

# Mössbauer line-shape parameters for $^{183}\text{W}$ and $^{191}\text{Ir}$ in metallic tungsten and iridium

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We have carried out precise Mössbauer line-shape analyses in tungsten and iridium metal using an exact representation of the line shape in transmission. By using exceptionally intense sources ( $\sim 70$  Ci for  $^{183}\text{Ta}$ ) and carefully chosen constraints between sets of Mössbauer-effect spectra, we have been able to make a quantitative test of the theory of final-state effects. The temperature dependence of the recoilless fraction,  $f_a(T)$ , for  $^{183}\text{W}$  in tungsten metal has been determined to about 1% accuracy, which is an order of magnitude better than previous Mössbauer or x-ray investigations, between 80 and 1067 K. The Debye model fits our results from 80 through 968 K, with a Debye Mössbauer temperature of 336.5 K, when a correction for thermal expansion is included. The recoilless fraction data were used to derive a value of 8.76(10) for the internal conversion coefficient for the 46.5-keV transition in  $^{183}\text{W}$ , with an approach based on the quasiharmonic approximation to the lattice vibrations, which determines the temperature dependence of the recoilless fraction. The interference parameters, times 100, that we find in this investigation of  $^{183}\text{W}$  in tungsten metal (46.5 keV) and  $^{191}\text{Ir}$  in iridium metal (129 keV), are  $-0.317(6)$  and  $-0.77(10)$ , respectively. These values are both greater in magnitude than the theoretically calculated values by about 10%, although the  $^{191}\text{Ir}$  case has errors large enough that the comparison with theory is inconclusive. These results differ with theory, and would indicate that the theoretical calculations of interference need refinement if they are to be used in studies of time-reversal invariance.

## I. INTRODUCTION

The Mössbauer effect permits a sensitive test of several nuclear and solid-state properties, among them recoilless fraction, which reflects lattice-dynamical properties, interference, and isomer lifetimes. Recoilless-fraction measurements complement specific-heat measurements, and precise measurements of recoilless fraction over temperature, made using well-resolved spectra and exact line-shape analysis, may serve to test theories of vibrations of crystal lattices. Interference, which is sometimes called a final-state effect, since it arises from the interference between competing modes of absorption and reemission of  $\gamma$  rays and electrons, is important, since crucial tests of time-reversal invariance (TRI) depend heavily on theoretical models that have never been adequately tested. The lifetimes of excited states of Mössbauer nuclei, or isomeric lifetimes, can also be measured quite precisely using the Mössbauer effect, and, in the absence of complicating solid-state effects, may be measured with greatest precision using this method.

This work represents a study of basic physical properties associated with two Mössbauer transitions, the 46.5-keV transition in  $^{183}\text{W}$  in tungsten metal and the 129-

keV transition in  $^{191}\text{Ir}$  in metallic iridium. We have obtained superior resolution in our spectra through our use of sources of very high intensity, in the range of 10–100 Ci and (in the case of the  $^{183}\text{W}$  transition) through the use of a monochromating crystal filter to separate the Mössbauer line from intense background radiation. We have, in addition, analyzed spectra using an exact representation of the transmission integral describing the Mössbauer line shape in transmission. The importance of fitting Mössbauer data to the transmission integral was first noted by Gerdau *et al.*,<sup>1</sup> although their approach to the problem was to fit data directly to the convolution integral rather than an analytic representation as used in the present study.

Although it is widely known that the experimental spectrum resulting from a Mössbauer-effect (ME) experiment done in transmission is not truly Lorentzian, the vast majority of such spectra are analyzed using this line shape. The ME spectrum is a Lorentzian only in the limit of vanishingly small absorber thickness with an ideal unsplit source, and, in an effort to realize this ideal line shape, experimenters conventionally use absorbers of thickness number four or less. Credible fits are obtained only by relaxing the width as an adjustable parameter, which destroys the theoretical basis for the Lorentzian

and such fits can then be regarded as nothing more than empirical. It has been shown,<sup>2</sup> e.g., that an exponential Lorentzian is a much better empirical fit requiring no greater computer time than a Lorentzian for a fit. Fundamental properties such as line width, interference, and recoilless fraction are then deduced from the parameters derived by least-squares fits to such spectra by any of a number of approximation methods. However, this (Lorentzian) treatment of ME spectra suffers from a number of drawbacks.

(1) The linewidth is determined by taking a succession of spectra with absorbers of various thicknesses and plotting the linewidth parameter versus the thickness number, and the linewidth is determined by the extrapolation to zero thickness. Not only is the extrapolation process itself suspect, because of possible contributions from hyperfine field or instrumental vibration, but constraints of limited counting time will usually mean that these redundant spectra are poorly resolved, especially for the thin absorbers, further compromising the accuracy of the method.

(2) Recoilless fraction measurements (in an absorber experiment) are usually carried out by estimating the area under the absorption curve. Since the Lorentzian does not give the correct value of asymptotic absorption (the baseline), the estimate of area may be greatly in error, especially in the resonance wings. The area method, furthermore, yields only a relative measure of recoilless fraction, and normalization to give absolute values is difficult. The resulting parameters will generally depend on the velocity range used to scan the spectrum, which is not the case for data fitted directly to the convolution integral.

(3) The estimate of interference will always be in error. The magnitude of interference is very small, and accurate measurements require extremely well-resolved spectra, the more so the thinner the absorber. Precision determination of the interference parameter requires very-high-resolution data fitted to the exact line shape.

We have used an exact representation of the Mössbauer line shape in transmission<sup>3</sup> to derive precise values of fundamental parameters associated with the 46.5-keV transition in <sup>183</sup>W and in the 129-keV transition in <sup>191</sup>Ir. This formulation permits the inclusion of interference and source-resonance self-absorption (SRSA), although the experiments reported here made the latter feature unnecessary, as SRSA was quite small. The use of the exact line shape to analyze data makes it possible to use absorbers of arbitrary thickness and, in contrast to the usual practice of Lorentzian fits, we find that thicker absorbers are altogether to be preferred to thin ones. This is because the symmetric component of the absorption saturates at lower thickness numbers than the asymmetric component, so that interference is more easily determined from thick absorbers and because saturation of the symmetric component helps to make clear the relative contribution of absorber thickness and source recoilless fraction to the amplitude of the resonance.

## II. THEORY

### A. Line shape

Data were fitted to the theoretical line shape

$$C(x) = C_0 \left( (1 - f_{so}) + \frac{2f_{so}}{\pi} \int_{-\infty}^{\infty} \frac{\exp[-t\mathcal{L}(2x')]}{1 + 4(x - x')^2} dx' \right), \quad (1)$$

which represents the experimental spectrum resulting from unsplit Lorentzian emission and absorption profiles. Here,  $x = E_0(v - v_0)/\Gamma c$  and  $x'$  are dimensionless variables representing the relative source-absorber velocity and photon energy, respectively, where  $E_0$  is the transition energy and  $v_0$  is the peak position of the resonance in velocity units,  $f_{so}$  is the source recoilless fraction, and

$$\mathcal{L}(x) = \frac{1 - 2\beta x}{1 + x^2}, \quad (2)$$

is the Lorentzian absorption profile plus a term representing interference. We have adopted the minus sign in front of the asymmetric  $\beta$  term, which is required if  $x > 0$  for energies above the resonance peak. Several authors use the opposite convention ( $x < 0$  for energies above the resonance peak), which changes the sign of the interference term to plus. The relative velocity  $v$  between source and absorber is taken to be positive for the absorber approaching the source.  $\Gamma$  is the level width in energy units,  $\hbar/\tau$ , where  $\tau$  is the mean life of the excited state. The absorber thickness number  $t$  is defined by

$$t = f_a a_{a1} n_a \sigma_0, \quad (3)$$

where  $f_a$  is the absorber recoilless fraction,  $a_{a1}$  is the fraction of atoms in the absorber represented by the Mössbauer isotope,  $n_a$  is the number of atoms of all types per unit area in the absorber, and  $\sigma_0$  is the resonance cross section

$$\sigma_0 = \frac{\lambda^2}{2\pi} \frac{2I_e + 1}{2I_g + 1} \frac{b}{1 + \alpha}. \quad (4)$$

Here  $\lambda$  is the wavelength of the resonant photons,  $I_e$  and  $I_g$  are the spins of the nuclear excited and ground states,  $b$  is the branching ratio, equal to one for the cases considered herein, and  $\alpha$  is the internal conversion coefficient. Since  $\alpha$  is generally not well known, values of  $t$  can be used to find values of  $f_a/(1 + \alpha)$ , and these will give  $f_a$  directly only when  $\sigma_0$  is accurately known.

Correlation among parameters, in particular  $f_{so}$  and  $t$ , and to a lesser extent  $\Gamma$ , makes it generally difficult to obtain a precise fit of individual spectra to Eq. (1). This property has been noted before<sup>4-6</sup> and derives from the fact that both  $f_{so}$  and  $t$  contribute nearly linearly to the amplitude of the spectrum, especially when  $t$  is small compared to unity, and even for  $t$  of order 3, a commonly used value in Mössbauer spectroscopy. This is a minor drawback and is easily corrected<sup>4,7</sup> by simultaneously fitting multiple spectra with any of several constraints on the fitted parameters and especially on the correlated pa-

rameters. The most basic constraint, of course, is that  $\Gamma$  and  $\beta$  be the same (for all spectra taken in the same transition), and under suitable conditions, such as when the radiation is essentially free of background from having been scattered,  $f_{\text{so}}$  is the same. In addition there may be a known relation between the thickness numbers characterizing the individual spectra, as when the ratio of physical thicknesses is known and the absorbers are at the same temperature. Of course, if a data set is sufficiently precise (high count statistics), the parameters will assume nearly correct values in an individual fit. The joint fitting of spectra with known constraints then is a way of improving the efficiency of finding line-shape parameters, since the requirements of precision are not nearly as severe as for individual fits. Fitting to changes in line shape as well as to line shape alone is also a good way to eliminate possible sources of systematic error, which could arise from unsuspected vibration or hyperfine interactions.

### B. Interference

Interference between resonant and Rayleigh scattering from a nucleus, as well as between the emission of internal conversion electrons and photoelectrons, leads to an asymmetry of line shape described by the interference parameter  $\beta$ . This is represented by the small dispersive term involving  $\beta$  in  $\mathcal{L}(x)$ , where the magnitude of  $\beta$  is usually of the order of the fine-structure constant. Precise analyses of Mössbauer spectra must include the interference parameter to obtain the correct isomer shift.<sup>3</sup>

The chief interest in interference, however, lies in its relation to experiments to test time-reversal invariance in mixed transitions. If the mixing coefficient is written

$$\delta = \pm|\delta|e^{i\eta}, \quad (5)$$

such an experiment seeks a value of the phase shift  $\eta$  different from zero or  $\pi$  as evidence of time-reversal violation. But interference produces an additional phase shift<sup>8,9</sup> (in an  $M1/E2$  transition)

$$\beta_T = \beta(E2) - \beta(M1), \quad (6)$$

so that the mixing ratio for the transition becomes

$$\delta = \pm|\delta|e^{i(\eta+\beta_T)}, \quad (7)$$

and such experiments measure  $\eta + \beta_T$  and not  $\eta$ . Since  $\eta$  may be quite small in relation to  $\beta_T$ , precise measurements of the Mössbauer interference parameter  $\beta$  are essential to testing the theoretical models used to calculate  $\beta(E2)$  and  $\beta(M1)$  from which  $\beta$  and  $\beta_T$  are determined, with  $\beta$  being given by

$$\beta = \frac{\beta(M1) + \delta^2\beta(E2)}{1 + \delta^2}. \quad (8)$$

## III. EXPERIMENTAL METHODS

### A. Spectrometer

The experiments were carried out at the Research Reactor Facility of the University of Missouri (MURR)

using the QUEGS (quasielastic gamma-ray scattering) instrument.<sup>10</sup> This is intended to be a brief review of the description in Ref. 10, and such details as differ from that reference and are common to both the experiments with tungsten and iridium will be described here.

Sources generated by neutron irradiation are installed in a heavily shielded source cask, which can be cooled by liquid nitrogen to about 77 K. The source material itself is confined to an aluminum can and mounted to a rod extending from the top to the bottom of the can.<sup>11,12</sup> Thermal contact between the source can and liquid-nitrogen jacket is improved by a constant flow of helium gas into the space between them (see Fig. 3, Ref. 10). Near the exit window in the source cask for the photon beam, there is provision for the mounting of a monochromating crystal.

The Doppler shift energy required to scan the Mössbauer spectrum was supplied to the absorber by a translating stage capable of a maximum speed of 14 cm/s. This translator consisted of a platform mounted on Thomson rods and using Teflon ball bearings to minimize vibration, on which either a cryostat or furnace could be mounted. A large auxiliary flywheel was mounted on the end of the countershaft, in order to reduce the amplitude of angular speed variations due to inertial loading. These variations were found to be less than  $\pm 0.3\%$ , and correcting for these small variations in joint fits to data produced negligible differences in results. The velocities obtained using a crank are not a pure sinusoid and the exact motion was used to calculate the velocities. The  $\gamma$  beam was detected with an intrinsic germanium detector, and the resulting pulses were selected by a single-channel analyzer and gathered by a multichannel scaler. The collimation confined the beam to an angle of about  $\pm 0.002$  radians in the horizontal and about  $\pm 0.007$  radians in the vertical; the total source-detector distance was about 1.5 m. With this geometry, distortion of the spectrum due to "cosine smearing," that is, due to noncollinearity of photon trajectories, was almost completely absent. In addition, all Mössbauer spectra were taken in approximately 512 channels, so that distortion due to channel averaging may be neglected.

### B. Tungsten experiments

Sources were strips of natural tantalum foil 0.003 inches thick, and measuring about  $0.25 \times 1.25$  in.<sup>2</sup>, which are mounted in aluminum cans. The sources were each irradiated for 6 days in a flux of about  $3 \times 10^{14}$  neutrons/cm<sup>2</sup> s, giving an activity of about 70 Ci for the 5.1 day half-life  $^{183}\text{Ta}$ . The principal activity produced is  $^{183}\text{Ta}$ , resulting from double neutron capture by  $^{181}\text{Ta}$ , so that such background as may have been present after scattering decayed largely at the same rate as that of the 46.5-keV line. For sources of this intensity, source-resonant self-absorption (SRSA) can seriously distort line shape if  $t_{\text{RS}}$ , the effective thickness of the source treated as if it were an absorber, is too large.<sup>3</sup> All sources

were fresh, that is, had not been previously irradiated, so that maximum  $t_{RS}$  during the course of the experiment was held to about 0.05 and did not differ by more than about 0.03 for any of the spectra. Experimental tests<sup>11</sup> of our calculations of  $t_{RS}$  have substantiated this estimate of SRSA. The radiation from the sources was scattered using the (200) reflection of a prestressed lithium fluoride crystal and the 46.5-keV  $\gamma$  rays, essentially free of background, were subsequently collimated through heavy shielding. Dead time for the detection system was 20  $\mu$ s for this experiment, and the counting rate was held to about 2000 counts per second with the absorber in place. Fits including dead time made a negligible difference in parameter values.

The absorber for experimental runs at room temperature and above consisted of seven tungsten foils, each nominally 0.001 in. thick, enclosed in a pillbox made of boron nitride, to ensure uniformity of temperature over the surface of the foils. Additionally, boron nitride baffles were used on each side of the absorber assembly to prevent convection. The foils were placed in a quartz tube in an electric furnace, designed after the technique of Mullen and Knauer.<sup>13</sup> A constant flow of argon gas was maintained through the chamber containing the absorber during all experiments with the furnace.

Two chromel-alumel thermocouples were in contact with the pillbox above and below where the beam struck. A subsequent calibration based on the Curie temperature of iron and direct comparison with a National Institute of Standards and Technology calibrated thermocouple indicated that the thermocouples read high by 6 K (0.5%) at the highest temperature, and the readings were adjusted in compensation. The temperature of the absorber was taken as the average of the two thermocouple readings;

in any event, they did not differ by more than 1 K, and the temperature measurement is held to be accurate to 1 K.

For the measurement at 77 K, a liquid-nitrogen cryostat was used containing four foils, each nominally 0.001 in. thick, from the same stock used for the furnace foils, and fastened to an oxygen-free copper block attached to the liquid-nitrogen container, and a platinum resistance thermometer (RTD) was used to measure temperature. The RTD was checked at liquid-nitrogen temperature (77 K) and at room temperature and found to be accurate to 1 K without correction.

### C. Iridium experiments

The two sources used were prepared from 330 mg of natural osmium (26.4 atm. %  $^{190}\text{Os}$ ) powder, pressed into a cavity 0.3 cm wide  $\times$  2.50 cm high  $\times$  0.088 cm deep and contained by an aluminum can of the same dimensions as the cans used for the tantalum sources. The first and second sources were irradiated for three and four weeks, respectively, at a flux of about  $2.5 \times 10^{14}$  neutrons/cm<sup>2</sup> s, yielding estimated activities of  $^{191}\text{Os}$  of 14 Ci and 16 Ci, respectively. SRSA was quite small; maximum  $t_{RS}$  was less than 0.005. A pulse-height spectrum of the  $^{191}\text{Os}$  source, taken using the QUEGS intrinsic-germanium detector, is shown in Fig. 1, and the 129-keV line is very well resolved, even without a monochromating crystal.

Absorbers were foils of natural iridium metal, each nominally 0.01 in. thick. Due to the high energy of this transition, it was not possible to scatter efficiently using the crystal mentioned above, unless a thicker crystal than was available to us were used. Therefore, it was decided to take spectra directly in an unscattered photon beam.

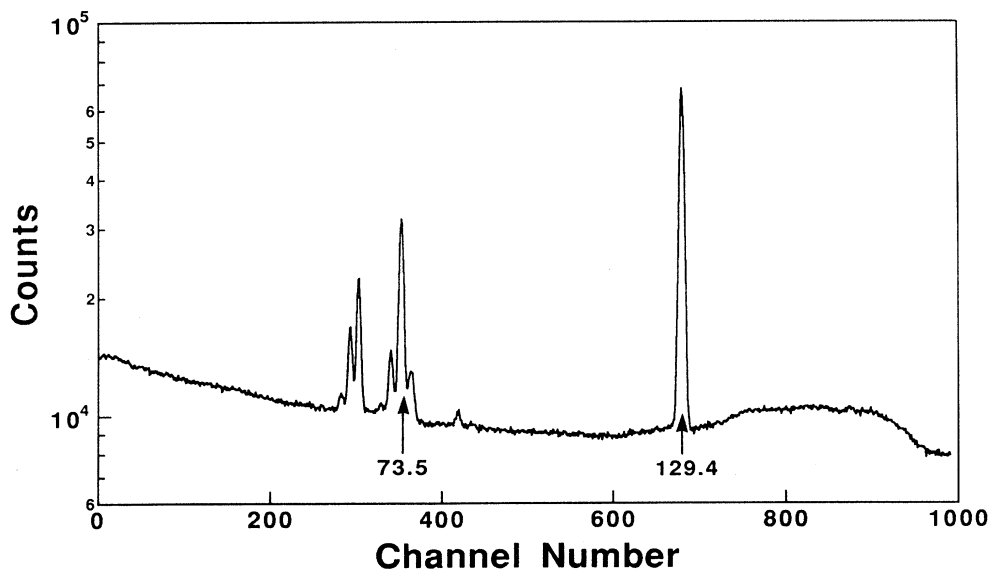


FIG. 1. Pulse-height spectrum of the  $^{191}\text{Os}$  source.

Spectra were taken at liquid-nitrogen temperature, one with two foils and one with three.

The accumulation of spectra in a direct beam meant that the source fraction could not be constrained to be the same for both spectra, an arrangement that is less than optimum for exact line-shape analysis. This experiment could have been carried out to a much higher degree of accuracy if absorber foils enriched in  $^{191}\text{Ir}$  had been available, or if our facility had been able to cool source and absorber to liquid-helium temperature. This would have made it possible to either increase the absorber effective thickness, conduct the experiment in scattering geometry, or both. We attempted to locate enriched  $^{191}\text{Ir}$

foils, but were unable to find any at costs that were acceptable.

#### IV. RESULTS AND DISCUSSION

##### A. Tungsten

Figure 2 shows the ME spectra taken at temperatures 80 – 1067 K in tungsten metal and the residuals, that is, the experimental points less the theoretical points. The data were analyzed in two groups of ten spectra each; one group, set A, consisted of spectra taken only with the furnace, and the other, set B, of spectra taken with the

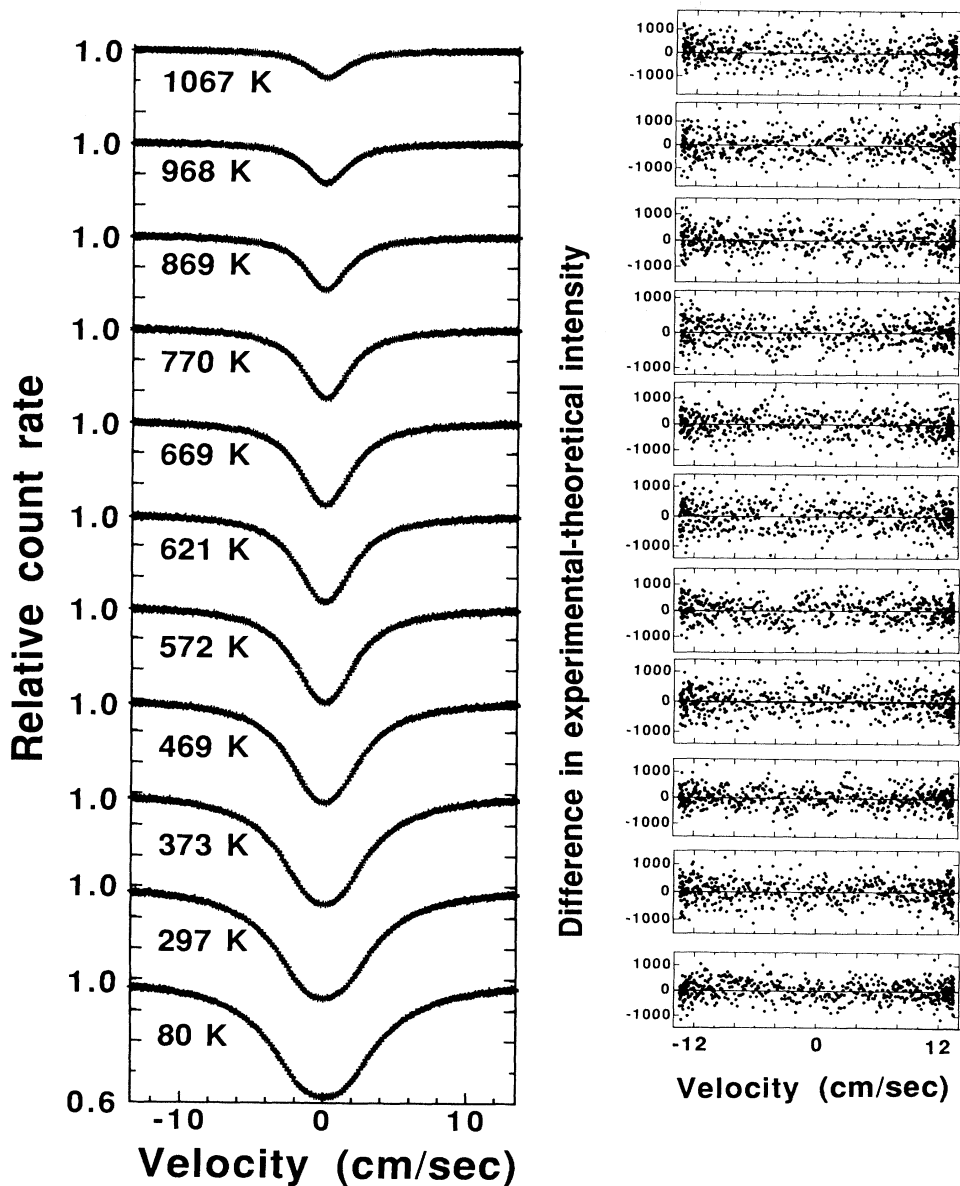


FIG. 2. Mössbauer spectra of tungsten metal absorbers as a function of temperature and residuals after fitting to transmission integral.

furnace and the cryostat, as well as some spectra taken at room temperature in an open holder. This was done with a view towards assuring consistency and checking the validity of assumptions regarding constraints on individual parameters. Our representation of the exact line shape made it possible to constrain certain fundamental parameters to be the same for all spectra in each fit, namely, the line width, interference, and, for spectra of absorbers at the same temperature,  $v_0$ , the peak position of the resonance curve. In addition, the source recoilless fraction was constrained to be the same in subgroups of spectra, taken with the same source and at the same radioactivity level. This was done, since cooling of the sources as the radioactivity diminished became apparent from separate spectra taken with an open holder, with source temperatures at the start of a run being about 2 K higher than at the end of a run (one week later). This was also confirmed from simple model calculations. The differences in thickness number resulting from this strategy were small but significant.

The reduction in the source recoilless fraction due to SRSA is estimated to have been 1%, corresponding to a source resonance thickness number  $t_{RS} = 0.05$ .<sup>3</sup> This is very small, but still gave rise to concerns that our absorber thickness number would differ by an amount roughly equal to  $t_{RS}$ . Tests made by fitting artificially generated spectra indicate that the effect of this small value of  $t_{RS}$  is to reduce the estimate of absorber thickness numbers by about 0.4%, for all values of thickness number. Since this 0.4% is within the experimental errors claimed here for our absorber thickness numbers, we have neglected this small correction.

The second-order Doppler shift with temperature was too small to measure, given the large line width, and so to guarantee accuracy of the interference measurements, the thermal shift was fixed for each spectrum not at room temperature, relative to the room-temperature peak position, using the Josephson formula<sup>14</sup> and values of  $C_p$  from the tables.<sup>15</sup> That is, only the peak position of the spectra at room temperature was fitted as a parameter, and the peak positions of spectra not at room temperature were fixed relative to the room-temperature peak position. This was done in order to produce the best possible estimate of the interference parameter  $\beta$ , since an incorrect value of  $v_0$  will affect the value of  $\beta$ .<sup>3</sup> We tried fits with no constraints on peak positions and found essentially the same results for  $\beta$ , but with a somewhat higher scatter.

Due to the importance of line width and interference, a separate experiment was done with two absorbers at room temperature to fix  $\Gamma$  and  $\beta$ . Two high-resolution spectra were accumulated, one with an absorber of four 1-mil foils (1 mil = 0.001 in.) and one with seven, and counting continued until each had a baseline of between one and two million, or roughly ten times that of the individual spectra used for the measurements of  $f(T)$ ; separate source fractions were used for the two spectra. These high-resolution spectra are shown in Fig. 3. A

fit allowing separate thickness numbers for the two spectra returned values that agreed with the ideal 7:4 ratio to within 0.4%, and holding the thickness number of the seven-foil spectrum to be 7:4 times that of the four-foil spectrum produced values of  $\Gamma$  and  $\beta$  within returned errors for the first fit. Since this degree of error is well within the range of error that might have been produced by slight differences in thickness between the two absorbers or by differences in absorber temperature, the values returned by the first fit were taken as final. To ensure optimum accuracy in the determination of recoilless fraction, sets A and B were fitted one last time with constraints on peak positions as noted above, and using the values of  $\Gamma$  and  $\beta$  determined in the fit to the high-resolution data as defined constants.

### 1. Mean life of the 46.5-keV state

In initial fits to sets A and B,  $\Gamma$  was allowed to vary so as to gauge the consistency of the two sets. The level width  $\Gamma = \hbar/\tau$  resulting from the fit to set A was 1.598(4) cm/s and 1.604(4) cm/s for set B, leading to an average value of 1.601(4) cm/s. The value of  $\Gamma$  resulting from

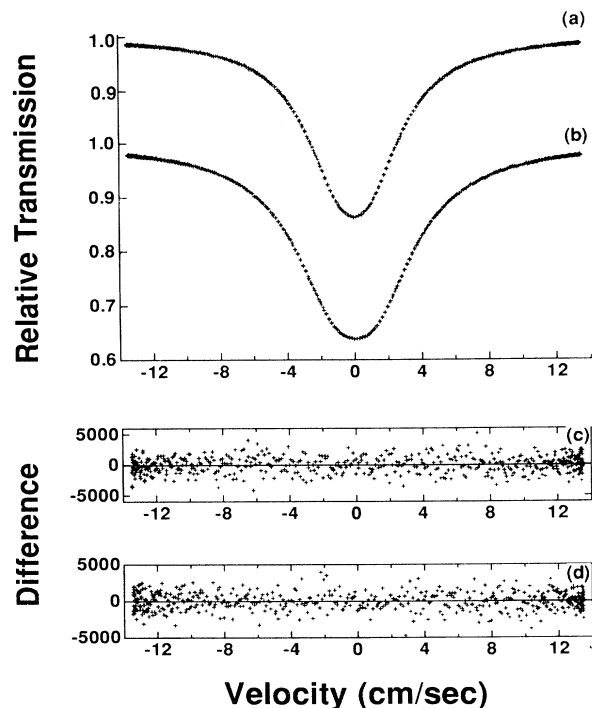


FIG. 3. High-resolution spectra and residuals after fitting to transmission integral: (a) spectrum with absorber of four 25- $\mu$ m tungsten foils, (b) spectrum with absorber of seven 25- $\mu$ m tungsten foils, (c) residuals of (a), and (d) residuals of (b).

the high-resolution spectra at room temperature was  $\Gamma = 1.600(7)$  cm/s. Since this last value is within the errors for the simultaneous fits to set A and to set B, this value, with the indicated error, was taken to be the line width of the 46.48-keV transition. This implies a mean life for the 46.48-keV state of 265(1) ps, or a half-life of 184(1) ps. Table I gives a compilation of some measured values for the lifetime of this state, in various units; the references are cited in chronological order, and some of the entries were calculated by us from values cited in other units.

With the exception of our earlier work, Ref. 21, all of these values were derived by the usual method of taking successive spectra with absorbers of various thicknesses, fitting the data with Lorentzians and extrapolating to zero absorber thickness. Most of these spectra except for those of Ref. 21 were poorly resolved, in addition, since most of the experiments did not use a monochromator, or had sources of rather low intensity. The work of Ref. 21 was later found to have been affected by vibration, a constant hazard in Mössbauer drivers, and especially in nontransducer types. Our current procedure of carrying out simultaneous fits to spectra with carefully chosen constraints is a check against such experimental artifacts being present in the data reported herein.

### 2. Isomer shift

In the final fit to data, center velocities for all spectra not at room temperature were constrained to have a fixed offset relative to the room-temperature peak position, as outlined above. The isomer shift returned from the fit to set A was 0.019(1) cm/s, and that from set B was 0.020(1) cm/s, while the isomer shift returned by the high-resolution spectra was 0.016(1) cm/s. The formal disagreement between the fits to sets A and B and to the high-resolution spectra, however, amounts to only about  $\frac{1}{40}$  of a channel at the peak position of the spectrum. The foils in the high-resolution spectra had not been thermally cycled, and this might be the origin of the small discrepancy, since tungsten's physical properties are sensitive to thermal history.

### 3. Interference

In joint fits to sets A and B, where the interference parameter was allowed to "float," that is, not constrained to

TABLE I. Lifetime of the 46.48-keV state in  $^{183}\text{W}$ .

$\tau_{1/2}$ (ps)	$\Gamma$ (cm/s)	$\Gamma$ ( $\mu\text{eV}$ )	Reference
150(10)	2.0(2)	3.1(3)	16
158(3)	1.86(4)	2.88(6)	17
184(5)	1.60(4)	2.48(6)	18
174(6)	1.69(6)	2.62(9)	19
188(4)	1.56(3)	2.42(5)	20
189(3)	1.55(2)	2.40(3)	21
184(1)	1.60(1)	2.48(1)	This work

be the same for each spectrum, the value returned by the fitting program held roughly steady at about  $-0.003$ , until data above 600 K was analyzed, where a large scatter appeared in the points, shown in Fig. 4. This signifies nothing more than that the ratio of signal to noise for the antisymmetric component of the spectrum declined to the point that the amplitude of the interference signal could not be recovered with any precision.

Since there was no evidence for a temperature variation of  $\beta$ , and such a temperature variation has not been predicted theoretically, interference was constrained to be the same for a further joint fit to sets A and B. Constraining  $\beta$  to be the same for all spectra caused no significant increase in  $\chi^2$ . The value obtained for the interference parameter  $\beta$  for set A was  $-0.00314(12)$  and for set B,  $-0.00327(7)$ . The value resulting from the high-resolution room-temperature spectra was  $\beta = -0.00317(6)$ , and this is the value used for the final set of joint fits to sets A and B.

Only two prior measurements have been made of the interference parameter using the 46.48-keV transition in  $^{183}\text{W}$ . The first, by Wagner *et al.*,<sup>22</sup> resulted in a value for  $\beta$  of  $-0.0005(6)$ , using Lorentzian fitting techniques without corrections for absorber thickness. A second measurement of  $\beta$ , carried out by the Purdue-Mössbauer group, Ref. 21, found a value of  $-0.0025(1)$ , which is much closer to the present determination and to theoretical values but is still in disagreement with both. It has been found that the experimental apparatus of Ref. 21 was affected by vibration, and perhaps by angular speed variations. The basic spectrometer used by us is nearly identical to the one used in Ref. 21; however, the present study used Teflon rather than steel bearings for the Thomson rod assemblies, and a large flywheel was used to reduce angular speed variations. Also, the earlier result in Ref. 21 did not have the check of simultaneous fittings to two absorber thickness numbers, as was the case for our present high-resolution spectra.

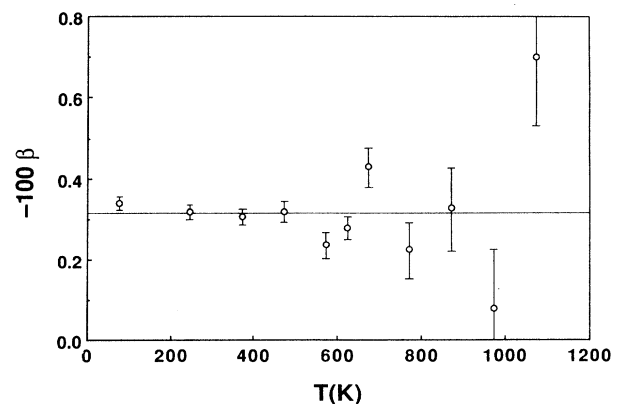


FIG. 4. Interference parameter vs temperature for tungsten spectra.

Theoretical predictions of  $\beta$  have been made by Goldwire and Hannon<sup>8</sup> and Davis *et al.*<sup>9</sup> Goldwire and Hannon predict  $\beta = -0.0030$ , while Davis *et al.* predict a value of  $-0.0028$ . In spite of the more detailed treatment of the subject by Davis *et al.*, it will be seen that our value of  $-0.00317$  agrees more closely with the earlier result of Goldwire and Hannon. The derivation of the interference parameter is closely related to that of the internal conversion coefficient, and Davis *et al.* made an attempt to check their results by calculating  $\alpha$  and comparing these with other theoretical calculations of  $\alpha$ ; however, this apparently was not done for all transitions tabulated, and no value was listed for the 46.5-keV transition in <sup>183</sup>W. It would be useful if future tabulations of theoretical values of  $\beta$  included, as well as estimates of the internal conversion coefficient calculated on the same assumptions; as will be seen later, Mössbauer line-shape experiments may yield a value of  $\alpha$  as well as of  $\beta$ , giving a valuable cross check on the theoretical calculations.

#### 4. Recoilless fraction

The results for  $f_a(T)$  are shown in Table II and plotted in Fig. 5. Since a wide range of values of  $\alpha$ , the internal conversion coefficient, have been published, we have cited both our values of  $f_a/(1+\alpha)$  and values of  $f_a$  determined using the value  $\alpha = 8.76$  derived by us (see below). It may be seen from Fig. 5 that, although the general variation of recoilless fraction with temperature behaves as expected at lower temperatures, at higher temperatures  $f$  begins to fall off more rapidly with increasing temperature, indicating the presence of anharmonicities. It has been suggested<sup>23</sup> that, to a good approximation, the effect of anharmonicities may be corrected to first order by a simple correction for thermal expansion. In Fig. 6, we have shown a plot of the difference between our  $\ln f_a(T)$  values and values derived using the Debye model, assuming a Debye temperature of 336.5 K and an internal conversion coefficient of 8.76. The points marked with a square were made using the original fits to our data and those marked with a circle are made using our data

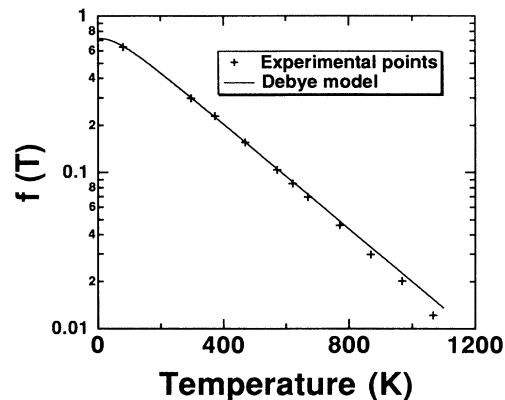


FIG. 5. Recoilless fraction in tungsten metal without corrections for thermal expansion, using 46.5-keV transition, and  $\alpha = 8.76$ ; solid line is the Debye model using  $\Theta_M = 336.5$  K.

after a simple correction for thermal expansion. It will be seen that, on this greatly expanded scale, the effect of anharmonicities has been greatly reduced by the addition of the thermal expansion correction. The thermal expansion corrections were employed, together with our values of  $f_a/(1+\alpha)$  to determine an experimental value for  $\alpha$ .

Sumbaev *et al.*<sup>16</sup> found, in the first work done on the 46.48-keV transition in <sup>183</sup>W, a value of  $\Theta_M = 320_{-40}^{+70}$  K, using an interesting early variation of simultaneous fitting of spectra taken with two absorbers. In this study, a value for  $\alpha$  of 11.0, which now appears to be 20% too large, as well as an inaccurate value for the level width, was used, and the velocity range of  $\pm 3.5$  cm/s was inadequate to fully scan the spectrum. In spite of the dispersion, the quoted value of  $\Theta_M$  is in surprisingly good agreement with our result (336 K) derived in the next section.

TABLE II. Recoilless fraction in tungsten metal, without corrections for thermal expansion.

Absorber temperature (K)	Thickness no.	$100f(T)/(1 + \alpha)$	$f(T), \alpha = 8.76$
80	14.33(5)	6.50(2)	0.634(2)
297	11.81(4)	3.06(1)	0.299(1)
373	9.058(40)	2.35(1)	0.229(1)
469	6.148(21)	1.59(1)	0.155(1)
572	4.100(17)	1.06(1)	0.104(1)
621	3.350(13)	0.868(3)	0.0847(3)
669	2.751(14)	0.713(4)	0.0696(4)
770	1.818(8)	0.471(2)	0.0460(2)
869	1.178(6)	0.305(2)	0.0298(2)
968	0.7993(32)	0.207(1)	0.0202(1)
1067	0.4824(24)	0.125(1)	0.0122(1)



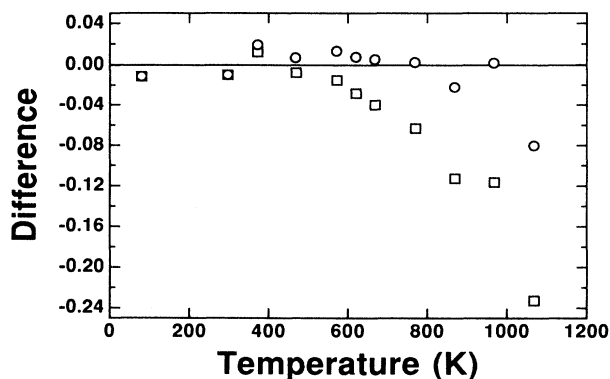


FIG. 6. Difference between  $\ln f_a$  values derived using the Debye model with  $\Theta_M = 336.5$ , and our data using  $\alpha = 8.76$ ; points marked with a square are uncorrected, while those marked with a circle have been corrected for thermal expansion.

### 5. Internal conversion coefficient

The values of  $f/(1+\alpha)$  derived from the joint fit were used together with thermal expansion corrections to derive a value for the internal conversion coefficient for the 46.5-keV transition. After Willis,<sup>23</sup> we have assumed that the recoilless fraction, in the presence of anharmonicities, may be corrected to first order by a simple allowance for thermal expansion:

$$\ln f(T) = \frac{\ln f'(T)}{1 + 6\gamma_G \epsilon}, \quad (9)$$

where  $f(T)$  is the recoilless fraction at constant volume, that is, in the absence of thermal expansion, and  $f'(T)$  is the recoilless fraction as measured. Here,  $\gamma_G$  is the Grüneisen parameter for tungsten, 1.62,<sup>24</sup> and  $\epsilon$  is the total linear thermal expansion, relative to room temperature, which we took from standard tables.<sup>15</sup> The assumption has been made here that  $\gamma_G$  does not vary with temperature. This is only approximately true; although  $\gamma_G$  is nearly constant at room temperature and above, it declines at low temperatures, so that the correction at 80 K is assumed to be negligible.

Fitting the values of  $f_a/(1+\alpha)$  to the Debye model and including the corrections for thermal expansion yielded a value of  $\alpha = 8.76(10)$ , and a Debye temperature of  $\Theta_M = 336.5(7)$  K, where the highest point was excluded from the fit. As a cross check, independent of the Debye model, we fitted data for temperatures from 373 K through 968 K, and obtained a value of  $\alpha = 8.83(12)$ . All fits to the data using either the linear approximation or the Debye model showed a dramatic increase in  $\chi^2$  when the last point, at 1067 K, was included.

Alternatively, it is possible to deduce  $\alpha$  by comparing our results for  $f_a/(1+\alpha)$  with values of the recoilless

fraction in tungsten calculated by Raj and Puri<sup>25</sup> using phonon dispersion data derived from inelastic neutron scattering in tungsten at room temperature. These authors cite values of recoilless fraction at several temperatures, of which 77 and 300 K are closest to two of ours. Using the Debye model to interpolate these data to our temperatures yields for the data of Raj and Puri  $f_a(80) = 0.6395$  and  $f_a(297) = 0.2977$ . Combining these with our values of  $f_a/(1+\alpha)$  gives, for the value at 80 K,  $\alpha = 8.84$ , and at 297 K,  $\alpha = 8.73$ . It should be noted that here the corrections for thermal expansion were not used.

Values ranging from about 8 to as high as 40 have been cited in the literature for  $\alpha$  for this transition.<sup>2,26-29</sup> Our best value of 8.76(10) agrees with the most recent theoretical value of 8.63,<sup>29</sup> but does not agree with the only other experimental values of 11 (no error was given for this value),<sup>28</sup> or with 13(3),<sup>2</sup> although the latter value was only a rough estimate and essentially agrees with the present result when the large error is taken into account.

### B. Iridium

As noted above, spectra taken with the 129-keV transition in iridium metal were taken mostly in direct beam, without a monochromating crystal. Although, as may be seen from Fig. 1, the 129-keV line is well separated from other lines, pulse-height spectra at much higher energies showed the presence of many high-energy lines above the 129-keV line. These spectra indicated that, ignoring the declining efficiency of the  $\gamma$  detector, over half the beam energy lay above the 129-keV line, and considering that the efficiency of such a detector falls off exponentially at higher energies, by far the greater part of the beam intensity lay above 129 keV. The extremely high background intensity meant that downscatter necessarily compromised the source fraction, so that it was no longer justifiable to hold this parameter to be the same for both spectra. The final joint fit was done holding line width and interference to be the same for both spectra, and constraining the effective thickness of the three-foil set to be 1.5 times that of the two-foil set. Figure 7 displays the final Mössbauer spectra for the two-foil and three-foil sets and the residuals after fitting to the transmission integral.

The value of  $\Gamma$  returned by our fit is 1.15(4) cm/s, corresponding to a half-life for the 129.4-keV state of 92(3) ps. This is to be compared to other Mössbauer experimental values of<sup>30</sup> 89.4(14) ps [which indicates a width of 1.18(2) cm/s] and<sup>22</sup> 1.13(2) cm/s [which indicates a half life of 93.6(16) ps]. A recently published value<sup>31</sup> for the half-life of this transition of 123(4) ps was derived as a weighted average of several measurements made using various methods, not including Mössbauer or Coulomb excitation. Measurements made using Mössbauer methods consistently give a half-life of around 90 ps, while a cited value<sup>31</sup> for  $B(E2)$  of 0.90(2) $e^2b^2$  gives a half life of 93(5) ps, using  $\alpha = 2.84$  and  $\delta^2 = 0.16$ . The reason given by the evaluator<sup>31</sup> for adopting the value of  $\tau_{1/2}$  of 123

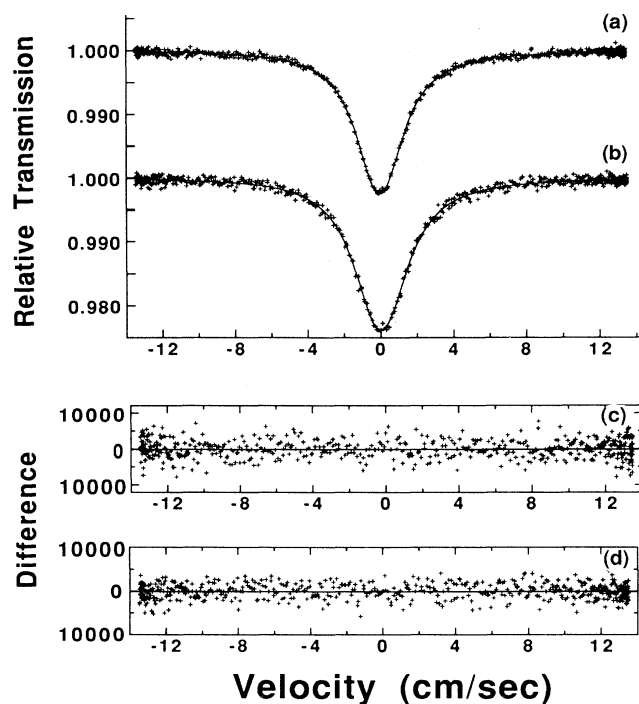


FIG. 7. Mössbauer spectra using the 129-keV transition in  $^{191}\text{Ir}$ : (a) two-foil spectrum, (b) three-foil spectrum, (c) residuals after fitting (a) to transmission integral, and (d) residuals after fitting (b) to transmission integral.

ps is that solid-state effects may give rise to a broadening of the Mössbauer line; however, our results indicate no hyperfine or vibrational broadening. A half-life of 123 ps implies a Mössbauer level width of 0.86 cm/s, and unresolved broadening of this magnitude would certainly have caused a poor  $\chi^2$  for our fit, which in fact was 0.974.

The effective thickness of the two-foil absorber was 2.6(3), yielding a value of the recoilless fraction in iridium metal at 80 K of 0.036(5). This corresponds to a characteristic Debye temperature of 335(9) K. This is in perfect agreement with a value of  $\Theta_M = 335(13)$  K found by Steiner *et al.*,<sup>30</sup> although the errors indicate the agreement is fortuitous. This is especially true, since the measurements of Ref. 30 were made at liquid-helium temperature, and one would expect a slightly different Debye temperature. Unfortunately, the value of  $\alpha$  used to arrive at their recoilless fractions was not given, making comparisons uncertain.

Our chief aim in doing this experiment was to resolve the discrepancy between theoretical estimates of the interference parameter in this transition and the only other Mössbauer measurement. Our value for the interference parameter derived from the joint fit is  $\beta = -0.0077(10)$ . This disagrees with the value of Wagner *et al.*<sup>22</sup> of  $-0.0050(12)$ . The theoretical estimate for the interference parameter in this transition by Goldwire and Hannon<sup>8</sup> is  $-0.0071$ , while that of Davis *et al.*<sup>9</sup> is

$-0.0069$ . Although our value agrees with both of these theoretical values within experimental error, it may be seen that our value of  $\beta$  is again larger in magnitude than the theoretical estimates.

Gimlett *et al.*<sup>32</sup> have measured the phase shift  $\beta_T = -0.0047(3)$  in this transition, and, using the theoretical estimate of  $\beta_T$  of  $-0.0037$  of Goldwire *et al.*,<sup>8</sup> concluded that there is evidence for a small time-reversal-like phase shift. Davis *et al.*,<sup>9</sup> however, calculate a value of  $\beta_T = -0.0043(4)$ , removing evidence of violation of time-reversal invariance. Our results indicate that  $\beta$  is larger than either of the values calculated in Refs. 8 or 9, and since this transition is principally  $M1$  in nature,  $\beta(M1)$  constitutes the bulk of the calculated value of  $\beta$ , implying that the true value of  $\beta_T$  is smaller than either of the theoretical values. This means that the results of Gimlett *et al.* need to be reexamined in the light of these new interference values, and we are remeasuring  $\beta$  for  $^{191}\text{Ir}$  to higher accuracy using an enriched  $^{191}\text{Ir}$  foil to more critically test the theoretical calculations of interference in this important system.

## V. CONCLUSIONS

Simultaneous fitting of complementary Mössbauer spectra to the exact line shape has been shown to be the most useful method for directly extracting the values of basic physical parameters associated with the Mössbauer line shape. Our representation of the line shape in terms of fundamental physical parameters produces physical values directly and without approximation. This method of line-shape analysis has permitted the first precision determination of absolute values of recoilless fraction over a large temperature range without using a theoretical value for the internal conversion coefficient. A similar study of recoilless fraction in metallic gold by Erickson *et al.*<sup>33</sup> produced values of comparable precision over a temperature range of about 100 K; however, their method of line-shape analysis was not clear, and parameter values were determined by iterative fits to spectra, rather than simultaneous fits. In addition, the internal conversion coefficient was determined with the aid of a complex analysis by others.

We have determined the value of the mean life of the first excited state in  $^{183}\text{W}$  to be 265(1) ps, and this is in good agreement with values derived by Coulomb excitation, if a reasonable value is used for  $\delta^2$ , the mixing coefficient of this transition. Our value for the interference parameter  $\beta$  of  $-0.00317(6)$  is about 10% higher in magnitude than theoretical estimates. We have determined the internal conversion coefficient for this transition to be 8.76(10), in good agreement with the current theoretical value of 8.63 (for which no errors were given), and much closer to this value than other experimental determinations. Our results for  $f(T)$ , the recoilless fraction in tungsten agree very well with the theoretical estimates of Raj and Puri, incidentally serving to corroborate our value of  $\alpha$ , and which display the expected properties of a clas-

sic crystal lattice, when a small correction for thermal expansion is included.

The measured mean life of the 129-keV level of  $^{191}\text{Ir}$  of 133(4) ps is fully in agreement with other published values for this quantity, including those derived from Coulomb excitation, and it is expected that even better agreement would have resulted if it had been possible to do the experiment under more nearly ideal circumstances. Most importantly, we have determined the interference parameter for this transition, and found it to agree within experimental error with both theoretical estimates, but with a nominal value that is slightly higher than either. If further experiments should prove that this value is in fact higher than both theoretical values, it will give new importance to a measurement by Gimlett *et al.*,<sup>32</sup> which could reopen the question of a possible

breakdown of the principle of time-reversal invariance in the electromagnetic decay of the mixed 129-keV transition of  $^{191}\text{Ir}$ .

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