Mössbauer line-shape parameters for ^{159}Tb in $TbAl_2$ and Tb_4O_7

B. R. Bullard and J. G. Mullen
Physics Department, Purdue University, West Lafayette, Indiana 47907

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Precise line-shape analyses of Mössbauer spectra using the 58-keV transition in ^{159}Tb have been made using an exact representation of the line shape in transmission. Spectra were made using a Dy_2O_3 source at liquid-nitrogen temperature and absorbers of Tb_4O_7 and $TbAl_2$ at several temperatures from 81 to 297 K. We have measured the recoilless fraction as a function of temperature between 115 and 297 K for $TbAl_2$ and at 81 and 294 K in Tb_4O_7. If the theoretical value of the internal conversion coefficient of 11 is accepted, we cannot fit our results to a Debye model, even in a rough approximation. The mean lifetime of the first excited state of ^{159}Tb was determined to be 77(1) ps. We have found the value of the interference parameter for this transition to be −0.0058(7), which appears larger in magnitude than predicted by theory.

I. INTRODUCTION

Few investigations of the Mössbauer effect using the 58-keV transition in ^{159}Tb have been made, and a wide variety of linewidths have been reported, ranging from $W_0 = 3.6$ to 16 cm/s. Most previous work has been based on spectra of rather poor resolution analyzed with Lorentzians. The most recent studies[1] have indicated linewidths that are near the top end of this range, and more nearly in agreement with a half life of 54(2) ps, derived from Coulomb excitation. Our interest in this transition derives from its suitability for conversion-electron Mössbauer spectroscopy,[2] and the ease with which absorbers can be fabricated (natural terbium is 100% ^{159}Tb), as well as its large linewidth of 8.5 μeV, which makes it an excellent candidate for the study of low-energy excitations in solids. Moreover, we believe that the unpopularity of this transition in the past is due to its large linewidth, which makes analysis by the usual Lorentzian methods difficult, due to the limited range of reduced velocity that is swept out using many of the readily available spectrometers.

We have used an exact representation of the line shape[3] and the technique of joint fitting of complementary spectra to determine the linewidth, as well as several other parameters of interest, with much greater precision than in previous work. This method has been applied to complementary Mössbauer spectra taken in cubic $TbAl_2$, and to a separate set in Tb_4O_7, a complex substance that contains both Tb^{3+} and Tb^{4+} ions,[4] and that does not have cubic point symmetry at all Tb sites. Fitting these spectra as unsplit lines yields excellent agreement in the linewidths and has enabled us to determine the fundamental linewidth to a precision of about 1% directly and without the approximations involved in the conventional Lorentzian method.

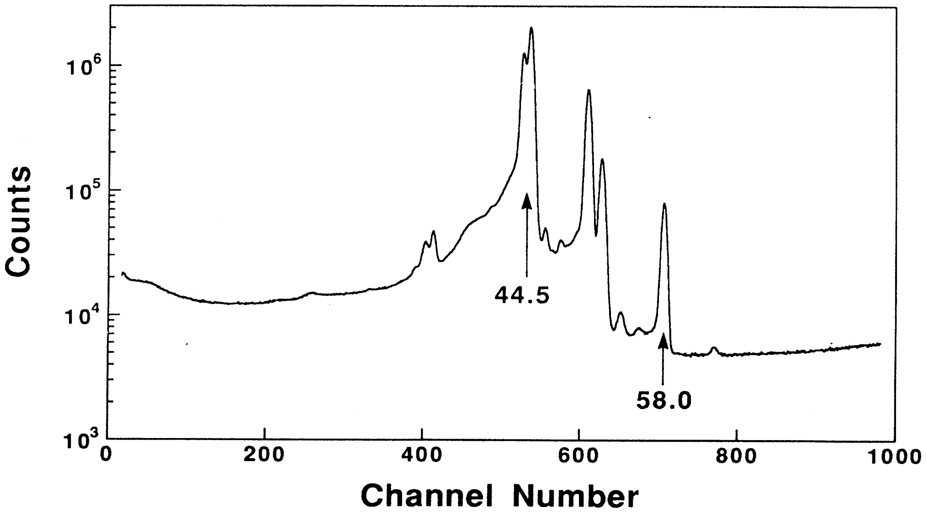

FIG. 1. Pulse height spectrum of $^{159}Dy_2O_3$ source used for experiments with $TbAl_2$.

II. EXPERIMENTAL METHODS

Sources were made of Dy_2O_3 enriched to 20.8 at. % in ^{158}Dy, and irradiated in a thermal neutron flux of about 3×10^{14} neutrons/cm^2 s at the Research Reactor Facility of the University of Missouri, for 2 – 4 weeks, to produce ^{159}Dy (lifetime, $t_{1/2} = 144$ d). The source intensity that can be obtained by this method is limited due to an exceptionally large burn-out cross section (8±2 kb) for ^{159}Dy,[5] but we were able to make sources of about 50 mCi activity. Source-resonance self-absorption was almost nil; we estimate $t_{\rm RS}$ (the source thickness number[3]) to be less than about 0.001 for all sources used. Sources were held at about 77 K for all experiments. The spectrum of one of the sources is shown in Fig. 1; the 58-keV line is the highest-energy line shown, and there were essentially no detectable γ lines above it in energy. For absorbers, the compounds $TbAl_2$ and Tb_4O_7 were used. The $TbAl_2$ was prepared by Ames Laboratory, and was ground and sifted to produce an average particle size of about 5–10 μm, and then encapsulated in Transoptic plastic. The Tb_4O_7 was obtained from Aesar as a fine powder and was similarly encapsulated without further grinding. Two absorbers of $TbAl_2$ were used, one containing 77.1 mg/cm^2 of $TbAl_2$ and the other 38.2 mg/cm^2. These absorbers were used individually and in combination: spectra were taken with both, for 115.3 mg/cm^2 at 115 and 297 K, and with the 77.1 mg/cm^2 absorber alone at 115 and at 150 K. These spectra are displayed in Fig. 2. Since the Curie temperature of $TbAl_2$ is about 108 K,[6] single-line spectra could not be taken below this temperature. For the experiments with Tb_4O_7, a single absorber of 73.1 mg/cm^2 Tb_4O_7 was used, and two spectra were taken with the Tb_4O_7 absorber, one at 81 K and the other at 294 K. The Mössbauer spectra taken using the absorber of Tb_4O_7 are shown in Fig. 3.

The Doppler energy shift was provided by a moving source cryostat mounted on Thomson rods and driven by a crank. The crank was attached to a countershaft driven in turn by a three-phase synchronous motor. Two different crank offsets were used: the one used for the Tb_4O_7 experiments gave a maximum speed range of ±9 cm/s, while that used for the $TbAl_2$ experiments gave a maximum speed range of ±14 cm/s, with the available pulleys. In spite of two flywheels attached to the countershaft, small angular speed variations due to inertial loading were present, of less than 1%, which were measured and included in the calculations of velocities. The source was contained in a 40-lb tungsten holder, which was enclosed in a stainless-steel liquid-nitrogen Dewar. The entire assembly weighed about 80 lb and was driven in a reciprocating motion by the precisely machined crank. The absorbers were mounted in a separate cryostat that could be heated to obtain absorber temperatures above 77 K, and temperatures were measured using a platinum resistance thermometer. The intrinsic germanium detector had a resolution of less than 200 eV at the transition energy of 58 keV. Total source-detector distance was greater than 80 cm, and the source to detector distance, which varied with position, required a correction for intensity as a function of crank angle.

Data were fitted to the theoretical line shape

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

where $f_{\rm so}$ is the source recoilless fraction, t is the absorber resonance thickness number x and x' are dimensionless variables representing relative velocity between source and absorber (taken as positive when the source was moving towards the absorber), and the variable of integration

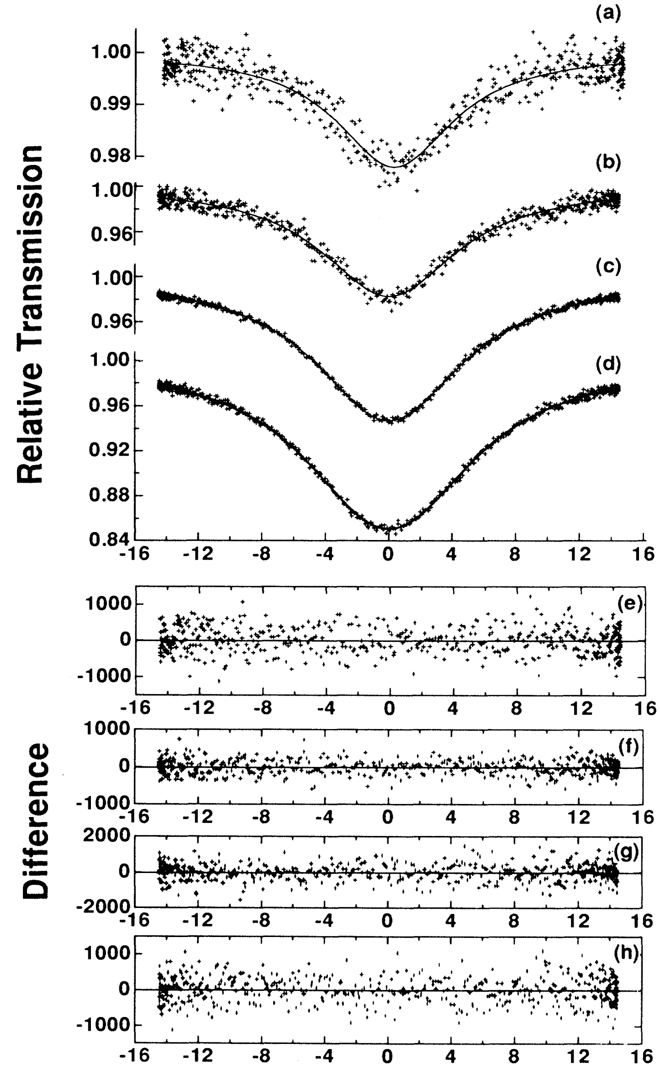

FIG. 2. Mössbauer spectra of $TbAl_2$ absorbers and residuals after fitting to transmission integral: (a) 115.3 mg/cm^2 absorber at 297 K, (b) 77.1 mg/cm^2 absorber at 150 K, (c) 77.1 mg/cm^2 absorber at 115 K, (d) 115.3 mg/cm^2 at 115 K, and (e), (f), (g), and (h) are residuals of (a), (b), (c), and (d), respectively.

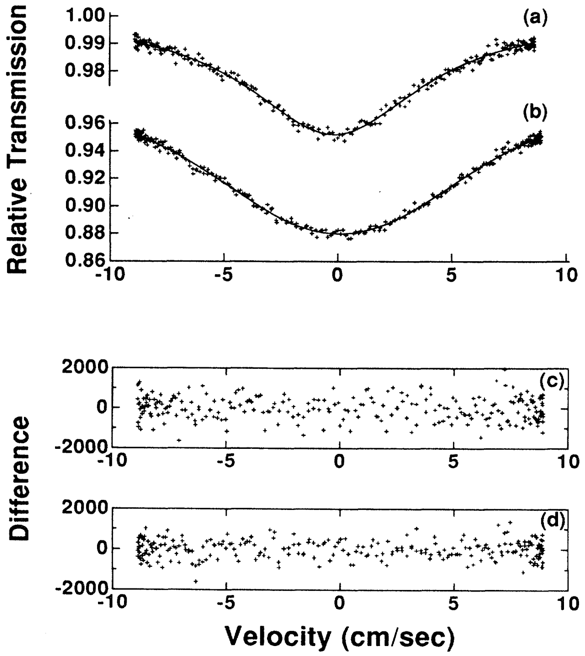

FIG. 3. Mössbauer spectra of Tb_4O_7 absorber and residuals after fitting to transmission integral: (a) spectrum at 294 K, (b) spectrum at 81 K, (c), residuals of (a), and (d) residuals of (b).

over energy, respectively, and $\mathcal{L}(x)$ is the Lorentzian plus an interference term, i.e.,

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

where β is the interference parameter. The variable $f_{\rm so}$ here is not the true recoilless fraction of the source but rather an "effective" recoilless fraction, to the extent that a certain amount of background was present. As pointed out by others,[7-9] correlation between certain of the parameters, especially $f_{\rm so}$ and t, is too great to permit accurate fits of individual spectra to Eq. (1). For this reason, all spectra taken with absorbers of $TbAl_2$ were fitted simultaneously, and a separate simultaneous fit was made to the Tb_4O_7 spectra. In each fit, linewidth, source recoilless fraction, and interference were held in common for all spectra in each fit, but no constraint was made to restrict any of the parameters from the two fits to be the same, and hence the values arrived at independently could be compared for a consistency check.

III. RESULTS AND DISCUSSION

The value of Γ, the level width in velocity units, derived from the fit to the $TbAl_2$ data is 4.40(3) cm/s, and that derived from the fit to Tb_4O_7 data is 4.41(10) cm/s, where the errors are those returned by the curve fitting program, and represent one standard deviation.[10] The agreement is the more remarkable due to the very different experimental conditions for the two sets of experiments; although $TbAl_2$ provides cubic symmetry at the Tb sites, commercial Tb_4O_7 is not a simple compound, and does not provide a cubic point symmetry surrounding for the Tb ions. The similar compound Tb_2O_3 has Tb^{3+} ions at two sites; three-quarters of the Tb ions are at sites with symmetry C_2 and one-quarter have symmetry C_{3i}. The apparent absence of broadening, as evidenced by values of χ^2 near unity for all individual and joint fits of spectra, indicates that quadrupole splitting in Tb_4O_7, as well as in the Dy_2O_3 source, must be quite small in relation to the linewidth of this transition in this temperature range.

Since the lifetime of the 58 keV state of ^{159}Tb is rather long, there is a possibility that "aftereffects" might have distorted the line shape of the Tb_4O_7 spectra by producing a variety of charge states and isomer shifts. However, $TbAl_2$ is a good conductor of electricity, and, since fits to the $TbAl_2$ spectra gave almost the same linewidth as the Tb_4O_7 spectra, we have concluded that aftereffects have not seriously distorted the spectrum. Also, the large K-fluorescence yield of 0.937 for terbium[11] indicates that disturbances of line shape due to this effect should not be very large.

The structure of Dy_2O_3 is nearly identical to that of Tb_2O_3, giving rise to concerns that a quadrupole splitting might be present in the source. Using the 25-keV transition in ^{161}Dy, quadrupole splittings corresponding to $e^2qQ/4$=200–300 MHz have been observed[12,13] at liquid-helium temperatures in Dy_2O_3. However, a study[14] using the same system with the Dy_2O_3 absorber at the temperature of liquid nitrogen shows no resolved splitting. In addition, artificial computer-generated spectra were made representing a quadrupole splitting in the source corresponding to the largest electric field gradient seen at liquid-helium temperature, and these were fitted simultaneously. It was found that, although the peak-to-peak splitting was about 10% of the experimental linewidth W_0, deviations of parameters derived by fitting from those expected for an unsplit spectrum were very small, the largest variation being in the level width Γ, which was found to be too large by 0.6%. This serves to substantiate the remarks of Agresti *et al.*[7] that simultaneous fitting of spectra tends to overcome such disturbances of line shape.

The extremely broad natural linewidth, one of the broadest of the transitions found in Mössbauer spectroscopy, goes far to obscure such disturbing influences. Owing to the greater number of spectra taken with the $TbAl_2$ absorbers and their better resolution, as well as the minimal hyperfine interactions expected to have resulted from the cubic structure of $TbAl_2$, the value of 4.40(3) cm/s is taken to be the natural linewidth of the 58-keV transition. This value does not agree well with most other values found, except the most recent work of Endres *et al.* who found Γ = 4.1±1.3 cm/s. Table I displays these values, and some values derived from other work using various methods.

TABLE I. Linewidth of 58-keV transition by various methods.

Method	Γ (cm/s)	$\tau_{1/2}$ (ps)	$\Gamma(10^{-6}$ eV)	Ref.
Coulomb excitation	4.41(13)	53.5(1.5)	8.53(25)	15
Coincidence	1.8(6)	130(40)	3.5(1.2)	16
Mössbauer effect	2.5(1)	96^{+37}_{-21}	4.8(2)	17
Mössbauer effect	7.9(9)	30(3)	15(1)	18
Mössbauer effect	2.25(37)	105(15)	4.34(54)	19
Classical nuclear resonance			7.7(1.7)	1
Mössbauer effect	4.1(1.3)	58(14)	7.8(1.9)	1
Mössbauer effect	4.40(3)	53.6(4)	8.51(6)	This work

As may be seen from the table, our value for the lifetime of this state is in disagreement with all but one of the Mössbauer measurements,[1] the most recent aside from ours. The earlier measurements are characterized generally by spectra that are poorly resolved and with very few points, some of them containing less than 50 channels. These earlier linewidths have in addition been derived on the basis of fits using Lorentzians, coupled with the usual process of extrapolation to zero absorber thickness. The occurrence of linewidths that are less than those found by us is hard to understand, since all of our spectra give, when fitted with Lorentzians, linewidths greater than our value for the natural linewidth, and those at room temperature give linewidths only slightly greater. The work of Endres *et al.*[1] is notable for determining the linewidth by both classical nuclear resonance, using a high-speed rotor, and through conventional Mössbauer methods. The Mössbauer measurements in particular used 10 spectra to deduce the natural linewidth of this system; a sample spectrum is rather well resolved, even if in only about 100 channels, and their velocity range was ±20 cm/s. It is likely that such heroic efforts would easily have produced a more accurate value for the linewidth if the exact line shape had been used for analyzing data, rather than Lorentzians.

The results for $f(T)$ are shown in Table II and plotted in Fig. 4. These values are derived using the theoretical value $\alpha = 11.04$ from Ref. 20. Errors represent both errors derived from the fitting program and errors from determining the physical thickness of absorbers.

The last column in the table is the Debye temperature corresponding to each value of recoilless fraction, and it may be seen that it rises with temperature in both compounds. Endres *et al.*[1] found very similar results for $f(T)$ in the compound Tb_2O_3, in the sense that no single Debye temperature could even approximately represent the entire dependence of f on T. These workers found that their data indicated $\Theta_M = 160$ K at 9 K, and $\Theta_M = 250$ K at 380 K.

Our values for $f(T)$ in $TbAl_2$ are slightly larger (1–15 %) than those found by Endres *et al.* at corresponding temperatures. A constant Debye temperature of 225 K for $TbAl_2$ would result if the internal conversion coefficient were chosen to be 14.3 rather than the tabulated value of 11.04. Values of Θ_M of 230 and 233 K have been cited[21] for the similar rare-earth compounds $TmAl_2$ and $YbAl_2$, respectively.

The fact that the oxides of rare earths do not obey the Debye model has been attributed by Kagan and Maslov[22] to optical modes. The optical modes are excited at much higher temperatures than acoustic modes, leading to a slower decline in the recoilless fraction than would be expected from the Debye model. This weaker dependence of the recoilless fraction on temperature would then be interpreted in the Debye model as a Debye temperature that increases with temperature. It is also important to realize that a value of internal conversion coefficient that is in error may produce the phenomenon of a Debye temperature that is apparently strongly dependent on temperature. The data presented here are insufficient to make this claim, however, and further investigations are required to clarify this issue.

The value of interference derived from the fit to $TbAl_2$ data is $-0.0058(7)$. The two spectra at 115 K, which

TABLE II. Recoilless fraction in terbium compounds. The column labeled "Thickness" is the physical thickness of the absorber, in units of milligram of compound per cm^2.

Compound	Temperature (K)	Thickness	Thickness no.	$f(T)$	Θ_M (K)
$TbAl_2$	115	115.3±1.5	3.20±0.08	0.108±0.003	211.0
$TbAl_2$	150	77.1±0.8	1.30±0.03	0.0659±0.0017	214.5
$TbAl_2$	297	115.3±1.5	0.206±0.005	0.00699±0.00019	219.1
Tb_4O_7	81	73.1±0.3	5.05±0.31	0.237±0.015	232.1
Tb_4O_7	294	73.1±0.3	0.661±0.012	0.0309±0.0006	261.3

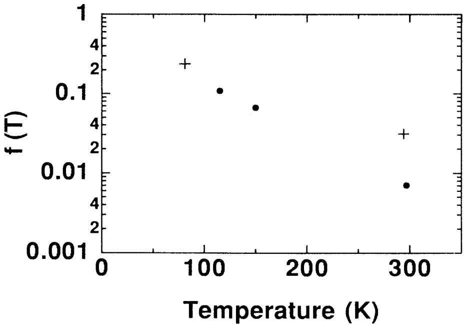

FIG. 4. Recoilless fraction in $TbAl_2$ and Tb_4O_7 vs temperature. Crosses represent results for Tb_4O_7 and circles represent the results for $TbAl_2$.

chiefly determine this value, when fitted individually yield interference parameters of −0.0066(11) for the 115.3 mg/cm^2 absorber and −0.0050(13) for the 77.1 mg/cm^2 absorber. These values do not agree with one another but individually agree rather well with the value from the joint fit. The spectra taken with Tb_4O_7 were not sufficiently precise to yield a reliable value for interference.

Although no theoretical values are available for β in this transition, Goldwire and Hannon[23] provide tables for the calculation of β using known values of the transition energy and character. This calculation in the case of the 58-keV transition in ^{159}Tb involves some extrapolation from the tabulated values; however, a value of $\beta = -0.0044$ was estimated.

IV. CONCLUSIONS

The use of the exact transmission integral rather than simple Lorentzians, combined with the technique of joint fitting of spectra, has produced much more precise results for the linewidth of the 58-keV transition in ^{159}Tb than previous work. Although direct use of the transmission integral to fit data requires much better-resolved spectra than when simple Lorentzians are used, in compensation, fewer spectra are required, and deducing the values of fundamental parameters such as linewidth, recoilless fraction, and interference requires no resort to approximations. This technique has also been shown to be resistant to small disturbances of line shape, such as unresolved splitting and vibration, in that simultaneous fits to such distorted spectra will return parameter values that are close to those that would be obtained from unbroadened spectra.

The agreement of our results for the linewidth in the $TbAl_2$ and Tb_4O_7 spectra implies that broadening due to hyperfine interactions in Tb_4O_7 and Dy_2O_3 must be small; if broadening were present in Tb_4O_7, it would presumably also be present in Dy_2O_3, and yet no difference was found in the linewidths derived from the two systems (Dy_2O_3,Tb_4O_7) and (Dy_2O_3,$TbAl_2$). Our value for the linewidth does not agree well with most earlier studies, as summarized in Table I, possibly because the earlier studies had very poorly resolved spectra. Our values for $f(T)$ for Tb_4O_7 and $TbAl_2$ agree fairly well with values at similar temperatures in Tb_2O_3 and $TbAl_2$ by Endres, although it appears our values are systematically higher by about 10%. The character of the variation of the recoilless fraction, especially in $TbAl_2$, indicates failure of the Debye model for this case, although a temperature-independent Θ_M can be obtained if α is 14.3 instead of the theoretical value of 11.

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