Isomer shift and influence of the chemical environment on the lifetime of the Mössbauer nucleus ^{119}Sn

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The influence of the chemical enviornment on the lifetime of the 23.87-keV state in ^{119}Sn was measured. The result together with Mössbauer measurements gives an experimental determination of the change in the nuclear charge radius during the Mössbauer transition, which is $\Delta R/R = +(1.69 \pm 0.22) \times 10^{-4}$.

I. INTRODUCTION

The isomer shift (IS) as measured by the Mössbauer effect is[1]

$$\delta = \tfrac{4}{5}\pi Z e^2 R^2 \frac{\Delta R}{R} \Delta\rho(0) = C\Delta\rho(0) , \quad (1)$$

where $\Delta\rho(0)$ is the difference of the electron density at the nucleus in different chemical environments, Ze is the nuclear charge, and ΔR is the change of the nuclear radius during a γ transition.

The radius R is related to the mean-square-charge radius by $R^2 = \frac{5}{3}\langle r_n^2 \rangle$ and corresponds to the radius of a uniformly charged sphere. In order to evaluate $\Delta\rho(0)$ from IS data, one has to know the "calibration constant" C of the corresponding Mössbauer transition. The present paper describes the experimental determination of $C = \frac{4}{5}\pi Z e^2 R \Delta R$ for ^{119}Sn.

Expression (1) is correct under the assumption that the electron density is constant over the nuclear volume, and that a chemically induced change of $\rho(0)$ does not affect the nuclear size. The justification of these assumptions for the case of ^{119}Sn is discussed in the Appendix.

Many attempts of IS calibration for ^{119}Sn have been made. An incomplete list of $\Delta R/R$ values obtained is given in Table I. The values of Uher and Sorensen[2] and of Belyakov[3] are based on nuclear-model calculations. Ruby, Kalvius, Beard, and Snyder[4] did self-consistent-field calculations for varius electronic configurations. Micklitz and Barrett[5] tried to remove some of the ambiguities in the assignment of the electronic configurations by measuring the IS of tin atoms embedded in rare-gas matrices. A purely experimental determination of $\Delta R/R$ was performed by Bocquet, Chu, Kistner, Perlman and Emery.[6,7] These authors measured with a β spectrometer the ratio of the $O:N$ conversion-electron coefficients for β-Sn and SnO_2. Together with IS measurements, the tabulated values of $\Delta R/R$ were obtained. An interesting calibration by Rothberg, Guimard, and Benczer-Koller[8] is based on a comparison of IS and NMR-Knight-shift measurements.

In the present paper the influence of the chemical environment on the lifteime of the 26.39-nsec Mössbauer level of ^{119}Sn is measured. This level decays by a partially converted $M1$ transition. Raff, Alder, and Baur[9] showed for $M1$ transition that the following relation is valid within 1%.

$$\alpha_s^{(i)} = \text{const}\rho_s^{(i)}(0) ; \quad i = K, L, M \ldots . \quad (2)$$

The proportionality of $\alpha_s^{(i)}$ and $\rho_s^{(i)}(0)$ for ^{119}Sn is illustrated by Table II. The change of the lifetime may be written as

$$\frac{\Delta\tau}{\tau} = -\frac{\Delta\lambda}{\lambda} = -\frac{\Delta\alpha}{\alpha+1} = -\frac{\alpha_s}{\alpha+1}\frac{\Delta\rho_s(0)}{\rho_s(0)} , \quad (3)$$

where α is the total and α_s the s-electron conversion coefficient, respectively, $\rho_s(0)$ is the total s-electron density of the shells contributing to the conversion. Since the IS in ^{119}Sn is mainly due to the s electrons (the non-s contribution to $\rho(0)$ is only 2.4%), $\Delta\rho(0)$ of Eq. (1) may be replaced by $\Delta\rho_s(0)$. Equations (1) and (3) combined give

$$\frac{\Delta R}{R} = \tfrac{5}{4}\pi \frac{1}{Ze^2R^2} \frac{\alpha_s}{\alpha+1} \frac{1}{\rho_s(0)} \frac{\delta}{\Delta\lambda/\lambda} . \quad (4)$$

For the evaluation of $\Delta R/R$ the following values were used: $\rho_s(0) = 24\,400$ a.u. (Table II); $\alpha = 5.10$; $\alpha_s = 4.63$; $R = 5.90$ pm.[12] The combined error of these constants is estimated to be less than 5%.

II. MEASUREMENTS

The sources were selected according to the following criteria: (i) To get large and measurable values of $\Delta\lambda/\lambda$, source combinations with large IS were chosen. (ii) To decrease the disastrous effects of resonance absorption in the source, sources with low recoil-free factors were used.

The resonance absorption effect was described by Lynch *et al.*[10] The intensity of the γ radiation after passing through a resonance absorber is

$$I(t) = I_0 e^{-\lambda t}[J_0((\beta\lambda t)^{1/2})]^2 , \quad (5)$$

where J_0 is the zero-order Bessel function and $\beta = N\sigma_0 f$ (N is the number of resonance nuclei per cm^2, σ_0 is the resonance cross section, f is the recoil-free factor of absorber nuclei). In the case

TABLE I. Most significant determinations of $\Delta R/R$ for ^{119}Sn.

Author	Date	$10^4\,\Delta R/R$
Boyle *et al.* (Ref. 13)	1962	1.1
Belyakov (Ref. 3)	1965	−2.5
Uher and Sorensen (Ref. 2)	1966	0.76
Bocquet *et al.* (Ref. 6)	1966	3.3
Ruby *et al.* (Ref. 4)	1967	1.2 ± 0.4
Emery and Perlman (Ref. 7)	1970	1.84 ± 0.37
Rothberg *et al.* (Ref. 8)	1970	1.8 ± 0.4
Micklitz and Barrett (Ref. 5)	1972	0.73 ± 0.05

investigated, the Mössbauer nuclei are homogeneously distributed in the "absorber." Equation (5) must therefore be modified to

$$I(t) = I_0\, e^{-\lambda t}(1 - f' + f'\{[J_0((\beta\lambda t)^{1/2})]^2 + [J_1((\beta\lambda t)^{1/2})]^2\}), \tag{6}$$

where f' $(=f)$ is the recoil-free factor of the emitter nuclei. For $\beta\lambda t \ll 1$ this formula may be expanded to

$$I(t) = I_0\, e^{-\lambda t}\left(1 - \frac{N\sigma_0 f^2 \lambda t}{4} + \cdots\right) \cong I_0 \exp\left[-\lambda t\left(1 + \frac{N\sigma_0 f^2}{4}\right)\right]. \tag{7}$$

In order to determine $\Delta\lambda/\lambda$ with an accuracy of 10^{-5} one requires $\frac{1}{4}N\sigma_0 f^2 \leq 10^{-5}$. For $f = 4\%$ and $\sigma_0 = 1.4\times10^{-18}$ cm^2, the allowed areal density of ^{119}Sn is $N = 2\times10^{16}$ cm^{-2}. The sources were prepared from the commercially available radioactive ^{119}Sn, which was produced by neutron irradiation of 90% enriched ^{118}Sn. The fraction of ^{119}Sn in these sources is estimated to be 1%. From these data, 0.4 mg/cm^2 is found to be an upper limit for the source thickness. With a typical source strength of 10 μCi and a specific activity of 200 mCi/g the active area should be ≥ 10 mm^2.

In two independent series, the following sources were used:

(i) $Sn(SO_4)_2$, SnS_2, β-Sn, $SnCl_2$,

(ii) $Sn(SO_4)_2$, SnI_4, β-Sn, SnS.

A typical source had a strength of 10 μCi and an area of 20 mm^2 and was sealed in a plexiglass capsule. For the lifetime measurements these capsules were mounted between lead apertures in order to reduce coincidences due to backscattering in the scintillators. The sources of each series were made to be of the same strength within approximately 10%. Source strength and background effects were found in the earlier ^{57}Fe measurements.[11] In this measurement no such effects could be detected.

The Mössbauer spectra of the sources were measured before and after the lifetime measurements with a standard spectrometer (Fig. 1). As absorber, $BaSnO_3$ at room temperature, was used. To reduce the x-ray background, 50 μm of Pd was used as an absorber before the NaI(Tl) detector. To increase the f factor of the sources, they were cooled to 80 K. The central shift of the various

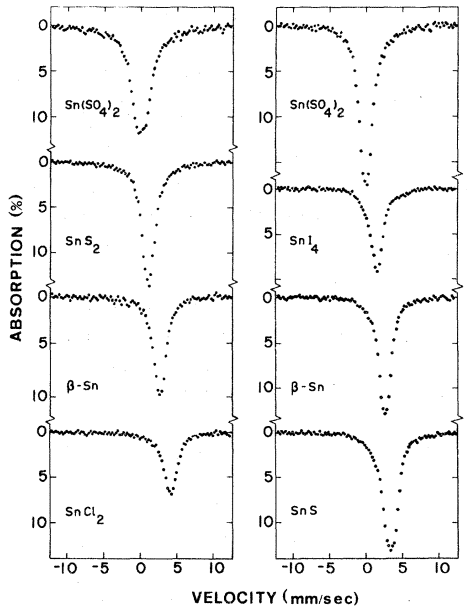

FIG. 1. Mössbauer spectra of the eight sources used in the lifetime measurements. As absorber $BaSnO_3$ was used. The sources were cooled to nitrogen temperature.

TABLE II. Internal-conversion coefficient α for the 23.781-keV $M1$ transition in ^{119}Sn ($5s^15p^3$) (Ref. 9). The last column illustrates the proportionality between α and the electron density at the nucleus, $\rho(0)$, for the various s shells contributing to the conversion. Some of the conversion coefficients were obtained from the Tables of Hager and Seltzer (Ref. 14) (1 a.u. = 0.675 $\times10^{25}$ cm^{-3}).

Shell	α	$\rho(0)$ (a.u.)	$\alpha/\rho(0)$
K	0	168417.70	•••
L_1	3.759	19737.40	1.90×10^{-4}
L_2	0.3060	476.09	
L_3	0.0800	0.05	
M_1	0.7219	3847.50	1.88×10^{-4}
M_2	0.0616	100.00	
M_3	0.0160	0.01	
M_4	0.0009	0.00	
M_5	0.0006	0.00	
N_1	(0.1394)	733.66	
N_2	(0.0106)	17.19	
N_3		0.00	
O_1	0.0150	78.78	1.90×10^{-4}
O_2		0.93	
O_3		0.00	

TABLE III. Isomer shifts of the various sources as measured before and after the lifetime measurements. As absorber $BaSnO_3$ was used. The source temperature was 80 K. The errors are ±0.05 mm/sec.

		Isomer shift (mm/sec)		
Run	Source	Before	After	Average
1	$Sn(SO_4)_2$	0.03	0.02	0.02
1	SnS_2	1.03	1.09	1.06
1	β-Sn	2.54	2.58	2.56
1	$SnCl_2$	3.98	3.79	3.88
2	$Sn(SO_4)_2$	0.07	0.04	0.06
2	SnI_4	1.49	1.47	1.48
2	β-Sn	2.63	2.57	2.60
2	SnS	3.35	3.27	3.31

sources are summarized in Table III. Since the second-order Doppler-shift corrections due to the different Debye temperatures of the sources are with certainty smaller than 0.02 mm/sec, the center shift was taken as the IS.

The lifetimes of the four sources have to be compared with each other with an accuracy of approximately 10^{-5}. By alternate measurements of the decay curve of the chemically different samples, it is possible to evaluate the difference of the decay times. Most systematic errors due to nonlinearities, drifts, etc., which would influence an absolute measurement, will thus cancel.

The lifetime of the 24-keV level ($\tau = 26.4$ nsec) was measured with the coincidence arrangement shown in Fig. 2. The principle of the measurement is as follows: The 26-keV x ray from the highly converted $M4$ transition which populated the 23.9-keV level in ^{119}Sn served as a start and the 24-keV γ ray as a stop pulse for the time to amplitude converter (TAC). As scintillators, 1-mm

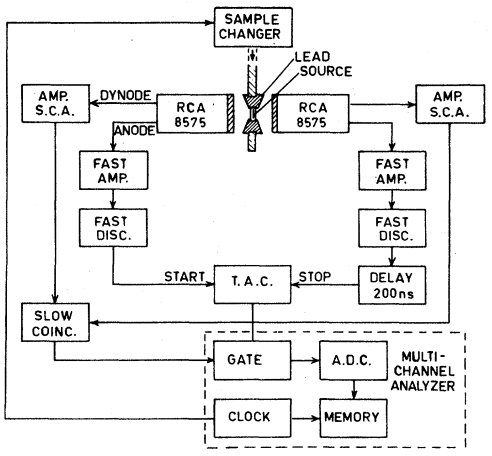

FIG. 2. Block diagram of the electronics used to measure the influence of the chemical environment on the decay constant of the 24-keV γ transition of ^{119}Sn.

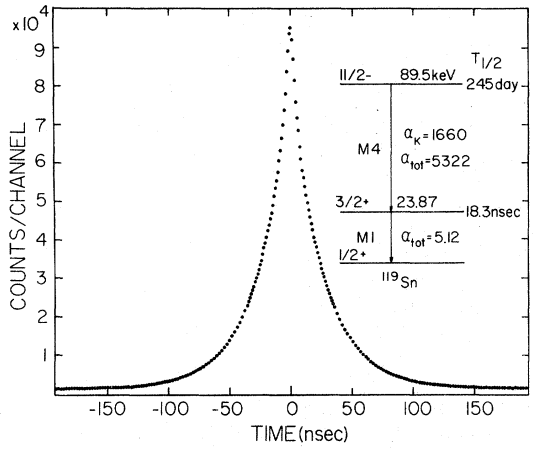

FIG. 3. Typical delayed coincidence curve of the 24-keV level of ^{119}Sn. The time spectrum is symmetric since the detectors do not distinguish between the x rays and the 24-keV γ rays used as start and stop pulses for the time-to-amplitude converter.

NaI(Tl), crystals were used. The four sources were mounted on a sample changer. The events were stored as a function of time in the four quadrants of a multichannel analyzer. Since the detectors cannot distinguish between start and stop pulses, the time spectrum is symmetric (Fig. 3). The sources were interchanged automatically every 8 min to average out electronic drifts. The time resolution of the spectrometer as determined with a ^{125}I source (27 keV) was 6 nsec at full width at half-maximum. The exact time scale was determined with a 100-MHz quartz "time calibrator."

III. RESULTS

From a least-squares fit of the function $N(t) = a + b\,e^{-\lambda t}$ the decay constant and its statistical error was obtained. Since the electronic drifts are larger than the expected effects, the average $\bar{\lambda}$ of the four sources was formed and subtracted from the decay constants of the four individual measurements. In this way 19 runs for the first and 13 runs for second set of sources were evaluated.

In Fig. 4 the decay constants obtained in the two series are plotted versus the isomer shift. For the slope of the straight line through the individual points one gets the following values:

$$\text{Series 1:}\quad \frac{\Delta\lambda}{\lambda\Delta\delta} = (3.48 \pm 0.56)\times 10^{-4}\ \text{sec/mm}\ ,$$

$$\text{Series 2:}\quad \frac{\Delta\lambda}{\lambda\Delta\delta} = (3.56 \pm 0.72)\times 10^{-4}\ \text{sec/mm}\ ,$$

$$\text{Average:}\quad \frac{\Delta\lambda}{\lambda\Delta\delta} = (3.51 \pm 0.44)\times 10^{-4}\ \text{sec/mm}\ .$$

The average lifetime for the 23.871-keV level in ^{119}Sn is

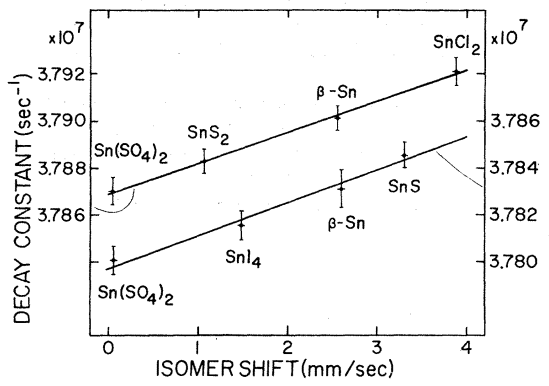

FIG. 4. Decay constant ($\lambda = \tau^{-1}$) plotted vs the isomeric shift. The straight line is the least-squares fit through 76 (=4×19) points obtained for the first and 52 (=4×13) points for the second series.

$$\tau = 26.39 \pm 0.13 \text{ nsec} .$$

The relatively large error bars of the eight sources in Fig. 4 are due to the fluctuations in the time scale. These fluctuations have almost no influence on the determination of the slope. From Eq. (4) one finds for $\Delta R/R$ and the calibration constant C

$$\Delta R/R = +(1.69 \pm 0.22) \times 10^{-4} ,$$

$$C = +(9.25 \pm 1.0) \times 10^{-2} \text{ a.u. sec/mm} .$$

The indicated errors are the statistical errors.

No indication of systematic experimental errors could be found. The total error introduced by higher moment corrections (see Appendix), by $\rho_s(0)$ (Table II), and by the assumption made in the derivation of Eq. (3) is estimated to be smaller than 10%. The value of $\Delta R/R$ determined is in good agreement with the values found by Emery and Perlman[7] and by Rothberg *et al.*[8] It is in disagreement with the recent value of Micklitz and Barrett.[5] We suspect that this is due to the questionable assumption that ^{119}Sn in a rare gas matrix has, in the 24-keV state, the electronic configuration of the free atom.

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APPENDIX

The electric monopole interaction is[1]

$$W_0 = -(4\pi e)^2 \int_0^\infty I_v \rho_n(r_n) r_n^2 dr_n - Ze^2 \int_0^\infty \frac{\rho_e(r_e) d^3 r_e}{r_e} , \quad \text{(A1)}$$

$$I_v = \int_0^{r_n} \left(\frac{1}{r_n} - \frac{1}{r_e} \right) \rho_e(r_e) r_e^2 dr_e .$$

For a spherical nucleus of radius R the electron density is

$$\rho_e(r_e) = \rho(0) \left[1 - \frac{1}{2} \left(\frac{Z\alpha}{R} \right)^2 r_e^2 + \cdots \right] , \quad \text{(A2)}$$

where α is the fine-structure constant. Together with (A1) one gets

$$W_0 = \tfrac{2}{3}\pi Z e^2 \rho(0) \left[\langle r_n^2 \rangle - \frac{3}{20} \left(\frac{Z\alpha}{R} \right)^2 \langle r_n^4 \rangle + \cdots \right] + W_p , \quad \text{(A3)}$$

$$\delta = \tfrac{2}{3}\pi Z e^2 \Delta\rho(0) \left[\Delta\langle r_n^2 \rangle - \frac{3}{20} \left(\frac{Z\alpha}{R} \right)^2 \Delta\langle r_n^4 \rangle + \cdots \right]$$

$$= \tfrac{4}{5}\pi Z e^2 R \Delta R \Delta\rho(0) [1 - \tfrac{3}{14}(Z\alpha)^2 + \cdots] .$$

For Sn the term $\frac{3}{14}(Z\alpha)^2$ is only 2.8% and is not taken into account.

A further assumption made in the derivation of Eq. (1) is that the electron density has no influence on the nuclear size and vice versa. For ^{119}Sn such an influence may be estimated from the nuclear compressibility. The energy due to the change of the nuclear radius is[2]

$$E_{\text{compr}} = \tfrac{1}{2} K \left(\frac{\Delta R}{R} \right)^2 , \quad (\Delta R = R_{\text{ex}} - R_{\text{gd}}) . \quad \text{(A4)}$$

By an increase of the electron density at the nuclear site the electrostatic energy changes by

$$E_{\text{Coul}} = -\frac{8}{5} \frac{Ze^2}{R} \pi R^3 \Delta\rho(0) . \quad \text{(A5)}$$

From the two equations, one gets the change of the nuclear radius due to the increase of the electronic charge in the nucleus

$$\frac{\delta R}{R} = -\tfrac{8}{5}\pi \frac{Ze^2 R^3}{K \Delta R} \Delta\rho(0) . \quad \text{(A6)}$$

To estimate $\delta R/R$, the following values may be used[2]: $R = 5.9$ fm, $\Delta\rho(0) = 100$ a.u., $K = 150A$ MeV, $A = 119$, $\Delta R/R = 1.7 \times 10^{-4}$.

The result of the crude estimate is $\delta R/R = 4 \times 10^{-8}$, a value which is more than three orders of magnitude smaller than the expected value for $\Delta R/R$, and will therefore be neglected.

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