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Change in the Decay Constant of ^{99m}Tc in BaTiO$_3$ by the Ferroelectric Transition

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The $BaTiO_3$ ceramic samples were prepared by sintering mixtures of $BaCO_3$, TiO_2, and $Na^{99m}TcO_4$ at 1400 °C. In these samples ^{99m}Tc atoms are located at the lattice site of the Ti atoms in the $BaTiO_3$ crystals, where an intense internal electric field acts. The relative change in the decay rate of the 2.17-keV $E3$ isomeric transition of ^{99m}Tc embedded in $BaTiO_3$ in the ferroelectric state (at room temperature) and the paraelectric state (at 170 °C) was measured. The result obtained is $\lambda[\mathrm{BaTi(^{99m}Tc)O_3}$ in paraelectric state$] - \lambda[\mathrm{BaTi(^{99m}Tc)O_3}$ in ferroelectric state$] = (2.6 \pm 0.4) \times 10^{-3} \lambda[\mathrm{BaTi(^{99m}Tc)O_3}$ in ferroelectric state$]$. Statistics and errors of the measurement are discussed. It is reasonable to conclude that the main contribution to the observed effect comes from a change in the $4p$ electron density near the nucleus caused by the influence of the internal electric field in $BaTiO_3$.

The decay rate of the 2.17-keV $E3$ isomeric transition of ^{99m}Tc ($T_{1/2} = 6.04$ h) through internal conversion in outer shells has been shown to be altered slightly by changes in the external environment, by chemical,[1] superconductivity,[2] and high-hydrostatic-pressure effects.[3-5] The changes in the decay rate are attributed to changes in the electron density at the nucleus imposed by these external effects. The imposition on ^{99m}Tc atoms of a strong internal electric field in a ferroelectric substance may provide such an external environmental influence on the decay rate of ^{99m}Tc. Recently, a change in the lifetime of ^{89}Zr due to the influence of the internal electric field in $BaTiO_3$ has been investigated by Huber *et al.*[6,7] The work presented in this paper was undertaken to observe a change in the decay constant of ^{99m}Tc embedded at the site of the Ti ion of this ferroelectric substance. The $BaTiO_3$ lattice is tetragonal and spontaneously polarized at room temperature, while above the Curie temperature, $T_c = 120$ °C, the lattice becomes cubic and the spontaneous polarization disappears. This fact means that the internal electric field at the site of the Ti ion in the ferroelectric phase can be eliminated by heating the sample above T_c. The idea of the present experiment lies in comparing the lifetimes of ^{99m}Tc in these two lattice states of $BaTiO_3$.

The $BaTi(^{99m}Tc)O_3$ ceramic samples (10-mm diam × 2 mm thick) were prepared by sintering mixtures of $BaCO_3$, TiO_2, and $Na^{99m}TcO_4$ at 1400 °C for about 10 min, followed by quenching at room temperature. Such a short time was chosen for sintering, because ^{99m}Tc is apt to escape from the samples during the process. The $Na^{99m}TcO_4$ solution was obtained by milking a commercial generator containing the longer-lived parent ^{99}Mo. Measurements of γ-ray spectra showed that the solution thus obtained was free from radioactive impurities. The ferroelectric properties of the samples prepared were examined by their spontaneous polarization using the Sawyer-Tower method[8] as well as by x-ray diffraction analysis of their lattice structure. The spontaneous polarization was found to be about 2 μC/cm^2, smaller than that for good $BaTiO_3$ ceramics (~ 5 μC/cm^2); but no anomaly was observed in the x-ray diffraction pattern of the samples. The rather small polarization observed may be due to the porosity in them. From the ionic radius of the Tc ion,[9] ^{99m}Tc is believed to be located probably at the site of the Ti ion, where an electric field of about 10^8 V/cm acts in the ferroelectric state of the sample.[10]

The experimental method used in the present work is, as is usually the case, based on the differential method. We measured the 140-keV γ rays immediately following the isomeric transition concerned. The measuring system is shown schematically in Fig. 1. The gains of two identical NaI(Tl) scintillation detectors were set almost equal by adjusting the applied voltages to the photomultipliers (Toshiba 7696). During the measurement, one of the samples was kept at about 170 °C by electric heating and the other at room temperature. The anode currents of both photomultipliers were fed to a high-input-impedance differential amplifier. The output was measured by a digital voltmeter as a function of time. A recorder was also used to monitor the performance of the whole measuring system.

The decay constants of ^{99m}Tc in samples in the ferroelectric (room temperature) and paraelectric (170 °C) states are assumed to be λ and $\lambda + \Delta\lambda$, respectively. If the offset voltage of the differential amplifier is almost compensated, the output voltage is given by

$$v_{fp}(t) = G(i_f e^{-\lambda t} - i_p e^{-(\lambda+\Delta\lambda)t} + i_d). \qquad (1)$$

Here G is a conversion factor of the differential amplifier from the input current to the output voltage, and can be given by $G = Rg$ as described later, where R is the value of the resistor in the first stage (current comparator; see Fig. 1) and g is the voltage gain of the second stage of the amplifier. i_f and i_p are the anode currents of the photomultipliers at $t = 0$, corresponding to the measured γ-ray intensities from samples in the ferroelectric and paraelectric states, respectively, and i_d is the difference in the dark currents of the photomultipliers. In order to reduce a contribution of i_d, we selected out of 20 photomultipliers a pair having smaller dark currents of almost equal magnitude. However, since the strict compensation of the dark current was not achieved, measurements using two samples (designated as $f1$ and $f2$) in the same lattice state, i.e., of the ferroelectric phase, were performed before and/or after each run of measurements of $v_{fp}(t)$. The output voltage in this case is given by

$$v_{ff}(t) = G[(i_{f1} - i_{f2})\, e^{-\lambda t} + i_d]\ . \tag{2}$$

If we choose the value of t in this equation to be the same as t in Eq. (1), from these two equations we can obtain the following expression:

$$V_{fp}(t)\, e^{\lambda t} = G(i_f - i_p - i_{f1} + i_{f2}) + G i_p \Delta\lambda t\ , \tag{3}$$

where $V_{fp}(t) = v_{fp}(t) - v_{ff}(t)$. From the slope of a least-squares line of observed values $V_{fp}(t)e^{\lambda t}$, the value of $\Delta\lambda$ can be estimated, provided we use the known values of λ and G, and the initial current i_p from the photomultiplier with the paraelectric sample.

As a numerical value of λ we adopted that measured by Bainbridge *et al.*[1] with metallic technetium: $\lambda(^{99m}\mathrm{Tc}) = 0.1148\ \mathrm{h}^{-1}$. The conversion factor of the differential amplifier G, and i_p in Eq. (3) were estimated by the following procedure. As shown in Fig. 1, the first stage of the amplifier acts as a current comparator and the output voltage from this stage is given by $R(i_1 - i_2)$, where R ($=10^6\ \Omega \pm 1\%$) is a value of the feedback resistors and i_1 and i_2 are currents through these resistors. Since the input bias current in this circuit is of the order of 10^{-12} A, i_1 and i_2 can be treated as being the same as the input currents from the photomultipliers. Therefore, by measuring the output voltage of the first stage, provided that either of the input currents is set at zero, the initial value of the input current can be measured. Applying this procedure to the input current from the photomultiplier for a paraelectric sample, we could estimate a value of i_p for each measurement of $v_{fp}(t)$. The voltage gain g of the second stage of the amplifier was measured independently as $g = 22.3 \pm 0.5$ by the use of a mercury cell and a variable resistor. From g and R, the factor G could be estimated as $(2.23 \pm 0.07) \times 10^7\ \Omega$.

In the present work the stability of the whole system was crucial to the success of the experiment. Since the scintillation efficiency of the NaI (Tl) crystal depends on its temperature, we had to take special precautions against this effect. In the course of the measurement of $v_{ff}(t)$, the temperature of the crystals could be maintained constant within ±0.5 °C. However, in the case of $v_{fp}(t)$, one sample was heated up to about 170 °C to make it paraelectric state. The surface temperature of the NaI(Tl) crystal for this sample was observed to rise by about 4 °C in the period of 3 h after switching on the heater of the sample. This rise resulted in an unfavorable effect on the values of $v_{fp}(t)$. To correct for this rise its effect was examined carefully by the use of a pair of ^{57}Co sources, one of which was heated by a device similar to that used in the actual experiment. The output of the differential amplifier was found to be stable about 3 h after initiation of the heating. The minute change in the measurement geometry due to the thermal expansion of the sample holder was examined and found to be negligibly small as long as temperature of the holder was kept at (170 ± 10) °C. In the course of actual measurements of $v_{fp}(t)$, fluctuation of the temperature was within ±1.5 °C at 170 °C.

Another vital factor was the stability of gains of the photomultipliers used. Troubles due to the gain drift caused by the small fluctuation of the applied voltage could be eliminated by setting the gains of both phototubes equal. The temperature dependence of the sensitivity of photocathodes and dynodes was found to be negligible in the present

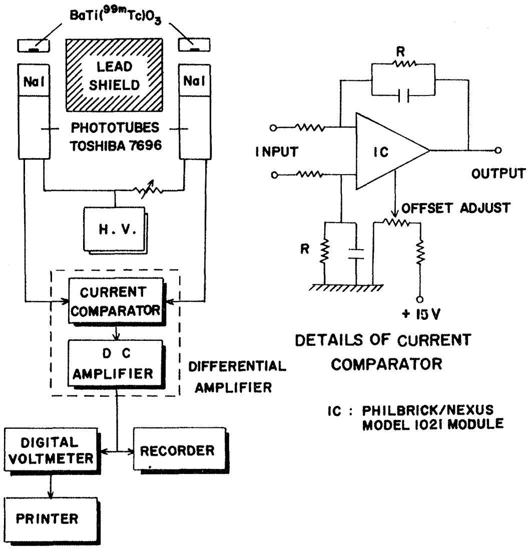

FIG. 1. Block diagram of the measuring system. The differential amplifier is composed of a current comparator and a dc amplifier. The feedback resistor in the current comparator is shown by R.

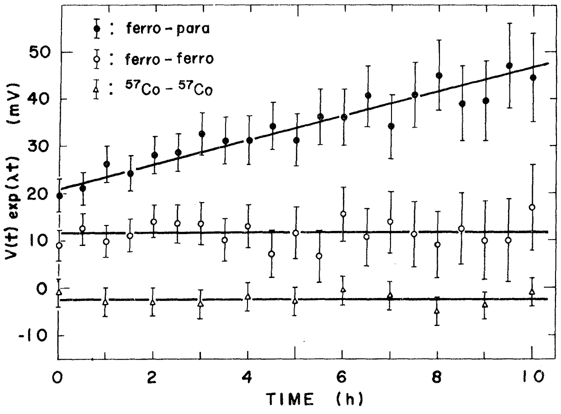

FIG. 2. Typical set of measured $V_{fp}(t)\,e^{\lambda t}$ and $V(t)\,e^{\lambda t}$. Two horizontal lines, $V(t)\,e^{\lambda t}$ obtained using the ferroelectric samples and using two ^{57}Co sources, were used for the stability test of the measuring system.

experiment. A troublesome problem encountered was the fatigue characteristic of the photomultiplier, which depends on anode current, temperature, and past history. The tubes selected for the present work were examined carefully to determine the dependence of their fatigue effects on the intensity of γ rays to be measured and on the applied voltage. The fatigue effect was observed to be greater for γ-ray intensities, yielding more than a few-μA anode current. Relatively low applied voltage was found to reduce fatigue effects to acceptable values.

By these careful examinations of experimental conditions, we decided to apply -640 ± 1 V to both photomultipliers, to adjust the source intensities of both samples so as to give about 0.5 μA at $t=0$ for the measurements of $v_{fp}(t)$ and $v_{ff}(t)$, and to start each run of measurements of $v_{fp}(t)$ 3 h after the heater for the paraelectric sample was switched on. In Fig. 2 a horizontal line is shown as the result of the stability test of the system obtained using two ^{57}Co sources with intensities giving about 0.4-μA anode current. For such a current range, the dependence of the anode current on the light input was believed to be satisfactorily linear.[11]

Furthermore, to check the stability of the whole measuring system, a pair of $v_{ff}(t)$'s obtained before and after each measurement run of $v_{fp}(t)$ was used. If the system has good stability, $V(t)e^{\lambda t}$ (given by the following relation) vs t is constant:

$$V(t)e^{\lambda t} = G(i_{f1} - i_{f2} - i'_{f1} + i'_{f2}) \,, \qquad (4)$$

where $V(t) = v_{ff}(t) - v'_{ff}(t)$. Here the prime denotes the quantities obtained after the measurement of $v_{fp}(t)$. The constant behavior of $V(t)e^{\lambda t}$ vs t could be used as an index for the stability of the system.

In the measurements of $v_{fp}(t)$ and $v_{ff}(t)$ obtained in the present work, the output voltages from the differential amplifier were measured 75 times during a 1-min period. Such measurements of 75 sampling outputs for 1 min were repeated every 30 min. The decay of the samples was pursued by such measurements for about 10 h. It is noted here that the measurement run of $v_{ff}(t)$ was performed before and after each measurement run of $v_{fp}(t)$ in order to examine the stability of the system by the use of Eq. (4). An entire set of measurements, composed of a $v_{fp}(t)$ run and two $v_{ff}(t)$ runs, was repeated 25 times. However, out of these 25 sets of measurements, only 15 sets were adopted for our purpose, because the stable performance of the measuring system could not be achieved for the other 10 sets.

A weighted least-squares line of $V_{fp}(t)e^{\lambda t}$ was obtained from each set of measured values of $v_{fp}(t)$ and $v_{ff}(t)$. A typical line is shown in Fig. 2, together with two horizontal lines for the stability tests of the measuring system. One horizontal line was obtained using two ^{57}Co sources and the other was $V(t)e^{\lambda t}$, given by Eq. (4), derived from two runs of measurements of $v_{ff}(t)$. From the slope of $V_{fp}(t)e^{\lambda t}$ we could estimate directly $\Delta\lambda/\lambda$ using numerical values i_p and the constants G and λ adopted as a standard of comparison. As mentioned above, we used numerical values, $\lambda = 0.1148$ h^{-1} of metallic ^{99m}Tc and $G = (2.23 \pm 0.07)\times 10^{7}$ Ω. The initial currents i_p differed from each other in the 15 sets of measurements; the average magnitude was 0.5 μA and the errors in its measured values were less than ±4.0%. From 15 values of $\Delta\lambda/\lambda$ thus estimated, we obtained the result as a weighted mean:

$$\frac{\lambda[\mathrm{BaTi}(^{99m}\mathrm{Tc})\mathrm{O}_3,\ 170\,^{\circ}\mathrm{C}] - \lambda[\mathrm{BaTi}(^{99m}\mathrm{Tc})\mathrm{O}_3,\ 20\,^{\circ}\mathrm{C}]}{\lambda(^{99m}\mathrm{Tc})} = (2.6 \pm 0.4)\times 10^{-3}. \qquad (5)$$

The main sources of errors contributing to the quoted standard deviation of 0.4×10^{-3} came from the measurements of $v_{fp}(t)$ and $v_{ff}(t)$. In this deviation are involved the standard deviations calculated from the weighted least-squares analysis of the selected 15 measurements of $V_{fp}(t)e^{\lambda t}$ taking into account the stability of the whole measuring system for each corresponding run. As mentioned above, the time-independent behavior of $V(t)e^{\lambda t}$ given by Eq. (4), observed before and after each run of measurements of $v_{fp}(t)$, was used as a criterion for the stability of the system. The gradient of the weighted least-squares line of $V(t)e^{\lambda t}$, designated as ΔV, was less than 0.5 mV/h, corresponding to a few tenths of $\Delta\lambda/\lambda$ at most. The standard deviation of the gradient, $\delta(\Delta V)$, was also about 0.5 mV/h. Since $\delta(\Delta V)$ contains an error due to the statistical fluctuation of $V(t)e^{\lambda t}$, adoption of $\Delta V+\delta(\Delta V)$ as the maximum error introduced from an instability of the whole measuring system, as we did, may result in a slight overestimation of the final error.

The second and minor source of errors came from the determination of G and i_p. As mentioned above, both of the errors associated with the measured values of these factors could be suppressed to only ±4.0%. Contributions to the final result from these errors, therefore, can be neglected in comparison with those just discussed in the preceding paragraph. As a standard numerical value of λ we adopted the decay constant of metallic ^{99m}Tc determined by Bainbridge *et al.*,[1] since their value is believed to be most accurate and reliable. This value is reasonably understood to be minutely different from λ of ^{99m}Tc embedded in ferroelectric $BaTiO_3$, probably by an order of 10^{-3}. In the present work a contribution from this very small difference to the quoted standard deviation in the expression (5) can also be neglected. Accordingly, our final result is $\lambda[\mathrm{BaTi}(^{99m}\mathrm{Tc})\mathrm{O}_3$ in paraelectric state$] - \lambda[\mathrm{BaTi}(^{99m}\mathrm{Tc})\mathrm{O}_3$ in ferroelectric state$] = (2.6\pm0.4)\times10^{-3}\ \lambda[\mathrm{BaTi}(^{99m}\mathrm{Tc})\mathrm{O}_3$ in ferroelectric state$]$.

This result confirms that the outer-shell electron density near the ^{99m}Tc nucleus in $BaTiO_3$ in the ferroelectric phase is smaller than that in the paraelectric phase by an influence of the internal electric field existing in the ferroelectric $BaTiO_3$. A similar tendency has been observed recently by Huber *et al.*[6,7] with ^{89}Zr embedded in $BaTiO_3$. The relative change of the decay constant, $\Delta\lambda/\lambda$, of the electron capture process of ^{89}Zr was found to be $(8.0\pm0.3)\times10^{-4}$ by measuring γ rays from two samples at room temperature and at 150 °C. Observations of the Mössbauer effect of ^{57m}Fe in the $BaTiO_3$ lattice by Bhide and Multani[12] in 1965 showed an abrupt change in the temperature dependence in the isomer shift at the Curie temperature. This effect implies an increase in the electron density concerned in going above the Curie temperature. Our result is consistent with these observations by other workers.

In the present work the embedded Tc atoms are assumed to be located substitutionally at the Ti site with a charge state of +7. However, one cannot deny the possibility of substitution of Ba ions by Tc ions in the sample we prepared. It is hoped that future study will clear up this ambiguity. The 2.17-keV $E3$ transition in ^{99m}Tc goes mainly by the M-shell conversion, and the relative contribution from the N shell has been measured to be about 14% compared with that from the M shell.[13,14] Referring to theoretical considerations provided by Slater[15] on the chemical effect of the internal conversion of ^{99m}Tc in $KTcO_4$ observed by Bainbridge *et al.*,[1] the change in the decay rate observed in the present work, $\Delta\lambda/\lambda\simeq$ a few tenths of a percent, may be due to a change of the electron density of the $4p$ electrons. The charge density of $4p$ electrons near the Tc nucleus in the sample is presumed to be decreased by an influence of the internal electric field in the ferroelectric state. However, since no detailed information on the electron configuration of the Tc atom embedded in $BaTiO_3$ has so far been obtained, no more detailed discussion can be presented. More accurate measurements of the characteristics of internal conversion in some nuclides, such as ^{99m}Tc, embedded in the lattice structure might provide valuable information on the electronic structure.

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