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Mössbauer Spectrometer Calibration Using TiFe*

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The splitting of the ^{57}Fe Mössbauer spectrum in TiFe has been carefully measured in a magnetic field and compared with the zero-field quadrupolar splitting of sodium nitroprusside. The comparison gives a value of 1.699 mm/s at 295 K for the sodium nitroprusside splitting. This determination makes use of the known Knight shift of Fe in TiFe and is independent of any velocity measurement. Comparison is made with the splitting of the inner two lines of a pure Fe spectrum.

Key words: Calibration; chemical shift; iron; Knight shift; Mössbauer effect; sodium nitroprusside; TiFe.

1. Introduction

The recent discovery [1][1] of the ^{57}Fe nuclear magnetic resonance in the non-ferromagnetic intermetallic compound TiFe makes this material useful as a reference material for use in Mössbauer effect spectroscopy.

The Mössbauer effect of TiFe in the absence of an external field gives a single resonance line. Applying a known external field splits this line and the separation of the resulting lines can be used to calibrate the Mössbauer effect spectrometer in magnetic field units, energy units, and velocity units. Conversely, if the velocity calibration is known, the TiFe spectrum can be used to determine the applied magnetic field. This is possible because the Knight shift of ^{57}Fe in TiFe is accurately known [1], and because TiFe has an ordered CsCl structure which places each Fe in a cubic site, giving a Mössbauer resonance with no resultant distortion due to the ^{57}Fe excited state electric quadrupole moment. Also the Knight shift of TiFe has the advantage that it is only weakly temperature dependent. By varying the applied field, the TiFe line splitting can be varied. Thus this material is useful for calibration over a wide range of velocities and for checking spectrometer linearity.

In this paper we present data comparing Mössbauer effect spectra of TiFe in a magnetic field of about [2] 50 kG and spectra of sodium nitroprusside (SNP) in zero field. Using this comparison we obtain a calibration for the quadrupole split lines of sodium nitroprusside. Although intrinsically no more precise than a direct velocity determination, this calibration is of interest because it is independent of any velocity measurement. Values quoted in the literature [2–7] for the room-temperature quadrupole splitting of sodium nitroprusside determined by direct velocity measurement vary from 1.65 to 1.85 mm/s. Several of the more precise of these determinations are compared in figure 1. The results obtained by the method used here are in close agreement with the direct velocity determinations of references [2] and [7].

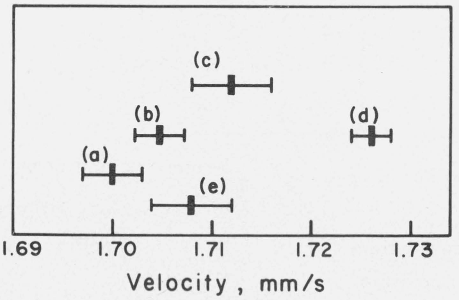

FIGURE 1. *Comparison of various results on the quadrupole splitting of sodium nitroprusside.*

(a) this work.
(b) reference [2].
(c) reference [4].
(d) reference [3].
(e) reference [7].

We have been informed that with new direct velocity measurements, Drs. J. R. DeVoe, J. J. Spijkermann, and J. C. Travis have obtained a value above 1.700 mm/s but within our error bar shown in (a).

The sodium nitroprusside calibration is of considerable interest in Mössbauer spectroscopy with ^{57}Fe. It has been issued [3] for use as a standard reference material for calibrating Mössbauer spectrometers and for comparing isomer shifts in iron-containing compounds. As previously noted by a number of authors [4, 8] sodium nitroprusside has several desirable characteristics for use as a standard. The fairly large

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[1] Figures in brackets indicate the literature references at the end of this paper.
[2] The field value was carefully measured using NMR, as explained in detail later.

quadrupole splitting is only weakly dependent on temperature (on the order [5] of 10^{-4} mm s^{-1} K^{-1} at room temperature). This is combined with an easily available high chemical purity and stability in addition to near natural resonance linewidths.

Using the results presented here, the Knight shifts and chemical shifts [3] of ^{57}Fe in Fe compounds can be measured to better than 0.5 percent by the Mössbauer effect. This is poor accuracy when compared with normal NMR results. However, it still offers the possibility of valuable results, since the NMR of ^{57}Fe in most compounds is much too weak to be measurable.

2. Experimental Procedure

The Mössbauer effect spectrometer-superconducting magnet system has been described in detail elsewhere [9]. A schematic of the experimental arrangement is shown in figure 2. The velocity drive unit was used in the constant acceleration mode and spectra were stored in a multichannel analyzer.

The source was about 100 mCi of ^{57}Co in a Pd matrix. It was prepared [4] by plating the requisite amount of carrier-free ^{57}Co in a 6-mm-diam circle on one side of a 25-μm foil of pure Pd. This was diffused in a hydrogen atmosphere at about 1270 K for 1 hr followed by a water quench.

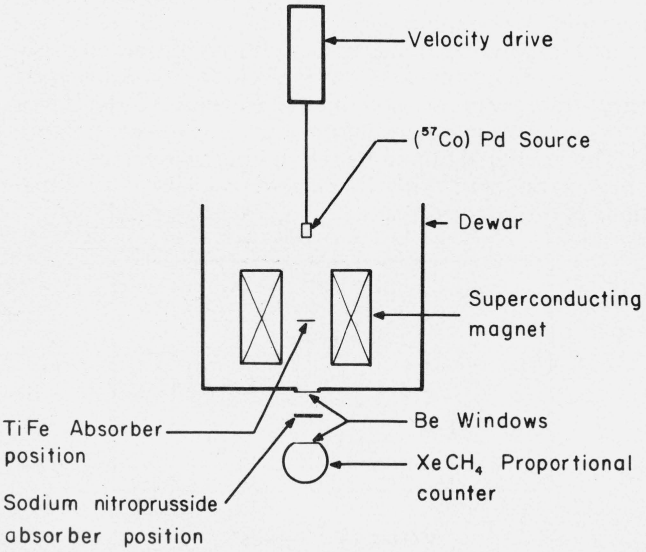

FIGURE 2. *Schematic drawing of the experimental arrangement.*
The source temperature was controlled at 210 K, the TiFe absorber at 120 or 60 K. The sodium nitroprusside temperature was 295 K. The source-to-detector distance was 0.33 m. The γ-ray beam was collimated to a 12-mm diameter at the TiFe absorber position.

The TiFe alloys were prepared by arc melting weighed quantities in an argon atmosphere. The ingots were turned and remelted three times during arc melting. The purity of the starting materials was Ti 99.97 percent and Fe 99.999 percent (no ^{57}Fe enrichment was used). An excess of one atomic percent Ti above the stoichiometric quantity was used. This gives a more perfectly ordered alloy, as evidenced by NMR signal strength [10] and ME line shape [11]. The arc-melted ingot was homogenized at 1470 K for 72 hr and then crushed to a powder. The powder was then annealed by sealing in an evacuated quartz ampoule, heating at 1170 K for 1 hr, then cooling to 870 K by reducing the temperature 30 K/hr. Two samples were prepared from separate melts and the measurements to be reported later detected no significant difference in their ME. (The same annealing procedure was used by Swartz et al. [1] for the TiFe samples in which ^{57}Fe Knight shift measurements were made.) From the annealed powders −200 mesh particles were obtained. These particles were embedded in a lucite disk about 12 mm in diameter and 2 mm thick with enough powder to give 0.02 μg/m^2 of ^{57}Fe.

The sodium nitroprusside sample [5] was in the form of a 10 mm square cut from a single crystal with the surface parallel to the *ac* plane of the crystal [2]. It was approximately 0.8 mm thick yielding 0.055 μg/m^2 of ^{57}Fe.

The magnetic field was calibrated by measuring the NMR frequency of Cu at 4.2 K with a super-regenerative detector. Details of this measurement are described more fully in the section on systematic errors.

Runs were made alternately on sodium-nitroprusside and TiFe. A total of eleven sodium nitroprusside spectra and nine TiFe spectra were obtained over a period of about 12 days.

3. Results

A summary of the measurement conditions for each run is given in table 1. The spectrum, $w(x)$, taken with no sample was used to determine the small perturbation introduced by the presence of Fe in the beryllium windows of the magnet dewar and proportional counter. This spectrum is a doublet and was least squares fitted to obtain its position, splitting, and width. Since the sodium nitroprusside is in a small fringing field of several hundred gauss, two runs were taken with the magnet coil de-energized. No significant difference was detected when compared to the spectra taken with the coil energized.

All spectra were least squares fitted using an equation of the form

$$y(x) = a + bx + cx^2 + dw(x) + \sum_{\alpha} h_\alpha D(x, \Delta_\alpha, C_\alpha, \Gamma_\alpha, \epsilon_{h\alpha}, \epsilon_{w\alpha})$$

where

$$D(x, \Delta_\alpha, C_\alpha, \Gamma_\alpha, \epsilon_{h\alpha}, \epsilon_{w\alpha}) = \frac{1+\epsilon_{h\alpha}}{\left[\frac{2}{\Gamma_\alpha(1+\epsilon_{w\alpha})}\right]^2 \left(x - \frac{\Delta_\alpha}{2} - C_\alpha\right)^2 + 1} + \frac{1-\epsilon_{h\alpha}}{\left[\frac{2}{\Gamma_\alpha(1-\epsilon_{w\alpha})}\right]^2 \left[x + \frac{\Delta_\alpha}{2} - C_\alpha\right]^2 + 1}. \qquad (1)$$

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[3] By chemical shift we mean the NMR frequency shifts often observed in nonmetals. The term chemical shift has sometimes been used to refer to the isomer shift, which is measureable only by ME.

[4] The source preparation was performed by the New England Nuclear Corp., Boston, Mass.

[5] Standard reference material 725; disodium pentacyanonitrosoferrate dihydrate ($Na_2Fe(CN)_5NO \cdot 2H_2O$). Otained from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. in October 1966.

TABLE 1. *Summary of measurement conditions and results obtained*

All runs taken with source at 210 K, magnetic field at 50.131 kG, SNP at 295 K, and TiFe at 120 K, except as noted. The Δ_1 ratios are obtained by averaging the SNP results before and after each TiFe run.

Run No.	Absorber	Δ_1	$\frac{\Delta_1(\text{SNP})}{\Delta_1(\text{TiFe})}$
010970.1	SNP	175.97	
010970.2	TiFe	169.20	1.0403
011070.1	SNP	176.06	
011070.2	TiFe [a]	169.26	1.0396
011170.1	SNP	175.88	
011270.1	SNP [b]	175.73	
011270.2	TiFe	169.03	1.0398
011370.1	SNP	175.80	
011470.1	None [c]		
011470.2	TiFe [a]	168.48	1.0446
011570.1	SNP [b]	176.18	
011570.2	TiFe	169.10	1.0409
011670.1	SNP	175.84	
011670.2	TiFe	168.59	1.0426
011770.1	SNP	175.72	
011770.2	TiFe [d]	168.79	1.0403
011970.1	SNP	175.47	
011970.2	TiFe [d]	168.85	1.0409
012070.1	SNP	176.03	
012070.2	TiFe [d]	168.30	1.0457
012170.1	SNP	175.94	

[a] Second of two samples of TiFe.

[b] No magnetic field.

[c] This run used to obtain window doublet parameters.

[d] TiFe at 60 K.

Here $y(x)$ refers to the amount of resonant absorption as a function of channel No. x. The parameters a, b, and c represent a background parabola arising from the fact that the source-detector distance is varied in the experiment. The doublet due to the presence of Fe in the beryllium windows, determined in the run with no absorber, is represented by $w(x)$ and d is the height of this doublet. For fitting the sodium nitroprusside spectra one doublet is used (see fig. 3) and the summation index α runs over only $\alpha=1$. The TiFe spectra are fitted to two doublets, an outer and a narrowly spaced inner (see fig. 4) and the summation index α runs over $\alpha=1$ and $\alpha=2$. The parameter Δ_α represents the doublet splitting, C_α the center of the doublet, Γ_α the full width at half maximum (FWHM) of each doublet line, $\epsilon_{h\alpha}$ any difference in the height of the two doublet lines, and $\epsilon_{w\alpha}$ any difference in the width of the two doublet lines.

The least squares fit was accomplished by an iterative procedure. The function $y(x)$ was expanded in a Taylor series with only the linear terms retained. Partial derivatives with respect to the various parameters were determined numerically. Initial estimates of a, h_α, C_α, and Γ_α could be made from the raw data to within 5 percent of their final value. The initial estimates for b, c, $\epsilon_{h\alpha}$, and $\epsilon_{w\alpha}$ were taken as zero. The initial estimate for d was determined from a spectrum taken with no absorber. On two of the spectra several least squares fitting procedures were used to determine the effect of deleting various combinations of the background parabola, window doublet, and assymmetry parameters. This is discussed in the next section on systematic errors.

Determination of the splitting of the outer doublet of the TiFe spectrum Δ_1(TiFe) in a known field calibrates the spectrometer. From the splitting of the sodium nitroprusside doublet in channels Δ_1(SNP), the splitting in velocity, v(SNP) is given by

$$v(\text{SNP}) = \lambda(1+3g_1/g_0)(1+K(T))\left(\frac{\gamma}{2\pi}\right)H\frac{\Delta_1(\text{SNP})}{\Delta_1(\text{TiFe})} \tag{2}$$

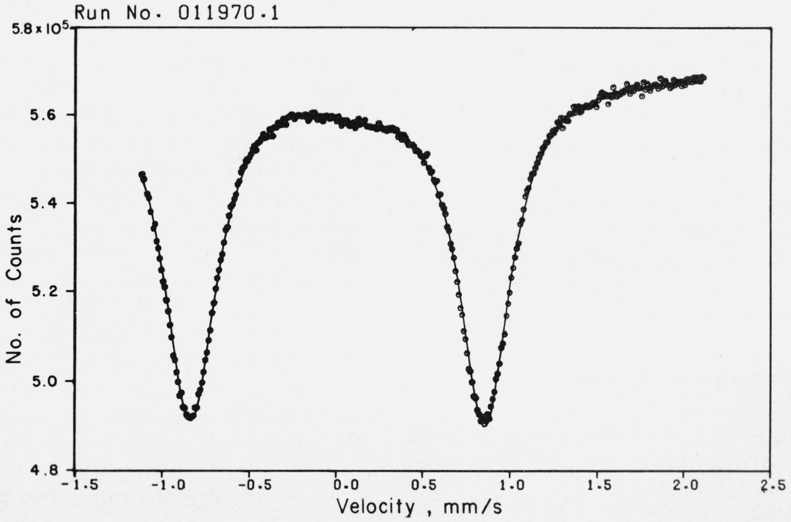

FIGURE 3. *Typical spectrum of sodium nitroprusside.*

Circles are experimental points and the solid line is the least squares fit. The direction of gamma-ray propagation is along the *b* axis of the crystal. Distortion of background due to Fe in beryllium windows is evident. Velocity zero is taken as the center of the two prominent peaks.

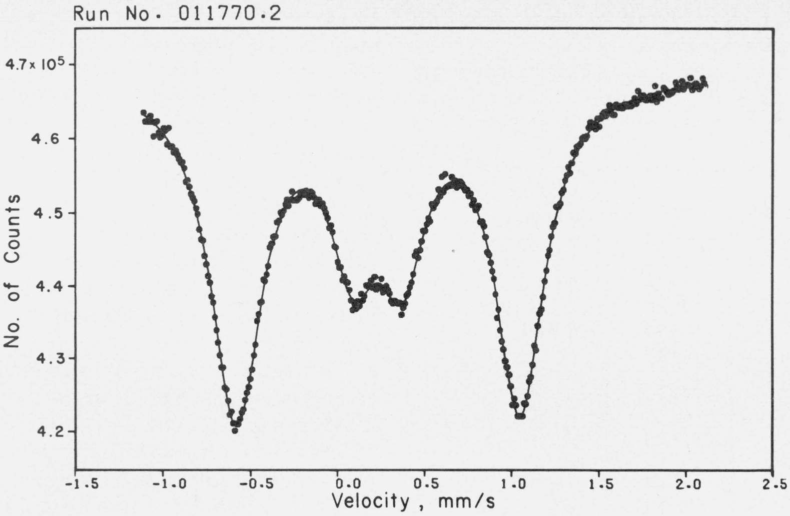

FIGURE 4. *Typical spectrum of* TiFe *in a magnetic field.*

Circles are experimental points and the solid line is the least squares fit. The sample was a polycrystalline powder. Velocity zero the same as for figure 2.

where λ is the wavelength of the Mössbauer effect gamma ray, g_1/g_0 is the ratio of the ^{57}Fe excited state level splitting to ground state splitting, $K(T)$ is the Knight shift of Fe in TiFe, $\gamma/2\pi$ is the gyromagnetic ratio of the ^{57}Fe ground state, and H is the applied field.

In table 1 are listed the 9 values obtained for the ratio $\Delta_1(\mathrm{SNP})/\Delta_1(\mathrm{TiFe})$. For the parameters we adopt

$$\lambda = 0.860231\ \text{Å}^{*}\ \text{[12][6]}$$

$$[1+K(T)]\,\frac{\gamma}{2\pi} = \begin{cases} 139.37\ \text{Hz/G at T} = 120\ \text{K}\text{[7]} \\ 139.42\ \text{Hz/G at T} = 60\ \text{K}\text{[7]} \end{cases}$$

$$3g_1/g_0 = 1.714.$$

The selection of these values and their contribution to the systematic error are discussed in the next section. Using these values, and the numbers listed in table 1, we obtain

$$v(\mathrm{SNP}) = 1.6993 \pm 0.0024\ \text{mm/s}$$

as a 90 percent confidence interval[8] for the sodium nitroprusside splitting at 295 K determined as described above. The contribution of the systematic errors are greater than the uncertainty in this value. They are discussed and estimated in the next section.

4. Systematic Errors

Besides the obvious sources of error, the determination of the position of a resonance line to within a few percent of its linewidth presents numerous difficulties. In this section we evaluate the known systematic errors in our determination of the sodium nitroprusside line splitting.

4.1. Magnetic Field Measurement

The magnetic field measurement utilized the ^{63}Cu nuclear magnetic resonance at 4.2 K. The Knight shift of Cu is accurately known [13] (0.232 %) and is nearly temperature independent. A super-regenerative detector of the type described by Rubinstein and Shtrikman [14] was used with a quench frequency of 20 kHz. The ^{63}Cu line was broadened to about 30 kHz by the field inhomogeneity. The accuracy of this method is better than one-half the resonance linewidth and is thus better than about 0.02 percent. No change in resonance frequency was detected when the superconducting magnet was switched to persistent mode. However, there was a field drift of 0.25 percent per hour in the persistent mode. To correct for this, the voltage drop across an 0.001Ω resistor required to give a field of 50.196 kG was measured. During the TiFe runs the field was readjusted every 0.5 hr to this value, giving an average field of 50.131 kG. Measurements of the field were made both before and after taking the ME spectra with no significant change detected. By moving the NMR probe in the magnetic field, the homogeneity of the field was estimated to be better than 0.1 percent over a 12.5-mm sphere. Considering all these factors, we estimate that the magnetic field error could contribute no more than 0.0015 mm/s to the systematic error.

4.2. Gamma-Ray Wavelength

The uncertainty in the value of λ[12] is less than 100 ppm. This is an order of magnitude smaller than the uncertainty of our measurement and will contribute

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[6] This value is based on comparison with $\lambda_{WK\alpha} = 0.2090100$ Å* [12]. Professor J. A. Bearden has kindly informed us that this is his most accurate value at present.

[7] Taken from ref. [1]. These values are based on an effective nuclear moment of ^{39}K in the reference salt (aqueous KI) of 0.39090 μ_N.

[8] Calculated as described by M. G. Natrella in NBS Handbook 91 (U.S. Government Printing Office, 1963) p. 2–2.

less than 0.0002 mm/s to the systematic error in the sodium nitroprusside splitting.

4.3. Knight Shift Values

The uncertainty in the product $[1+K(T)]\gamma/2\pi$ is likewise small and is given [1] as about 300 ppm. Since we use only the product and not $K(T)$ alone, any uncertainty in the ground state nuclear moment of ^{57}Fe does not affect our result. Also, there is no reason to expect a field dependence of the Knight shift of TiFe up to fields much larger than those used here. This view is supported by the fact that there is no detectable change in the TiFe spectra upon lowering the temperature from 120 K to 60 K. The contribution of the Knight shift value to the systematic error is less than 0.0005 mm/s.

4.4. Velocity Drive Linearity

A schematic diagram of the velocity feedback circuit is shown in figure 5. In this experiment we depend critically on the linearity of the reference signal, and the ability of the feedback circuit to reduce the error signal to zero. Throughout the experiment, the error signal was continuously monitored at the output of operational amplifier $A2$. Knowing the parameters of the velocity transducer and the values of R_1, R_2, R_3, and C_1, a correction could be made for the feedback error. However, in no case would this error have exceeded 0.03 channels (out of 175 channels peak separation) and hence it was neglected.

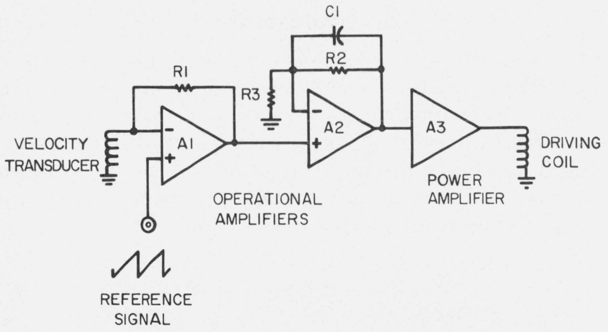

FIGURE 5. *Velocity spectrometer feedback circuit.*

Values of the parameters used were: R1 – 250 kΩ; R2 – 825 kΩ; R3 – 1 kΩ; C1 – 0.047 μF; velocity transducer – 19 kΩ, 2.4 Hr, with 20 vs/m sensitivity.

The channel address voltage of the multichannel analyzer was used to control the reference signal (as described by Ruegg et al. [15]). Operation can be linear only if the reference signal voltage is proportional to the analyzer channel number. This was checked by measuring the reference signal voltage with a precision voltmeter as a function of channel number. A small nonlinearity of ±0.15 channels over the 332 channels utilized was detected. However, since the TiFe peaks and the sodium nitroprusside peaks fall within 18 channels of each other, the change in Δ_1(SNP)/Δ_1(TiFe) by correcting for this nonlinearity would be only 0.0003 mm/s. This same reasoning applies for any nonlinearity in the velocity transducer. The transducer[9] was a magnetically shielded coil about 180 mm long with an O.D. of 15 mm and with a bar magnet about 110 mm long moving through the inside of the coil. The difference in position of the bar magnet between corresponding peaks of the TiFe and the sodium nitroprusside spectra was only 80 μm. We thus expect the nonlinearity in the velocity transducer to shift the peaks of both TiFe and sodium nitroprusside equally and thus not affect the ratio Δ_1(SNP)/Δ_1(TiFe) significantly. Our estimate of the total systematic error due to velocity drive nonlinearity is 0.0008 mm/s.

4.5. Nuclear Moment Ratio

The ratio of the excited state to the ground state ^{57}Fe moment, $3\,g_1/g_0$, appears in eq (2) and affects the accuracy of the results. (This ratio is actually negative but here we use $3\,g_1/g_0$ to refer to its absolute value.) It cannot be determined accurately from our own spectra because of the reduced intensity and very close spacing of the inner two doublet lines. We therefore use the value of $3\,g_1/g_0$ determined for pure Fe. Several precision measurements of pure Fe Mössbauer spectra have been made. Using an ultrasonic technique, Cranshaw and Reivari [16] obtained $3\,g_1/g_0 = 1.715 \pm 0.003$. Using an interferometer to calibrate their spectrometer, Fritz and Schulze [17] obtained $3\,g_1/g_0 = 1.711 \pm 0.002$. Using Moiré fringes for velocity measurement, DeWaard [18] obtained $3\,g_1/g_0 = 1.713 \pm 0.004$, and using the lead screw of a lathe as a velocity drive, Preston et al. [19] obtained $3\,g_1/g_0 = 1.715 \pm 0.004$. Considering these values we adopt $3\,g_1/g_0 = 1.714 \pm 0.003$. The uncertainty in this value for g_1/g_0 yields an uncertainty of 0.0019 mm/s in the sodium nitroprusside splitting.

We mention the possibility of an anomalous hyperfine field effect [20] which could cause the apparent value of $3\,g_1/g_0$ to be different for ^{57}Fe in TiFe and ^{57}Fe in pure iron. The anomaly arises from the fact that the distribution of magnetic dipole density over the finite nuclear volume may be different for different isotopes or for the ground and excited nuclear states of the same isotope. The effect has been observed, for example, for the Knight shifts of ^{85}Rb and ^{87}Rb in rubidium metal [21] which are, respectively, 0.6527 percent and 0.6502 percent. This anomaly would lead to an error in magnetic field of 0.002 percent using Rb. The anomalous effect is thus expected to be negligible for ^{57}Fe in different materials because it generally decreases with decreasing nuclear size. It has not been detected within the precision of any Fe Mössbauer experiments to date. We therefore feel confident in neglecting it for this experiment.

4.6. Background, Asymmetry, and Vibration

The background for the spectra obtained here were perturbed from an ideal straight line due to the presence of Fe in the Be windows of the dewar and due to

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[9] L. V. Syn Model 6LV2, Sanborn Electronics, Waltham, Massachusetts.

source motion. To correct for these perturbations they were included as the parabola and window doublet of eq (1). Also, as indicated in eq (1), the heights and the widths of the doublets were allowed to be asymmetric. The window doublet fraction, d, averaged about 5 percent and the background parabola about 0.5 percent of the total absorption area. The height asymmetry, ϵ_h, averaged about 0.01 and width asymmetry, ϵ_w, about 0.02.

To test the effect of these factors on the results, various fits were made to the data of one TiFe spectrum and one sodium nitroprusside spectrum under various constraints on the parameters of eq (1). The results are shown in table 2.

The Γ_α's obtained for all runs varied from 34 to 36 channels, corresponding to a FWHM of 0.34±0.01 mm/s. This is about 0.07 mm/s larger than the width of 0.27 mm/s exhibited by both the TiFe and the sodium nitroprusside samples under ideal conditions. The excess width is due to vibrations arising from nearby vacuum pumps, building vibrations, etc. The effect of such vibrations is to give the center of the doublets a Gaussian probability distribution. When this assumption is put into eq (1) and a least squares fit made with the parameters Γ_α constrained to correspond to 0.27 mm/s, the results shown in table 2, line (e) are obtained.

A statistical analysis of the various fits shows that the constraints introduced in (b), (c), and (d) of table 2 all result in a statistically significant (5% level or better) increase in the standard deviation of fit. The analysis also shows that the assumptions made in (e) give the best fit to the data. As seen from table 2, the value of Δ_1(SNP)/Δ_1(TiFe) is in all cases quite insensitive to the method of fitting the data. The values of Δ_1, though still relatively insensitive, vary considerably more than the ratio Δ_1(SNP)/Δ_1(TiFe). When vibrations may be a problem the results shown in table 2 suggest that the most appropriate method would be to fit with a Gaussian distribution of natural-width Lorentzians. The results presented here are quite insensitive to the choice of fitting method since they depend only on the ratio Δ_1(SNP)/Δ_1(TiFe).

TABLE 2. *Effect of constraints on lease squares fitting results for run No. 012070.2* (TiFe) *and run No. 012170.1* (SNP).

Parameters of fit	Δ_1(TiFe)	Δ_1(SNP)	$\frac{\Delta_1(\text{SNP})}{\Delta_1(\text{TiFe})}$	Percent change from [a]	s_{fit} [f]	
					TiFe	SNP
([a])	168.30	175.94	1.0454	....	0.013	0.012
([b])	168.07	175.77	1.0458	+0.04	.016	.015
([c])	167.88	175.64	1.0462	+.08	.014	.015
([d])	167.90	175.67	1.0463	+.09	.017	.016
([e])	168.19	175.79	1.0452	−.02	.012	.010

[a] Fit to eq (1), no constraints, all parameters allowed to vary independently.

[b] Fit to eq (1), background parabola terms b and c and asymmetry terms $\epsilon_{h\alpha}$ and $\epsilon_{w\alpha}$ constrained to be zero.

[c] Fit to eq (1), height of window doublet d constrained to be zero.

[d] Fit to eq (1), height of window doublet d, background parabola terms b and c, and asymmetry terms $\epsilon_{h\alpha}$ and $\epsilon_{w\alpha}$ constrained to be zero.

[e] Fit to eq (1), with h_α given a Gaussian distribution as a function of C_α. Widths Γ_α constrained to 28.0 channels (corresponding to 0.27 mm/s). No other constraints.

[f] Standard deviation of fit, $s^2_{\text{fit}}=(y-y_{\text{obs}})^2/(N-P)$, where N is the number of data points, P is the number of independent parameters used in the fit, and the data points y_{obs} have been normalized to lie in the range of zero to unity. Both runs had an average of about 5×10^5 counts in each of 330 channels.

As seen in table 2, no correction due to background, asymmetry or vibration greater than 0.1 percent is used. We estimate the systematic error due to these factors to be no greater than one-half this correction, 0.0008 mm/s.

The systematic error contributions are summarized in table 3. The result for the sodium nitroprusside splitting is then 1.6993 mm/s with a precision of ±0.0024 mm/s based on a 90 percent confidence limit for the mean value of all determinations, and with a maximum systematic error of 0.0021 mm/s, not including possible errors in 3 g_1/g_0, λ, and $K(T)$.

TABLE 3. *Contributions to systematic error in this determination of the sodium nitroprusside splitting*

The first four are independently determined constants. The last three are unique with this measurement.

Parameter	Estimated error contribution
	mm/s
γ...........................	0.0002
$K(T)$......................	.0005
$3g_1/g_0$....................	.0020
Hyperfine field anamoly...............	.0000
H.........................	.0015
Linearity.................	.0008
Background, etc.......	.0008

5. Discussion

The sodium nitroprusside splitting obtained here is compared with other results in figure 1. Within the limit of error, the results compare favorably with those of Grant et al. [2] and Fritz [7]. It is also interesting to compare the splitting obtained for the sodium nitroprusside with a pure iron spectrum. From the results of four runs we estimate

$$\frac{(g_0-g_1)}{\Delta_1(\text{SNP})}=0.9886\pm0.0010$$

where (g_0-g_1) is the splitting of the inner two lines of a pure iron spectra. Using this, and the previously quoted value for 3 g_1/g_0 and assuming $\Delta_1(\text{SNP})=1.699$ mm/s we obtain $g_0=3.918\pm0.004$ mm/s and $g_1=2.238\pm0.004$ mm/s for pure iron at 295 K. These values are compared with previous ME results and with NMR results [22] in table 4. The Mössbauer effect results are in good agreement and give confidence in the correctness of the SNP value. The NMR results are listed for reference. Though inherently more accurate than the ME results, they cannot be directly compared since NMR in ferromagnetic iron measures the splitting for ^{57}Fe atoms in domain walls, whereas the ME measures the splitting for ^{57}Fe atoms within the domains. As described by Schechter et al. [23], the values of g_0 and g_1 are useful for calibrating and checking linearity of spectrometers using pure Fe.

TABLE 4. *Comparison of* g_0 *and* g_1 *values obtained for* ^{57}Fe *in pure* Fe *at* 295 ± 1 *K.*

Technique and Ref.	g_0	g_1
	mm/s	*mm/s*
ME, this work	3.918 ± 0.004	2.238 ± 0.004
ME [a] [16]	3.911 ± 0.003	2.236 ± 0.003
ME [17]	3.931 ± 0.003	2.242 ± 0.002
ME [18]	3.916 ± 0.005	2.236 ± 0.006
ME [b] [19]	3.920 ± 0.008	2.240 ± 0.005
NMR [a] [22]	3.909 ± 0.001	....

[a] Results given in frequency units, which we have converted to velocity units.
[b] Interpolated between values given for 293 and 298 K.

The results presented for TiFe and sodium nitroprusside make it possible to measure Knight shifts and chemical shifts of Fe in suitable alloys and compounds to about 0.5 percent or better.

To obtain more accurate results, several modifications to the equipment within the state of the art would be useful. This would include an interferometer or Moiré fringe counter for direct velocity measurement while the data are being accumulated. This would allow a check on the internal consistency of the results and, once calibrated, an accurate determination of applied field using TiFe spectra. Higher fields than used here are desirable in order better to resolve the inner two lines of the TiFe applied field spectrum. This would provide a sensitive test for the possible presence of a small hyperfine field anomaly and would allow calibrations of materials such as pure Fe with larger internal field splittings. Also, a more homogeneous and stable magnet would be useful, since the magnet field drift and inhomogeneity gave the largest contribution to the systematic error of this experiment.

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6. References

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