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Chemically induced change in nuclear decay rate as a tool for calibrating Fe^{57} isomer shifts*

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The calibration constant of Fe^{57} has been determined to be $\delta R/R = -(2.3^{+2.6}_{-0.8}) \times 10^{-4}$, from the isomeric chemical shift of the 14.4-keV γ rays, resulting from decay of Co^{57} diffused into zinc and vanadium host lattices. The difference in electron density at the nucleus was obtained directly from the measured difference in decay constant of the isomeric level. The fractional difference in the decay constant of the Mössbauer level of Fe^{57} between zinc and vanadium was measured to be $(4.2 \pm 2.2) \times 10^{-4}$.

I. INTRODUCTION

The isomeric chemical shift[1] of a Mössbauer transition between a pair of chemical states can be written[2]

$$\Delta v = C \frac{\delta R}{R} (\Delta \rho) , \tag{1}$$

where C is a constant depending on the atomic number, the transition energy, and the nuclear radius R, δR is the difference in equivalent radius between the excited and ground nuclear states, and $\Delta\rho$ is the difference between the total electronic charge densities at the nucleus of the two different chemical states. The small differences in electron densities which can be determined in this way allow a wide range of applications to chemistry and solid-state physics.[3] Quantitative extraction of electron-density differences, however, requires a knowledge of $\delta R/R$ for the particular Mössbauer transition being used, or equivalently, a calibration of the isomer shift.

Initial attempts at isomer-shift calibration have been usually based on chemical arguments involving concepts such as bond ionicity. Such calibrations have seldom been unique, and have sometimes turned out to be in error by rather large factors. A more direct method, based on comparison of isomer shifts with changes in valence-electron conversion, has been introduced by Bocquet *et al.*[4] A still more direct method, applicable to Mössbauer transitions whose conversion coefficients are large and almost entirely due to magnetic dipole conversion, has been suggested by Raff, Alder, and Baur,[5] and by the present authors.[6] This method involves comparison of changes of half-life, of the state emitting the Mössbauer transition, with isomer shifts. The half-life changes, under these conditions, are proportional to changes in electronic charge density at the nucleus, the $\Delta\rho$ of Eq. (1), without the complication introduced by the $\delta R/R$ factor. The application of these methods is discussed in a recent review.[7]

We give in this paper the results of an isomer-shift calibration for the 14.4-keV transition of Fe^{57}, using the change-of-half-life method; some preliminary results were presented earlier.[6] The results are in excellent agreement with those recently reported by Rüegsegger and Kündig.[8] A still more complete account is contained in the thesis of one of us (R. N. V.).[9]

II. EXPERIMENT

Sources of Co^{57}, about 60 μCi strong, were prepared by electrodeposition from $CoCl_2$ onto foils of zinc (0.0010-in. thick, 99.99% pure) and vanadium (0.0005-in. thick, 99.5% pure). The sources on zinc and vanadium were then diffused for 2 h in a hydrogen atmosphere at temperatures of 370 and 1100 °C, respectively. The preparation of Co^{57} Mössbauer sources has been discussed in detail by Dezsi and Molnar,[10] Stephen,[11] Qaim *et al.*,[12] and Mustachi.[13] Two physically different sources were prepared for each matrix.

Isomer shifts for the sources were determined relative to the same single-line absorber $Na_4Fe(CN)_6 \cdot 10H_2O$ (1.0-mg/cm² Fe^{57}, 90.7% enriched). A standard Mössbauer spectrometer was used in the constant-acceleration mode. The isomer shift of the 14.4-keV γ ray from Fe^{57} in vanadium relative to that in zinc was found to be

$$v_V - v_{Zn} = 0.51 \pm 0.01 \text{ mm/sec} ,$$

which is in agreement with the value found from the measurements of Qaim.[14]

In view of the 143-nsec mean life of the Mössbauer level of Fe^{57}, and the availability of the 123–14.4-keV γ-γ cascade populating and depopulating the level, a fast-slow delayed coincidence technique, using NaI(Tl) detectors, was employed for the change-in-half-life measurements. The data-acquisition system was automated to accumulate time distribution curves for two different sources, alternately, in two separate sections of the multichannel-analyzer memory. The sources, to be viewed by the γ-ray detectors for the preceding and the delayed radiations, and the analyzer-memory sections, were switched every 5 min. In each 24-h run, about 3×10^6 true coincidence events were collected in each delayed time distribution. Data from more than 25 such runs were included in each decay-rate comparison. Time calibration of the system was done by the method of Taylor.[15] The decay-rate comparisons were performed with sources about 10 μCi strong, cut from the foil sources used for the isomer-shift measurements, to keep the chance-to-true ratio small.

Differences in decay rates for the 14.4-keV level in different environments were determined from the corresponding delayed coincidence distributions using the ratio method, which can be explained as follows: Let $f_1(x)$ and $f_2(x)$ be the true coincidence counts in channel x for Fe^{57} in source 1 and source 2. Let λ and $\lambda+\Delta\lambda$ be the corresponding decay constants. Using the formulation of Newton[16] it can be easily shown that

$$\ln[f_2(x)/f_1(x)]=A-(\Delta\lambda)x$$

for the region where $f(x)\gg P(x)$, where A is a constant, and $P(x)$ represents the prompt coincidence curve for the source and electronics. Thus, the ratio method consists in fitting $\ln(f_2/f_1)$ vs x by least squares to a straight line, and finding its slope. The initial channel is taken a few channels away from the maximum of the time distribution curve on the delayed side to avoid complications due to the prompt distribution of the system. The final channel is taken about three mean lives later to avoid possible systematic uncertainties in the tails due to subtraction of chance coincidences. Further, the initial and final channels must be chosen such as to give a value for the slope $\Delta\lambda$ which is independent of the exact end points of the region fitted within the statistical limitations. In this method $f_1(x)$ and $f_2(x)$ do not have to be normalized because the slope of $\ln[f_2(x)/f_1(x)]$ is independent of any multiplicative constant. Differential nonlinearities also cancel out. Using the known value of λ, which is of course checked by the time calibration, one finds $\Delta\lambda/\lambda$. Plots of $\ln[f_2(x)/f_1(x)]$ vs x for five typical runs are shown in Fig. 1. The values of $\Delta\lambda/\lambda$ for 31 runs for zinc versus vanadium, from which the weighted mean of $\Delta\lambda/\lambda$ was extracted, are tabulated in Table I.

III. RESULTS AND DISCUSSION

To check the performance of the experimental arrangement, a $\Delta\lambda/\lambda$ measurement was made using two sections of the same source of Co^{57} in zinc. From 28 pairs of time distribution curves it was found that $\Delta\lambda/\lambda=(0.1\pm1.8)\times10^{-4}$, consistent with a null result for identical environments of Fe^{57} within the statistical uncertainty.

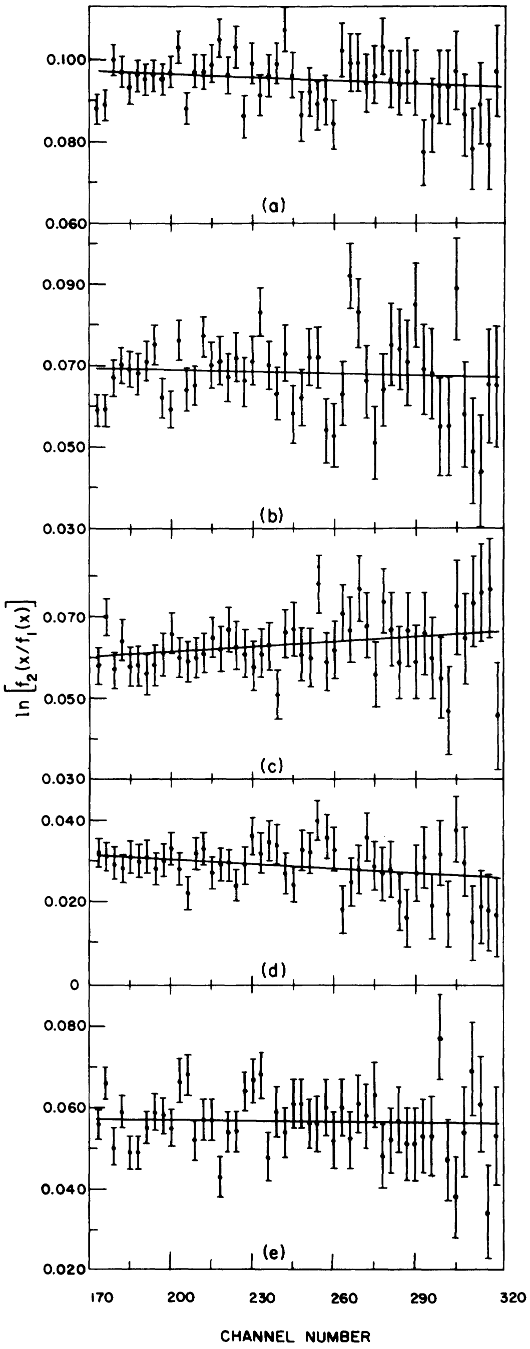

FIG. 1. Plots of $\ln[f_2(x)/f_1(x)]$ against x for five typical runs. $f(x)$ is the number of true coincidence counts in channel x. The subscripts 2 and 1 refer to the hosts vanadium and zinc, respectively. The ordinate of each point in the plots is the weighted mean of the quantity $\ln[f_2(x)/f_1(x)]$ for the channels $(x-1)$, x, and $(x+1)$. The statistical error in the ordinate is shown by the error bar. The values of $10^4\times\Delta\lambda/\lambda$ deduced from the slopes of the lines a, b, c, d, and e are -14.0 ± 10.3, -5.2 ± 13.0, $+23.2\pm12.1$, -15.8 ± 9.4, and -2.7 ± 11.4, respectively. The calibration constant of the analyzer system is 2.78 nsec/channel.

TABLE I. Individual values of $\Delta\lambda/\lambda$ for zinc vs. vanadium environments.

Pair No.	$\left(\frac{\lambda_{Zn}-\lambda_V}{\lambda}\right)\times 10^4$	Pair No.	$\left(\frac{\lambda_{Zn}-\lambda_V}{\lambda}\right)\times 10^4$
1	−14.0 ±10.3	17	+6.3 ±13.4
2	−11.4 ±13.4	18	−5.6 ± 9.8
3	+7.4 ±12.7	19	−2.7 ±11.4
4	−1.2 ±11.8	20	−10.3 ±12.5
5	−5.2 ±13.0	21	+32.4 ±15.8
6	−18.5 ±14.0	22	+0.1 ±14.0
7	−5.8 ±14.1	23	−30.0 ±14.2
8	−1.5 ±12.0	24	−26.1 ±11.7
9	+9.4 ±13.3	25	+20.4 ±10.9
10	+23.2 ±12.1	26	−5.1 ±13.3
11	−1.7 ±12.7	27	−0.6 ±12.6
12	−27.0 ±12.5	28	−10.2 ± 7.3
13	−17.0 ±13.6	29	−7.9 ±14.6
14	−15.8 ± 9.4	30	+19.5 ±12.6
15	+7.6 ±14.8	31	+3.5 ±14.7
16	−15.3 ±13.4		

Direct comparison between sources of Co^{57} in vanadium and in zinc, averaged from 31 runs, gave the result

$$(\lambda_V-\lambda_{Zn})/\lambda=(4.2\pm 2.2)\times 10^{-4}\ ,$$

where the quoted uncertainty represents one standard deviation.

Since for a magnetic dipole transition[4–6, 17]

$$\Delta\alpha/\alpha=\Delta\rho/\rho\ ,$$

where α is the total conversion coefficient and ρ the total electron density at the nucleus, and since

$$\lambda=\lambda_\gamma(1+\alpha)\ ,$$

one can express the fractional radius change between the ground and excited nuclear states as

$$\frac{\delta R}{R}=-\frac{\Delta v}{C(\Delta\lambda/\lambda)\rho}\ \frac{\alpha}{1+\alpha}\quad .$$

The adopted value for the total conversion coefficient of the 14.4-keV transition is 8.26 ± 0.20.[18] For the total relativistic electron density at the nucleus we use the value of Raff, Alder, and Baur[5] $\rho=(1.48\pm 0.07)\times 10^4$ a.u. With the electron density in those units the constant factor is $C=313$ mm/sec a.u. Using these values and the Δv from Sec. II, one finds the result

$$\frac{\delta R}{R}=-(2.3^{+2.6}_{-0.8})\times 10^{-4}\quad .$$

This result agrees, well within the statistical uncertainty, with the value $-(3.1\pm 0.6)\times 10^{-4}$ reported by Rüegsegger and Kündig,[8] who used an approach very similar to the one used here. Their method of data analysis was somewhat different. The present experiment was done with metallic environments to minimize any possible aftereffects of the preceding electron capture, while that of Rüegsegger and Kündig compared sources in four chemical environments, with the greatest contribution to increasing the statistical precision coming from the use of CoO, with its large isomer shift, as one of the environments.

The values for $\delta R/R$ found here, and by Rüegsegger and Kündig, are considerably smaller in magnitude than that originally proposed, on the basis of free-atom Hartree-Fock calculations, by Walker, Wertheim, and Jaccarino[19]: Their value, when corrected for relativistic effects, was -14×10^{-4}. Later estimates based on chemical arguments have tended to be somewhat smaller in magnitude: Goldanskii, Makarov, and Stukan[20] gave -9×10^{-4}, while Chappert, Regnard, and Danon[21] gave a calibration constant which converts to a $\delta R/R$ value of $\sim -7\times 10^{-4}$. Simanek and Sroubek[22] and Simanek and Wong[23] estimated values in the neighborhood of -4×10^{-4}, in rather good agreement with the present results. Others of the older estimates are tabulated by Kienle, Kalvius, and Ruby.[24] More recently, McNab, Micklitz, and Barrett[25] have provided an estimate of -10.6×10^{-4}, while Micklitz and Barrett[26] have given -8.7×10^{-4}; Duff[27] gives a calibration constant which converts to $\Delta R/R=-(5.7\pm 0.5)\times 10^{-4}$.

Changes in valence electron conversion were used by Pleiter and Kolk[28] to derive $\delta R/R=-(4.5\pm 1.5)\times 10^{-4}$. The interpretation of their result was made somewhat less clear by the discovery by Porter and Freedman,[29] that when studied at high resolution, the shapes of the conversion lines were not independent of the shell in which the conversion took place. The result of Pleiter and Kolk has also been discussed by Raff *et al.*[5] A high-resolution valence-shell conversion experiment has been performed by Fujioka and Hisatake,[30] who conclude that $|\delta R/R|\gtrsim 6\times 10^{-4}$.

The methods of the present experiment, and that of Rüegsegger and Kündig,[8] provide a much more direct determination of the quantity $\delta R/R$ than was previously possible. The results show that the magnitudes of the changes in the total electron density at the nucleus between different environments of the iron atom are somewhat larger than have usually been assumed, and that correspondingly the magnitude of the change in the nuclear charge radius in going from the ground to the first excited state of Fe^{57} is somewhat smaller than has usually been assumed.

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