

Isomer-shift calibration of ^{57}Fe by lifetime variations in the electron capture decay of ^{52}Fe

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Differential ionization chambers are used in order to measure the difference in the electron capture rate of ^{52}Fe nuclei in different chemical compounds. Combination with the corresponding Mössbauer isomer shifts of these Fe compounds permits the determination for the Mössbauer transition in ^{57}Fe of $\Delta\langle r^2 \rangle = -(33 \pm 3)10^{-3} \text{ fm}^2$.

I. INTRODUCTION

The Mössbauer isomer shift δ between a pair of chemical compounds is given by

$$\delta = \frac{2}{3} \pi Z e^2 \Delta\langle r^2 \rangle \Delta\rho(0) = \alpha \Delta\rho(0) \quad ,$$

where α is a constant depending on $\Delta\langle r^2 \rangle$, the change in mean-square charge radius of the nucleus during the Mössbauer transition, and $\Delta\rho(0)$ is the difference of the electron densities at the nucleus for the two chemical states. The calibration of the isomer shift consists in the determination of α , or $\Delta\langle r^2 \rangle$, by combination of estimated $\Delta\rho(0)$ values with the corresponding measured isomer shifts.

In order to estimate these $\Delta\rho(0)$ values one usually takes electron densities, calculated by self-consistent-field techniques, and corrected in some manner for the solid-state situation of the considered nuclei. However, the results obtained in this way are far from agreement.¹ Therefore experimental techniques have been used, e.g., conversion electron spectroscopy, where one supposes² that only the valence s shell contributes to the change in $\rho(0)$. But this assumption is not always satisfied, as shown in a recent conversion electron study of $\rho_{4s}(0)$ of an Fe-impurity atom in some transition and noble metals.³

Therefore, measurements of the change of nuclear lifetime in different compounds, that do not need this assumption, are at present in principle the most appropriate way to estimate $\Delta\rho(0)$. While the internal conversion probability is proportional to the elec-

tron density "near" the nucleus, i.e., in the region where the conversion takes place,⁴ the electron capture process is really local, so that $\Delta\rho(0)$ values, estimated by changes in electron capture rate, are exactly those that appear in the expression for the Mössbauer isomer shift.

Rüegsegger and Kündig⁵ compared the different values of the nuclear lifetime of the partially converted 14.4-keV level of ^{57}Fe in different atomic environments, resulting in a $\Delta\langle r^2 \rangle$ value lower than all other estimations. They measure λ and not directly $\Delta\lambda$, as is wanted for relative effects of about 10^{-4} . Moreover, such small effects are at the limit, if not below, of the reliability of the coincidence technique used. In the present work direct measurements of the difference in the electron capture rate in different ^{52}Fe -labeled compounds, are compared with the corresponding differences in isomer shift.

II. DIFFERENTIAL METHOD

The small differences $\Delta\lambda$ in the decay constants of two sources, with equal initial activity, were measured by the differential-ionization-chamber method, first used by Rutherford.⁶ The two essentially identical ionization chambers have opposite electric fields and connected collecting electrodes (Fig. 1). The current measured is the difference of the ionization currents in the two chambers, respectively. By putting

$$I_+(t) = I_+(0) e^{-\lambda_+ t}$$

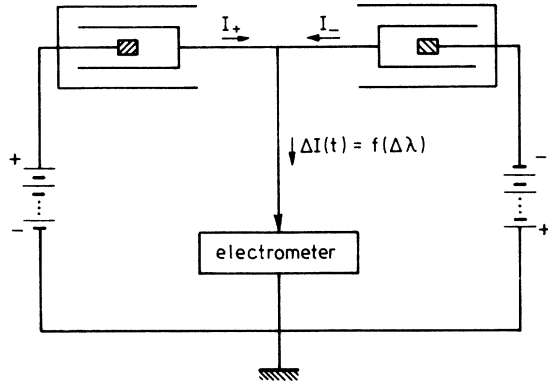


FIG. 1. Diagram of the setup of the differential ionization chambers.

and

$$I_{-}(t) = I_{-}(0)e^{-\lambda_{-}t} = I_{-}(0)e^{-(\lambda_{+} + \Delta\lambda)t}$$

+ and - indicating the respective polarities of the ionization chambers, this difference current can be approximated, for $t\Delta\lambda \ll 1$, as

$$\begin{aligned} \Delta I(t) &= |I_{+}(t)| - |I_{-}(t)| \\ &\approx e^{-\lambda_{+}t} [\Delta I(0) + I_{-}(0)t\Delta\lambda] \end{aligned} \quad (1)$$

Perturbing effects as different self-absorption in the compared sources or an efficiency difference of the two chambers largely cancel out by interchanging the sources.

The differential 4π ionization chambers used in these experiments, are a slight modification of the previously presented apparatus.⁷ The connection of the source holder via an insulator with a micrometer mechanism is modified in order to be able to remove this insulator during the experiment. The pressure of the argon gas was increased to 9.5 atm. In these conditions relative lifetime differences are reliable down to $\sim 2 \times 10^{-5}$. The difference current ($\leq 10^{-13}$ A) is measured by integration over the precision capacity of a Cary 401 vibrating reed electrometer.

III. DATA REDUCTION

A. Proportionality of $\Delta\lambda/\lambda$ and $\Delta\rho(0)/\rho(0)$

For electron capture (EC) the decay constant can be approximated⁸ by

$$\lambda_{\text{EC}} \approx \frac{g^2}{4\pi^2} C \sum_x q_{\nu x}^2 \rho_x(0) B_x, \quad x = s_{1/2}, p_{1/2}$$

The relative difference of the decay constant in two compounds is then given by

$$\frac{\Delta\lambda}{\lambda} \approx \frac{\sum_x [q_{\nu x}^2 \Delta\rho_x(0) B_x]}{\sum_x [q_{\nu x}^2 \rho_x(0) B_x]} \approx k \frac{\Delta\rho(0)}{\rho(0)}$$

The factors B_x take into account the effects of electron exchange as well as the imperfect overlap of the electron wave functions before and after the EC process, because of the change in nuclear charge during this transition. In particular, what started out as capture of an electron in a particular initial orbital can result in an inner-shell hole in a different final orbital. These effects seem to have been pointed out first by Benoist-Gueutal.⁹ Their consequences have been worked out in detail by Bahcall,¹⁰ who showed that exchange and overlap effects tend to cancel in total capture rates. Mostly these corrections are neglected, resulting in $k \approx 1.00$. However, a combination of the nonrelativistic one-particle electron wave functions of Watson and Freeman¹¹ with the B_x values calculated on this basis by Vatai¹² results in $k \approx 1.30$.

If the exact value of k is uncertain, we know that the influence of the B_x factors tends to increase k , and thus to decrease $\Delta\rho(0)$. This means that the $\Delta\rho(0)$ values derived with $k = 1$ can be interpreted as a maximum.

In the decay of ^{52}Fe (Fig. 2) only 44% proceeds by EC, the rest being β^+ . One can reasonably assume that the environmental effect on the probability of β^+ emission is at least an order of magnitude smaller than on λ_{EC} , and can thus be neglected. In this work the measured $\Delta\lambda$ is completely attributed to the ef-

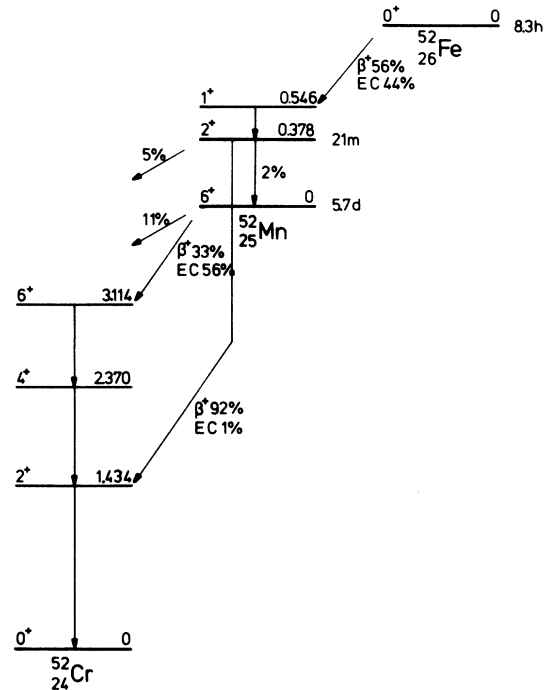


FIG. 2. Decay scheme of ^{52}Fe , with EC representing electron capture.

fect on the electron capture rate. This means that $\Delta\lambda = \Delta\lambda_{EC}$, and consequently

$$\left(\frac{\Delta\lambda}{\lambda}\right)_{\text{expt}} = \frac{\Delta\lambda_{EC}}{\lambda_{EC}} 0.44 = 0.44k \frac{\Delta\rho(0)}{\rho(0)} . \quad (2)$$

B. Differential measurements

The only Fe isotope suitable for differential lifetime-variation measurements is ^{52}Fe . Looking at its decay scheme (Fig. 2), it is clear that expression (1) has to be adjusted, due to the fact that ionization chambers integrate all the radiation present, and thus see the ingrowing daughter activity in both sources, implying new decay constants and also other transition energies and thus detection efficiencies. In gen-

eral the ionization current can be written as

$$I(t) = e \sum_i \lambda_i N_i(t) \sum_{E_i} p_{E_i} \xi_{E_i} \eta_{E_i} = e \sum_i \lambda_i N_i(t) \epsilon_i ,$$

with i representing different components and p_{E_i} being the relative intensity of E_i . ξ_{E_i} is the ionization chamber efficiency for E_i , and η_{E_i} is the emission efficiency of the source for E_i . Labeling $^{52}\text{Fe} = A$, $^{52m}\text{Mn} = B$, and $^{52}\text{Mn} = C$, the ionization current due to an ^{52}Fe source can then be written as

$$I(t) = e [\lambda_A N_A(t) \epsilon_A + \lambda_B N_B(t) \epsilon_B + \lambda_C N_C(t) \epsilon_C] .$$

The time evolution of the number of radioactive nuclei in the different states is given by

$$\begin{aligned} N_A(t) &= N_A(0) e^{-\lambda_A t} , \\ N_B(t) &= N_B(0) e^{-\lambda_B t} + \frac{\lambda_A}{\lambda_B - \lambda_A} N_A(0) (e^{-\lambda_A t} - e^{-\lambda_B t}) , \\ N_C(t) &= N_C(0) e^{-\lambda_C t} + 0.02 \frac{\lambda_B}{\lambda_C - \lambda_B} N_B(0) (e^{-\lambda_B t} - e^{-\lambda_C t}) \\ &\quad + 0.02 N_A(0) \frac{\lambda_A \lambda_B}{\lambda_B - \lambda_A} \left[\frac{1}{\lambda_C - \lambda_A} (e^{-\lambda_A t} - e^{-\lambda_C t}) - \frac{1}{\lambda_C - \lambda_B} (e^{-\lambda_B t} - e^{-\lambda_C t}) \right] . \end{aligned}$$

The differential measurements never started before $\lambda_A t = 0.4$, $t = 0$ being the moment of the chemical separation of Fe and Mn. In that case

$$e^{-\lambda_B t} / e^{-\lambda_A t} < 1.5 \cdot 10^{-4} ,$$

so that

$$\lambda_A N_A(t) \epsilon_A + \lambda_B N_B(t) \epsilon_B \approx \lambda_A N_A(t) \epsilon_{AB} ,$$

with

$$\epsilon_{AB} = \epsilon_A + \epsilon_B \lambda_B / (\lambda_B - \lambda_A) .$$

The equilibrium of ^{52m}Mn and ^{52}Fe can then be considered as a pure ^{52}Fe component, but with increased efficiency. Defining $\alpha(t) = N_C(t) \lambda_C / N_A(t) \lambda_A$, the ionization current can then be written as

$$I(t) \approx e \lambda_A N_A(t) [\epsilon_{AB} + \alpha(t) \epsilon_C] ,$$

or, with $\beta = \epsilon_C / \epsilon_{AB}$,

$$\begin{aligned} I(t) &\approx e \lambda_A N_A(0) e^{-\lambda_A t} \epsilon_{AB} [1 + \beta \alpha(t)] \\ &= I(0) e^{-\lambda_A t} [1 + \beta \alpha(t)] . \end{aligned}$$

Remark that $I(0)$ is *not* the ionization current that should be measured at $t = 0$, but an extrapolation to $t = 0$ of the current measured once the equilibrium between A and B is established, and before $\alpha(t)$ has to be taken into account [for $\lambda_A t = 1$, $\alpha(t) \approx 2 \times 10^{-3}$].

The differential current due to two ^{52}Fe sources, with respective decay constants λ_{A+} and $(\lambda_{A+} + \Delta\lambda)$ can then be written as

$$\Delta I(t) = |I_+(t)| - |I_-(t)| = I_-(0) e^{-\lambda_{A+} t} \left[\frac{\Delta I(0)}{I_-(0)} + t \Delta\lambda + \frac{I_+(0)}{I_-(0)} \beta_+ \alpha_+(t) - \beta_- \alpha_-(t) [1 - t \Delta\lambda] \right] .$$

The values $y(t) = \Delta I(t) e^{\lambda_{A+} t} / I_-(0)$ define approximately a straight line, $\Delta\lambda$ being the slope, if $\Delta\beta = 0$. If $\Delta\beta \neq 0$ this straight line becomes more and more curved in function of time (Fig. 3). For important $\Delta\beta$ values the sensitivity on $\Delta\lambda$ is lost. The efficiency ratios β are functions of the respective ionization

chambers as well as of the self-absorption in the sources. Measurements with identical sources showed that the part due to the ionization chambers can be neglected. In order to minimize self-absorption differences while comparing compounds a and b , an amount of the inactive compound b , equal

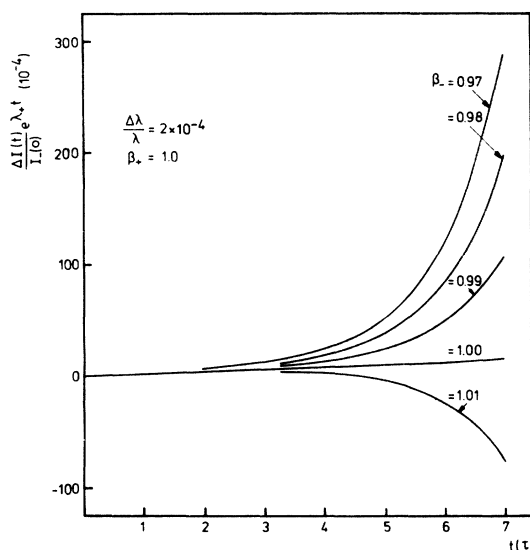


FIG. 3. Different curves $\Delta I(t)e^{+\lambda t}/I_-(0)$ as a function of the parameter β_- .

to the amount of the ^{52}Fe -labeled compound b , was added to the labeled compound a , and vice versa (except for one experiment). This means that compounds have to be chosen that do not interact chemically with each other.

For each experiment β_+ was determined using $I_+(t)$ values taken before and after the differential measurement. However, not the absolute value of the β 's, but only their difference $\Delta\beta$ has a significant influence on the estimation of $\Delta\lambda$. Therefore, a least-squares fit through the $y(t)$ values was made, with only three free parameters: $\Delta\lambda$, β_- , and $\Delta I(0)/I_-(0)$.

The integration time of 1000 s for one ΔI measurement was subdivided into ten parts of 100 s, and the deviation of these ten values around their mean used in defining the weight ($w_i = 1/\sigma_i^2$) of the measurement.

In evaluating $\alpha(t)$, $N_B(0)$ and $N_C(0)$ are neglected. Computer simulations indicate that they have to be of the order of 1% of $N_A(0)$ before $\Delta\lambda$ is significantly influenced. However, if the preparation of the two labeled compounds to be compared causes a different supplementary Fe-Mn separation, the ^{52}Mn -to- ^{52}Fe ratio in both sources can differ, even if $N_C(0) = 0$, because of the decay of the ^{52}Fe during the chemistry. This could introduce a slight difference between $\alpha_+(t)$ and $\alpha_-(t)$, apart from the difference due to $\Delta\lambda$. Computer simulations indicate that this difference in the function $\alpha(t)$ for the two compounds to be compared does not affect $\Delta\lambda$ but only the fitted β_- value, if $\Delta\beta \neq 0$. This means that $\Delta\beta$ changes its meaning, becoming composite, but retains its efficiency as a correction. Nevertheless, if possible, preparations with no possible different Fe-Mn separation were preferentially chosen.

Another question is the influence of a possible variation in the lifetime of the ^{52}Mn ground state (66% EC) on the estimation of the change in the ^{52}Fe decay constant, $(\Delta\lambda)_{52\text{Fe}}$. Estimations show that even for unexpected high effects on the lifetime of ^{52}Mn , $|(\Delta\lambda/\lambda)_{52\text{Mn}}| = 10^{-3}$, the deviation on an $(\Delta\lambda/\lambda)_{52\text{Fe}} = 10^{-4}$ effect, is less than 5%. Moreover, this deviation is quasi-independent of $\Delta\beta$.

IV. SOURCE PREPARATION

The ^{52}Fe activity is produced at the cyclotron of Louvain-la-Neuve using the reaction $^{55}\text{Mn}(p, 4n)^{52}\text{Fe}$, by a proton energy of 65 MeV. Most irradiation

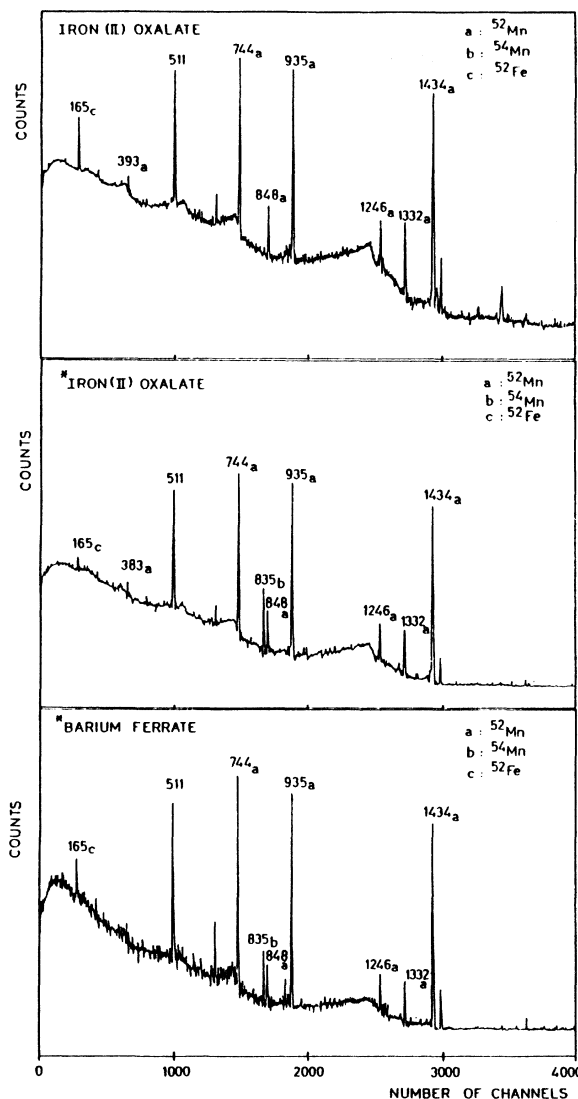


FIG. 4. γ spectra of different sources, five days after their production. In spectrum 1 there is no ^{54}Mn , whereas the ratio of ^{54}Mn to ^{52}Mn is the same in spectra 2 and 3, corresponding to two sources compared in one experiment.

tions were typically $8 \mu\text{A}$ during 4 h. The yield is about $100 \mu\text{Ci}/\mu\text{A h}$. Besides ^{52}Fe also other activities are produced: ^{53}Fe , ^{55}Fe , ^{51}Mn , ^{52}Mn , ^{54}Mn . The presence of ^{53}Fe , ^{55}Fe , and ^{54}Mn causes no problem, because of their respective lifetimes. However, ^{51}Cr ($t_{1/2} = 27.8 d$), daughter product of ^{51}Mn ($t_{1/2} = 45 m$) and ^{52}Mn ($t_{1/2} = 5.7 d$) have to be eliminated. This is done using anion exchange on two subsequent columns. The end of this separation is taken as $t = 0$. The purity of this separation was tested by γ spectroscopy, five days after the separation, i.e., after the differential measurement, an immediate test requiring too much time because of the bad signal-to-background ratio at that moment. Figure 4 shows typical γ spectra, i.e., with and without ^{54}Mn . The amount of ^{54}Mn in the sources, if any, was always small, and the ratio of ^{54}Mn to ^{52}Mn , for the two sources being compared, was always identical

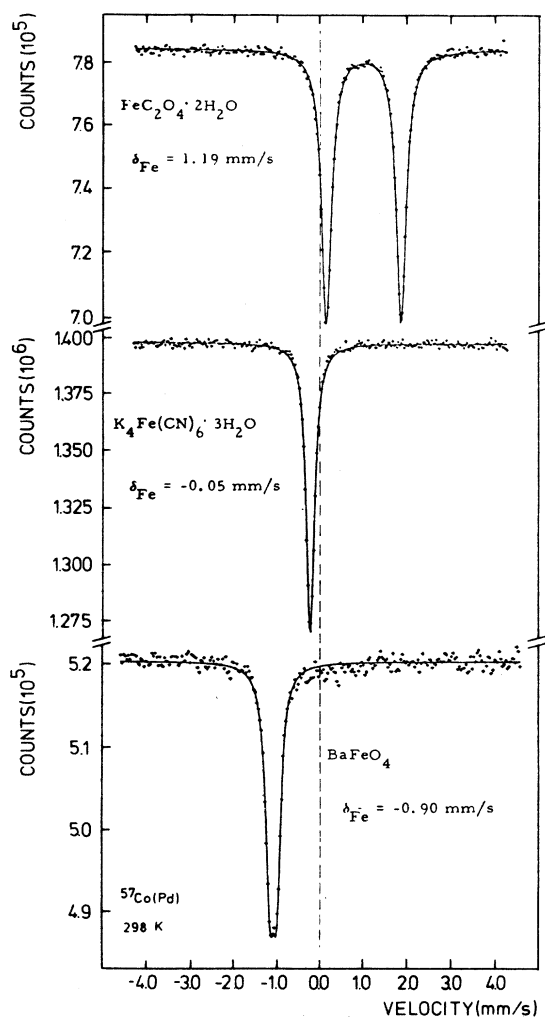


FIG. 5. Mössbauer spectra of the pure compounds, showing the large isomer-shift differences.

TABLE I. Different Fe compounds.

Compound	δ_{Fe} (mm s^{-1})
(O) : $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	$+1.19 \pm 0.02$
(G) : $\text{KFe}(\text{CH}_2\text{OCO}_2)_2\text{H}_2\text{O}$	$+0.40 \pm 0.01$
(H) : $\alpha\text{-Fe}_2\text{O}_3$	$+0.38 \pm 0.01$
(C) : $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	-0.05 ± 0.01
(F) : BaFeO_4	-0.90 ± 0.02

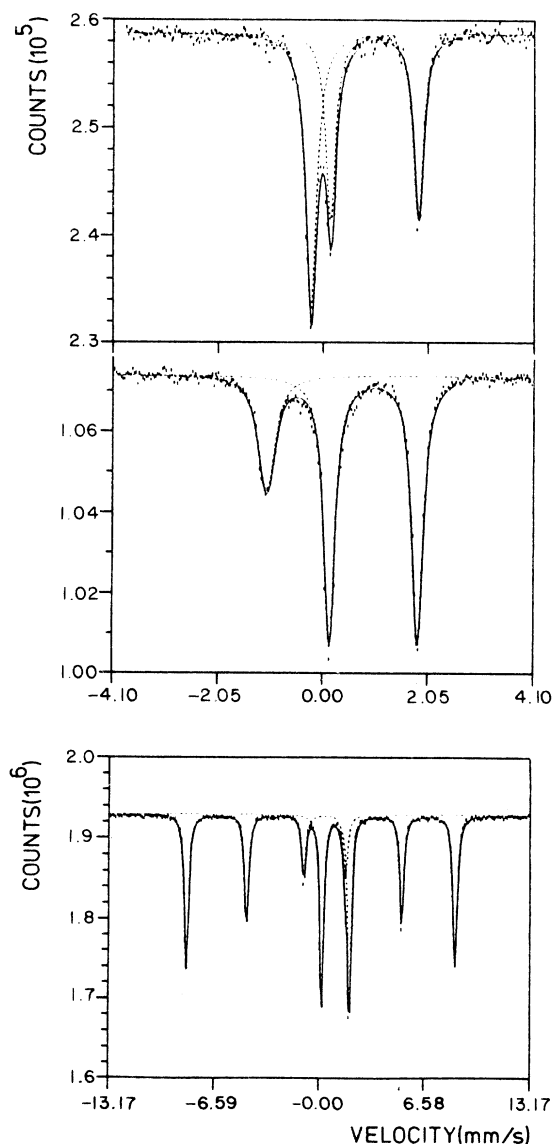


FIG. 6. Mössbauer spectra of the experimental sources, where the compounds to be compared are mixed: (a) $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O} + \text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; (b) $\text{BaFeO}_4 + \text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; (c) $\alpha\text{-Fe}_2\text{O}_3 + \text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

TABLE II. Experimental results.

Pair number	$\delta_- - \delta_+$ (mm s $^{-1}$)	Sources ^{a,b}		$I(0)$ (10 $^{-10}$ A)	$t(1)$ (s)	$\beta_- - \beta_+$ (10 $^{-4}$) ^a	$\frac{\lambda_- - \lambda_+}{\lambda}$ (10 4) ^a	$\frac{\Delta\lambda}{\lambda}$ (10 $^{-4}$) ^c	$\Delta\rho(0)$ ^c (a_0^{-3})
		+	-						
0	0.00	*G	*G	7.00 \pm 0.05	16 000	+(4 \pm 6)	+(0.19 \pm 0.17)		
	0.00	*O	*O	4.72 \pm 0.05	19 000	+(6 \pm 3)	+(0.16 \pm 0.16)		
1	-0.81 \pm 0.02	*O-H	*H-O	6.14 \pm 0.05	26 700	-(10 \pm 5)	+(0.83 \pm 0.18)	-0.71 \pm 0.20	-2.4 \pm 0.7
	+0.81 \pm 0.02	*H-O	*O-H	1.32 \pm 0.02	17 600	-(25 \pm 10)	-(0.59 \pm 0.35)		
2	-0.81 \pm 0.02	*O	*H	3.15 \pm 0.03	17 400	-(17 \pm 5)	-0.44 \pm 0.17	-0.89 \pm 0.18	-3.0 \pm 0.6
	+0.81 \pm 0.02	*H	*O	3.99 \pm 0.04	33 200	-(245 \pm 9)	-(2.21 \pm 0.33)		
3	-1.24 \pm 0.02	*O-C	*C-O	9.35 \pm 0.05	22 400	-(370 \pm 4)	+(1.19 \pm 0.14)	-0.92 \pm 0.11	-3.2 \pm 0.4
	+1.24 \pm 0.02	*C-O	*O-C	3.11 \pm 0.03	23 900	+(79 \pm 7)	-(0.70 \pm 0.27)		
	+1.24 \pm 0.02	*C-O	*O-C	4.94 \pm 0.05	23 200	+(193 \pm 5)	-(0.62 \pm 0.21)		
4	-2.09 \pm 0.03	*O-F	*F-O	2.36 \pm 0.03	28 600	+(1728 \pm 18)	+(1.19 \pm 0.43)	-1.75 \pm 0.29	-6.0 \pm 1.0
	+2.09 \pm 0.03	*F-O	*O-F	3.46 \pm 0.03	40 400	-(3848 \pm 6)	-(2.50 \pm 1.02)		
	+2.09 \pm 0.03	*F-O	*O-F	1.05 \pm 0.02	27 000	-(349 \pm 18)	-(2.31 \pm 0.43)		

^a+ and - refer to the sign of the collected current.

^b*Refers to the ^{52}Fe labeled compound; the symbols G, O, H, C, and F refer to the compounds as indicated in Table I.

^cArithmetic mean value of symmetric experiments for $\Delta\delta$ positive.

within the error. As mentioned above, such small imperfections of the initial separation do not significantly affect the experimental $\Delta\lambda$ value.

$\Delta\lambda$ being proportional to $\Delta\delta$, compounds were chosen with large isomer-shift differences. The compounds used are given in Table I. The synthesis of these compounds was tested by Mössbauer spectroscopy (Fig. 5). The initial activities were equilibrated by weighing on a precision balance corresponding quantities with an equal number of Fe nuclei. As the self-absorption of the sources was equilibrated by adding corresponding amounts of the nonradioactive complementary compound, the Mössbauer spectra of the sources after the differential measurement (Fig. 6), are each time a superposition of two spectra of Fig. 5.

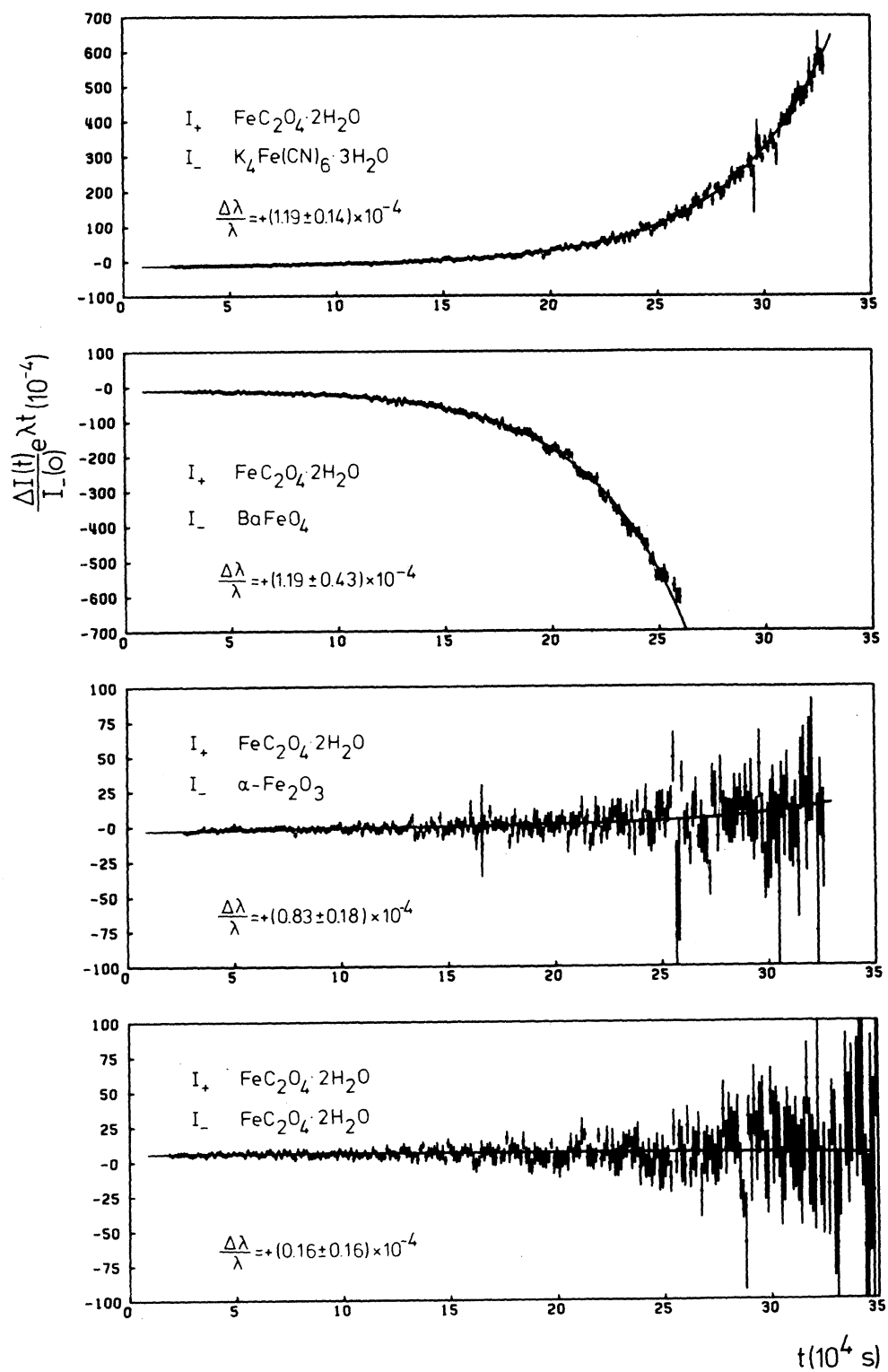
Except for the potassium diglycolate iron (III), that was only used in a "zero experiment" with two identical sources, each compound was compared to the Fe^{2+} oxalate. Haematite and potassium ferrocyanide are synthesized starting from Fe^{2+} oxalate: potassium ferrocyanide precipitates after adding a KCN solution to $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ whereas haematite is obtained by oxidation of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the air, at a temperature of 600 °C, during 30 min. In these

preparations there is thus no different supplementary Fe-Mn separation.

The synthesis of BaFeO_4 , which has a poor efficiency ($\sim 50\%$), is independent of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Moreover, it is accompanied by the production of more or less BaCO_3 , that cannot be eliminated in a simple way, so that the mass percent of Fe in this source is unknown. This means that self-absorption and activity are correlated and thus cannot be adjusted independently. This is the more troublesome as Ba is a heavily absorbing element, with a strongly changing absorption coefficient in function of the energies of ^{52}Fe and ^{52}Mn . This results in rather large $\Delta\beta$ values (cf. Table II) for the comparison of λ in BaFeO_4 and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

V. RESULTS AND DISCUSSION

The results are given in Table II. They are corrected for a $\sim 8\%$ systematic error in the experimental $\Delta I/I$ values, compared to the results presented at the International Mössbauer Conference, Kyoto 1978. The indices + and - indicate the signs of the respective ionization currents. Errors are purely statistical.

FIG. 7. Experimental curves $\Delta I(t)e^{+\lambda t}/I_-(0)$.

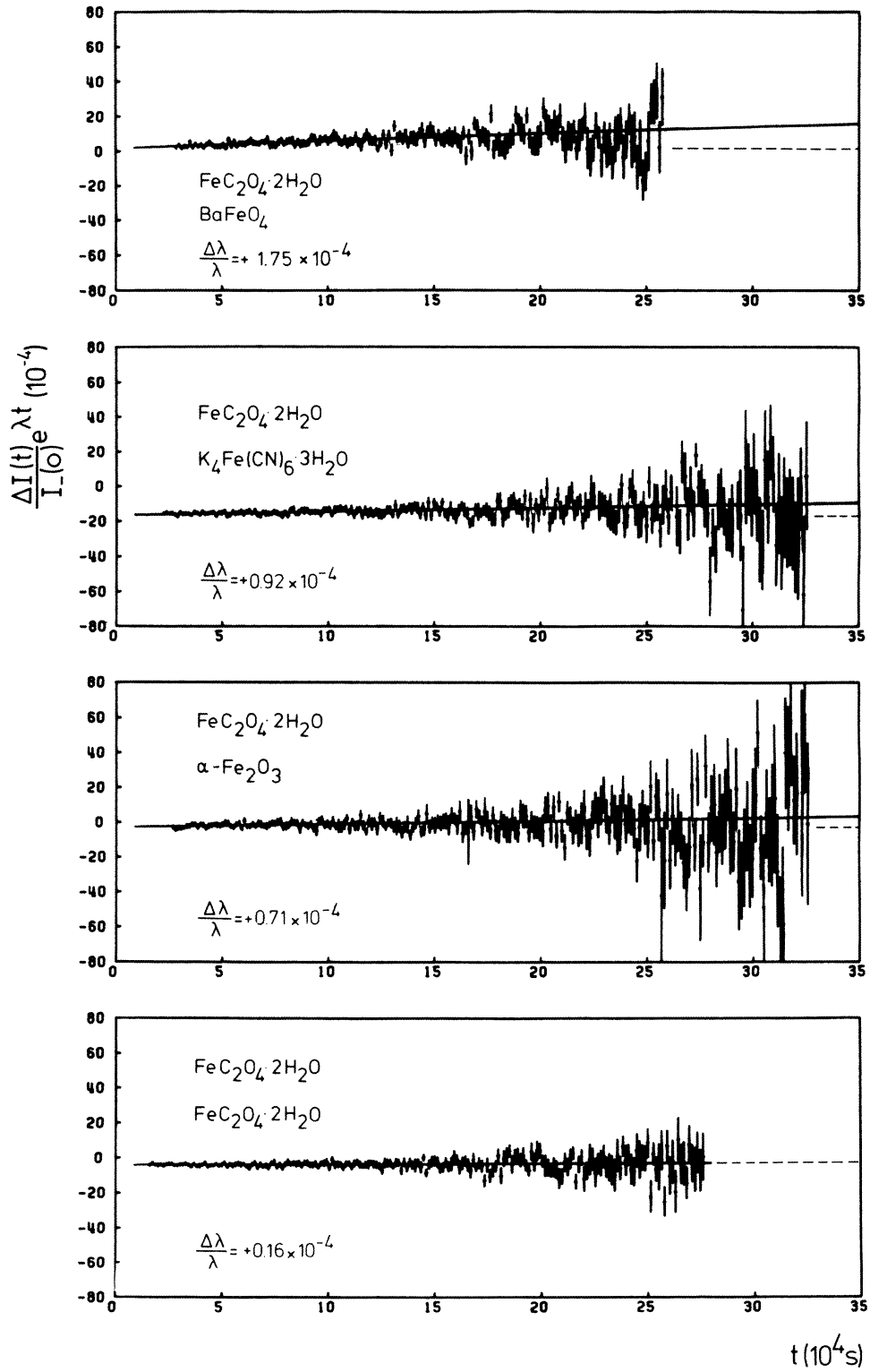


FIG. 8. Corrected curves $y_{ab}(t) = \frac{1}{2}[y_a(t) - y_b(t)]$, where the slope is proportional to $\Delta\rho(0)$.

$I(0)$ (column 4) is the reduction to $t=0$ of the ionization current of one source. Column 5 gives the time interval between the chemical separation of Fe and Mn, and the start of the differential measurement, whereas column 6 gives the differences between the efficiency ratios β . This $\Delta\beta$ is a good indication for the importance of the correction needed for the curvature of $\Delta I(t)/I(t)$. The error on $\Delta\lambda$ is function of $I(0)$ as well as of $t(1)$ and $\Delta\beta$. The relative difference in decay constant (column 7), is the fitted $(\lambda_- - \lambda_+)$ value, divided by the decay constant of ^{52}Fe as given in the literature,¹³ $\lambda = (2.327 \pm 0.002)\text{s}^{-1}$. While interchanging the source positions the experimental $\Delta\lambda$ value changes sign, as it should. The arithmetic mean of the absolute values of paired measurements (column 8) eliminates in first order the zero effect of the apparatus. For the pairs 1 and 3, where self-absorption in the sources and activity are well equilibrated, the zero effects eliminated in this way ($+0.11 \times 10^{-4}$ and $+0.25 \times 10^{-4}$) agree within the error with the effects measured with two identical sources (pair 0). In pair 2, the two sources have a different self-absorption resulting in a shifted zero effect ($\sim -1.30 \times 10^{-4}$). However, the arithmetic mean for this pair lies still within the error of the result of pair 1. As indicated above, the self-absorption and the activity cannot be decorrelated for the sources of pair 4. This results in a shift of the zero effect ($\sim -0.58 \times 10^{-4}$), be it smaller than in pair 2, on the one hand, and in rather large $\Delta\beta$ values, and thus a rather large error on the experimental $\Delta\lambda$ value, on the other hand. The last column of Table II gives the corresponding $|\Delta\rho(0)|$ values for $k=1$, and $\rho(0) = 15070a_0^{-3}$.¹⁴

Figure 7 shows some typical experimental $y(t) = \Delta I(t)/I(t)$ curves, for the different combinations of compounds. If one corrects these values for the fitted curvature, and then calculates for a pair of two measurements a and b , with interchanged source positions, the values $y_{ab}(t) = \frac{1}{2}[y_a(t) - y_b(t)]$, these $y_{ab}(t)$ values define a straight line, with $\Delta\lambda$ as slope. Figure 8 shows such $y_{ab}(t)$ curves for the different combinations of compounds; a and b are chosen in such a way that $\Delta\lambda$ is always positive.

As we find positive $\Delta\lambda$ and thus $\Delta\rho(0)$ values for negative $\Delta\delta$ values, the $\Delta\langle r^2 \rangle$ value for ^{57}Fe has to be negative, in agreement with the literature. In Fig. 9 $-\Delta\rho(0)$ is plotted against $\Delta\delta$. The slope of the least-squares-fitted straight line passing through the origin results in a calibration constant $\alpha = -(0.36 \pm 0.03)a_0^3 \text{ mm/s}$ corresponding to $\Delta\langle r^2 \rangle = -(33 \pm 3)10^{-3} \text{ fm}^2$. The absolute value is a lower limit, because of the uncertainty in the proportionality factor k between $\Delta\lambda/\lambda$ and $\Delta\rho(0)/\rho(0)$.

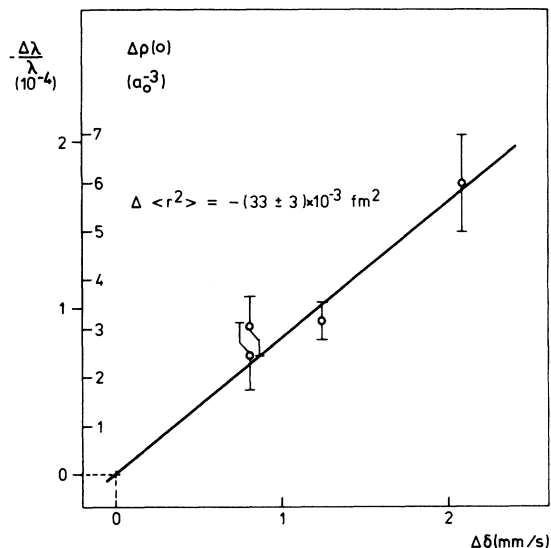


FIG. 9. Experimental differences in electron density at the nucleus, compared to the differences in isomer shift.

Our result is about four times larger than the $|\Delta\langle r^2 \rangle|$ value obtained in the comparison of direct lifetime measurements on the 14.4-keV level of ^{57}Fe in different chemical environments.^{5,15} However, as mentioned above, the sensitivity of their technique is doubtful, the standard deviation of a single measurement being three times as great as the mean (Ref. 15, Table I). In particular one should be sure that the spread of the results is purely statistical. Most recent estimations¹⁶ of $\Delta\langle r^2 \rangle$, based on molecular-orbital calculations of the electron density at the nucleus, yield a value around $-20 \times 10^{-3} \text{ fm}^2$, i.e., about 40% smaller than our experimental result. This could mean that the $\Delta\rho(0)$ values obtained from calculations are in general too large. However, we should remember that our analysis is based upon the assumption that the influence of chemical environment on the β^+ decay rate can be neglected. This point, even as the influence of overlap and exchange corrections on the proportionality factor k between $\Delta\lambda/\lambda$ and $\Delta\rho(0)/\rho(0)$, needs further investigation.

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