evidence of the *s* process since they have overabundances of the heavier elements, especially those with neutron magic numbers. The S stars and carbon stars also contain Tc and thus they indicate that both synthesis and mixing is taking place now or at least within the last few million years. Synthesis by the *s* process can produce Tc^{99} from Mo^{98}, Tc^{97} from Ru^{96}, and Tc^{98} from Tc^{97}. Since Mo^{98} can itself be produced by the *s* process while Ru^{96} cannot, the initial abundance of Tc^{99} is likely to be considerably greater than that of Tc^{97} (and of Tc^{98}). However, Tc^{97} can persist in stars for a much longer time after the neutron capture process has ceased because its half-life is about 12 times that of Tc^{99}.

Technetium-99 can also be produced in stars by the "*r* process,"[14] neutron capture at a *rapid* rate compared to the beta decay lifetimes. This is thought to occur in supernovae. If it should prove possible to identify the spectrum of Tc in the remnants of recent supernovae, such as the Crab Nebula, this would constitute direct evidence for the "*r* process." Of course, even better evidence would be the identification of transuranium elements in these residues.

An alternative mechanism for production of Tc in stars has been proposed by Greenstein.[10] He has postulated that variable magnetic fields in the atmosphere of certain stars can accelerate protons, which would interact with light elements by (p,n) reactions. The resulting neutrons could then produce Tc from Mo in the following cycle:

$$Mo^{98}(n,\gamma)Mo^{99}(\beta^-,\nu)Tc^{99}(\beta^-,\nu)Ru^{99}\text{-}$$
$$(n,\alpha)Mo^{96}(n,\gamma)Mo^{97}(n,\gamma)Mo^{98}.$$

Additional cycles such as the following might also occur:

$$Ru^{98}(n,p)Tc^{98}(\beta^-,\nu)Ru^{98},$$
$$Mo^{97}(p,n)Tc^{97}(K,\nu)Mo^{97}.$$

Mechanisms involving such reactions in the stellar surface require that there by very little mixing between the stars' atmospheres and their interiors, since otherwise it would not be possible to build up an appreciable concentration of Tc.

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[24] P. W. Merrill and J. L. Greenstein, Astrophys. J. Suppl. II, 225 (1956).
[25] One cannot completely rule out the possibility that there might exist a very long-lived isomeric state whose half-life is $>2\times10^8$ years.

ACKNOWLEDGMENTS

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