Mössbauer Effect in Tb^{159} †

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The linewidth of the Mössbauer resonance of the 58-keV radiation from Tb^{159m} has been measured with Dy^{159}(as Dy_2O_3) and Gd^{159}(as Gd_2O_3) sources and Tb_4O_7, Tb metal, and $Tb_2(CO_3)_3$ absorbers, all at 80°K. The measured linewidths, extrapolated to zero absorber thickness, are 5.0 ± 1.4 cm sec^{-1} for the Dy_2O_3-Tb_4O_7 system, 7.9 ± 1.8 cm sec^{-1} for the Dy_2O_3-$Tb_2(CO_3)_3$ system, and 11.5 ± 1.0 cm sec^{-1} for a 22 mg cm^{-2} Tb metallic absorber. A few measurements with a Gd_2O_3-Tb_4O_7 system gave 10.1 ± 1.0 cm sec^{-1} for a 27 mg cm^{-2} Tb_4O_7 absorber. The extrapolated value for the Dy_2O_3-Tb_4O_7 combination gives a calculated lifetime for this state of $(9.6_{-2.1}/^{+3.7})\times10^{-11}$ sec, in reasonable agreement with the value $(1.3\pm0.4)\times10^{-10}$ sec determined by delayed-coincidence methods. A discussion of line-broadening mechanisms and a comparison with some other rare-earth Mössbauer observations as well as a discussion of the use of this Mössbauer resonance in low-temperature phonon experiments is included.

INTRODUCTION

THE rare earths are particularly rich in Mössbauer isotopes; eight isotopes are now known to display Mössbauer resonances.[1,2] All rare-earth elements from Sm to Yb except Ho have observable Mössbauer resonances; Ho^{165} has an isomeric state at 95 keV ($M1$, $\frac{9}{2}\rightarrow\frac{7}{2}$) which may be usable for Mössbauer spectroscopy.[3] An observation of a Mössbauer resonance in Tb^{159} has been reported by Dezhi and Kestkheli.[2]

Tb^{159m} decays by gamma emission (58 keV, $\frac{5}{2}\rightarrow\frac{3}{2}$) to Tb^{159} which is 100% naturally abundant. The half-life of this transition has been measured by delayed-coincidence techniques to be $(1.3\pm0.4)\times10^{-10}$ sec.[4] This isomeric state can be populated by beta decay from either Dy^{159} (134-day) (e^- capture) or Gd^{159} (18.0-h) as shown in Fig. 1. Millicurie sources of Tb^{159m} have been prepared by thermal-neutron capture in Dy^{158} (using 10 mg of Dy_2O_3 enriched to 14% Dy^{158}) and Gd^{158} (using Gd_2O_3 enriched to 97.6% Gd^{158}). The neutron irradiation of Dy^{158} was carried out in a flux of 2.8×10^{14} neutrons cm^{-2} sec^{-1} at the Oak Ridge Research Reactor for a period of one week. Dy^{165} (139 min; β^-, γ) and Dy^{166} (82 h; β^-) (made by double neutron capture in Dy^{164}) were allowed to decay before attempting Mössbauer runs as the 81.1-keV gamma emission from Dy^{166} and other radiations are a serious source of interference. Several Gd^{159} sources were prepared, either by thermal-neutron irradiation at the same flux in the Oak Ridge Research Reactor or smaller sources at a flux of 10^{-12} neutrons cm^{-2} sec^{-1} in the Cornell University Triga II reactor. Highly enriched Gd^{158} is necessary as the starting material since naturally occurring Gd contains 14.7% Gd^{155} and 15.68% Gd^{157} which possess large thermal-neutron capture cross sections (6.1×10^4 and 2.4×10^5 b nucleus^{-1}, respectively). The irradiation period for the Gd sources was about 8 h in all cases.

Tb_4O_7 [5,6] (10.5 and 27.0 mg cm^{-2}) and $Tb_2(CO_3)_3$ (16 and 32 mg cm^{-2}) absorbers were made by evaporating to dryness water dispersions of the powders placed over aluminum foil as a substrate. After drying, a thin epoxy coating was applied to ensure mechanical stability. The 22 mg cm^{-2} Tb metal absorber was made by filing the metal to a powder and then following the above procedure.

The measured half-life of Tb^{159m} would correspond to a Mössbauer linewidth for unsplit source and absorber

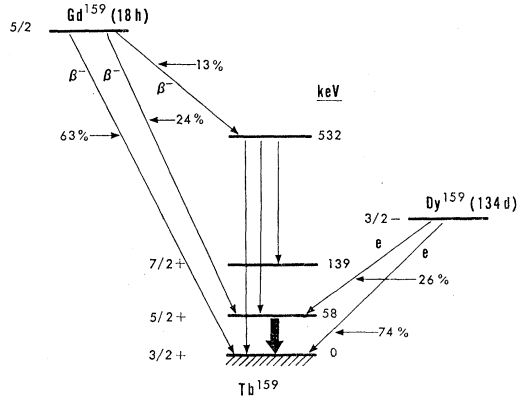

FIG. 1. Decay schemes of Gd^{159} and Dy^{159}. Some transitions have been omitted for clarity. The beta decay of Dy^{159} proceeds by electron capture.

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[1] Mössbauer Isotopes Table, Rev. Mod. Phys. **36**, 496 (1964); Mössbauer Effect Data Index, compiled by A. H. Muir, Jr., and K. J. Ando, North American Aviation Science Center, Thousand Oaks, California (unpublished).

[2] A Mössbauer resonance in Tb^{159} has been reported by I. Dezhi and L. Kestkheli, in *Proceedings of the Dubna Conference on the Mössbauer Effect* (translated by Consultants Bureau Enterprises, Inc., New York, 1963); however, the presented data do not display a resonance within statistical error or give any measure of a linewidth for this case.

[3] B. S. Dzhelepov and L. K. Peker, *Decay Schemes of Radioactive Nuclei* (Pergamon Press, Inc., New York, 1961), p. 482.

[4] E. E. Berlovich, M. P. Bonetz, and V. V. Nikitin, Izvest. Akad. Nauk SSSR, Ser. Fiz. **25**, 218 (1961) [English transl.: Bull. Acad. Sci. USSR, Phys. Ser. **25**, 210 (1961)].

[5] F. J. Darnell, Phys. Rev. **132**, 1098 (1963).

[6] W. C. Koehler, H. R. Child, E. O. Wollan, and J. W. Cable, J. Appl. Phys. **34**, 1335 (1962).

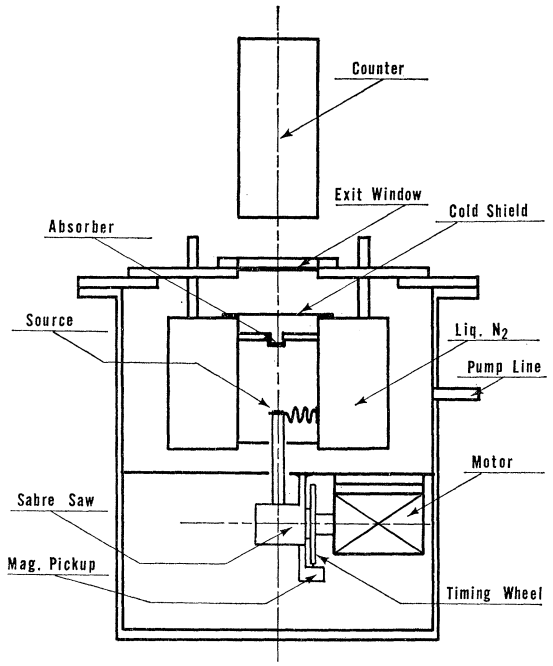

FIG. 2. Experimental arrangement for the observation of Tb^{159} Mössbauer resonances.

of 3.6 cm sec^{-1} (2Γ) thus indicating that a more rapid source mover must be supplied than is usually encountered in Mössbauer spectroscopy. As the ground-state nuclear magnetic moment of Tb^{159} is 1.52 nm,[7] the Tb metal sample should display magnetic hyperfine structure over a ± 10 cm sec^{-1} range.

METHOD

The source mover, a sinusoidal device providing velocities up to ± 40 cm sec^{-1} was a modified commercial jigsaw head driven by a 300-rpm synchronous motor.

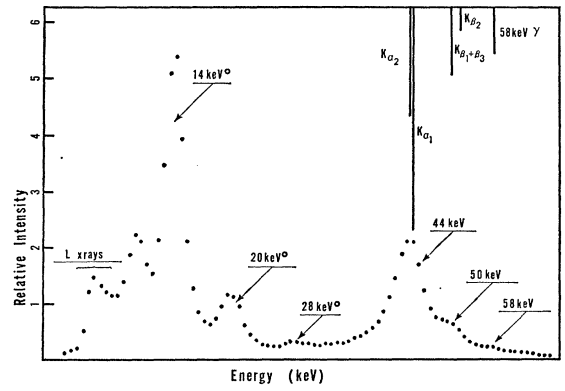

FIG. 3. Theoretical line intensities and experimental Xe-CH_4 proportional counter intensities for radiations from Dy^{159} millicurie source. Superscript zeros denote escape peaks.

[7] J. M. Baker and B. Bleaney, Proc. Phys. Soc. (London) A68, 257 (1955); NMR Table, Varian Associates, Palo Alto, California (4th ed.), 1964 (unpublished).

The saw blade was replaced by a stainless steel tube with a Lucite source holder mounted on the end. Figure 2 shows the placement of the source-absorber combination in the liquid-nitrogen Dewar. A synchronization signal was produced when an iron insert in the brass flywheel on the mover shaft traversed a magnetic pickup.[8] This signal, when amplified and pulse-shaped, opened a gate allowing a series of channel advance pulses from an external oscillator to advance the address of an RIDL multichannel analyzer. The gate was closed by the address reset pulse from the multichannel analyzer.

The most crucial part of the apparatus is the gamma-ray detector which must assist the accompanying electronics in discriminating against the abundant x radiation. Figures 3 and 4 illustrate this problem by displaying a bar graph of the expected intensities and energies of all radiations near the desired 58-keV radiation (Gd^{159} source and $\alpha = 10$) with a pulse-height distribution from a Xe-CH_4 proportional counter and then with the NaI(Tl) scintillation counter acually

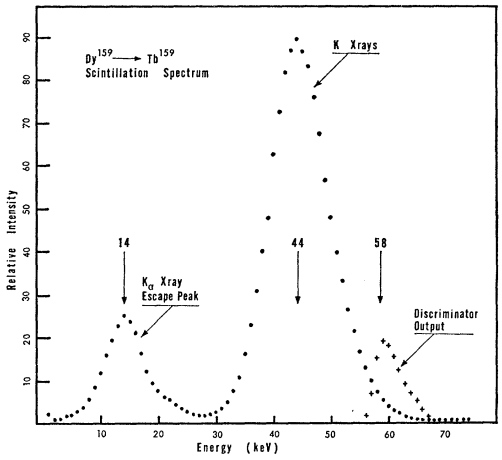

FIG. 4. Pulse-height spectrum from Dy^{159} recorded with a 1.25-in.-diam, 0.080-in.-thick NaI(Tl) scintillation crystal mounted on an EMI 9578S photomultiplier.

used. Xe-CH_4 proportional counters, used at first, did not display the necessary long-term stability and energy resolution although the energy resolution obtainable with a fresh counter permitted more certain identification of the radiation components. The scintillation detector consisted of a 1.25-in.-diam, 0.080-in.-thick NaI(Tl) crystal mounted with silicone grease on the photocathode of a 3-in.-diam, 13-stage EMI 9578S photomultiplier tube. The spectral region containing the 58-keV gamma radiation was selected from the pulse-height distribution by a single-channel pulse-height discriminator and discriminator pulses were accumulated in the channels of the multichannel analyzer operated in time, or multiscaler, mode.

[8] The magnetic pickup assembly was Type 3055-A supplied by the Electro Products Laboratory, Inc., Chicago, Illinois.

As the source-detector distance is not constant because of the motion of the source, a correction must be made to the data for the "solid-angle effect." After each Mössbauer run another spectrum was obtained under the same conditions except that the settings on the pulse-height selector were changed to allow discriminator pulses to be obtained only for x radiation. The x-ray data were then normalized to the same number of average counts per analyzer channel as previously recorded in regions of no Mössbauer absorption with the 58-keV gamma radiation. The normalized x-ray data were then subtracted from the gamma data in the same channel leaving only recoilless radiation information.

The velocity V_i in channel A_i is given by

$$V_i = V_0 \sin[2\pi(f_0/f_1)(A_i - A_0)],$$

where V_0 is the maximum velocity, f_0 is the transducer frequency, f_1 is the channel address frequency, and A_0 is the zero-velocity channel. A_0 was determined by measuring the high point on a curve drawn through the x-ray data.

RESULTS

The Mössbauer resonance obtained with a Dy^{159} (Dy_2O_3) source and a 10.5 mg cm^{-2} Tb_4O_7 absorber is shown in Fig. 5. Both source and absorber were at 80°K. The observed linewidths [full width at half-maximum (FWHM)] are (8.8±0.7) cm sec^{-1} for a 27 mg cm^{-2} absorber and 6.4±1.1 cm sec^{-1} for the 10.6 mg cm^{-2} absorber. The percent resonances observed were 2.3 and 1.3%, respectively. When the Gd^{159} (Gd_2O_3) source was substituted for the Dy^{159} (Dy_2O_3) source a larger percent resonance was obtained with the 27 mg cm^{-2} absorber (3.6 instead of 2.3%) but the linewidth was slightly broader (10.1±1.0 cm sec^{-1}). The lower x-ray intensity of the Gd^{159} source (due to β^- decay rather than e^- capture) accounts for this increase in percent resonance.

The linewidth (FWHM) for the Dy_2O_3-Tb_4O_7 system extrapolated to zero absorber thickness is 5.1±1.4 cm sec^{-1} corresponding to a half-life (assuming centered single emission and absorption lines) of $(9.6_{-2.1}{}^{+3.7}) \times 10^{-11}$ sec, in reasonable agreement and comparable accuracy with the measurement by delayed-coincidence of $(1.3\pm0.4)\times10^{-10}$ sec. As Tb_4O_7 is not a simple compound,[9] it should display different isomer shifts corresponding to Tb^{159} nuclei at different lattice sites. In order to compare such chemical effects, $Tb_2(CO_3)_3$ absorbers were measured. They displayed even broader single resonances: The extrapolated zero absorber thickness was 7.9±1.8 cm sec^{-1}.

The Mössbauer resonance in Tb metal was more easily observed using the Gd^{159} (Gd_2O_3) source because of the higher percent resonance. A broad line of 11.5 ±1.0 cm sec^{-1} linewidth was observed as shown in Fig. 6.

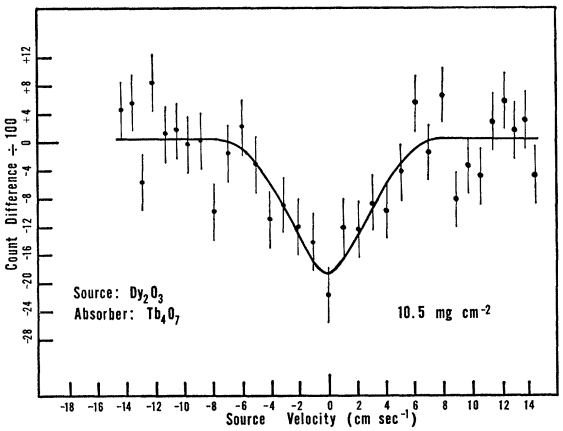

FIG. 5. Mössbauer resonance spectrum of Dy^{159} (Dy_2O_3) source and 10.5 mg cm^{-2} Tb_4O_7 absorber.

DISCUSSION

Magnetic splitting in a Gd_2O_3-Dy^{161} (Dy_2O_3) Mössbauer combination has been observed[10] using the 26-keV radiation from Dy^{161m}. At 80°K the splitting corresponds to an effective magnetic field at the nucleus of 9×10^5 Oe. A similar magnetic field would account for the line broadening observed in these experiments and also might account for the difference in linewidth observed between the Dy^{159} (Dy_2O_3) and Gd^{159} (Gd_2O_3) sources with the same Tb_4O_7 absorber.

The observed resonance in Tb metal with the Gd^{159} (Gd_2O_3) source is about 10% broader then the resonance in Tb_4O_7. Unfortunately there is no resolution of hyperfine lines so that no conclusions can be drawn about the magnetic interactions in Tb metal from this Mössbauer data.

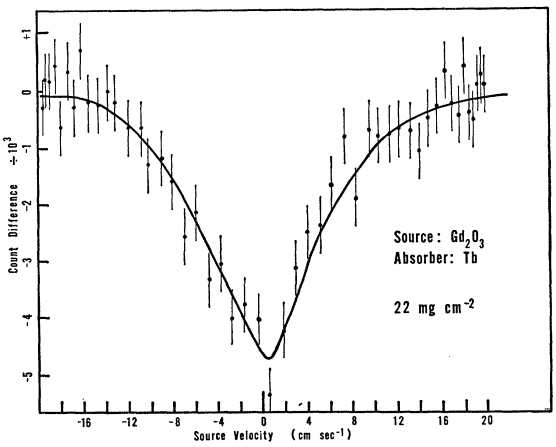

FIG. 6. Mössbauer resonance spectrum of Gd^{159} (Gd_2O_3) source and 22 mg cm^{-2} metallic Tb absorber.

[9] F. Vratny, J. Chem. Phys. 34, 1377 (1961).

[10] V. V. Skylarevski, B. N. Samoilov, and E. P. Stepanov, Zh. Eksperim. i Teor. Fiz. 40, 1874 (1961) [English transl.: Soviet Phys.—JETP 13, 1316 (1961)].

The linewidths observed both by Mössbauer spectroscopy and delayed-coincidence methods in Tb^{159} have energy widths of 4×10^{-2} °K as compared with an energy width of only 5.3×10^{-5} °K for unsplit source-absorber combinations using the 14.4-keV transition in Fe^{57m}. Several Mössbauer experiments involving phonon spectra are suggested by the presence of this wide (by Mössbauer-spectroscopy standards) line. An unsuccessful attempt to observe the predicted low-energy optical mode (3.4°K) in rare-earth (lanathanum and holmium) ethyl sulfates[11–13] was made. Using a Tb $(C_2H_5SO_4)_3\cdot 9H_2O$ absorber with Gd^{159} and Dy^{159} sources cooled to 80°K failed to yield any increased "single-phonon" absorption when the absorber was cooled to 1°K over a velocity range from 0 to 120 cm sec^{-1}. This velocity range is less than satisfactory for this experiment but further measurements of the specific heat of holmium ethyl sulfate do not require the low-lying mode for an explanation.[14]

[11] I. P. Morton and H. M. Rosenberg, Phys. Rev. Letters 8, 200 (1962).
[12] R. Orbach, Phys. Rev. Letters 8, 393 (1962).
[13] H. Meyer and P. L. Smith, J. Phys. Chem. Solids 9, 285 (1959).

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[14] D. G. Onn, R. Gonano, and H. Meyer, in *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964* (Plenum Press, Inc., New York, 1965).

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Accelerated Currents in Superconductors*

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It is shown that the ratio of the accelerated currents of energy and matter induced in a superconductor by a long-wavelength electric field is equal to the chemical potential of the system.

1. INTRODUCTION

WHEN a long-wavelength electric field is applied to a superconductor it induces accelerated flows of matter and energy. In this note it is shown from a microscopic point of view that, at all temperatures below the critical temperature, the accelerated energy current is precisely given by the product of the chemical potential and the accelerated component of the matter current. The result is intuitively extremely plausible: The accelerated flows arise from the motion of the condensate for which the energy per particle is the chemical potential. On this physical basis, Luttinger,[1] in a paper that has greatly clarified the concepts underlying calculations of the thermal conductivity of superconductors, has already conjectured what is proved here.

Luttinger also conjectured that the same relationship holds for the accelerated energy and matter currents induced in a superconductor by a temperature gradient. Using these conjectures, he showed that the thermal conductivity of a superconductor may be exactly written in terms of an autocorrelation function of the current

$$\mathbf{U}=\mathbf{J}^E-\mu\mathbf{J},$$

where $\mathbf{J}^E$ and $\mathbf{J}$ are the energy and matter currents, respectively, and μ is the chemical potential. The expression for the thermal conductivity of superconductors so obtained in Ref. 1 had in fact already been used as the starting point for several calculations.[2] However, it was not previously realized that negligibly small errors [of order $(kT/\mu)^2$] were not thereby introduced at the outset, as they would be for the normal Fermi system.

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[1] J. M. Luttinger, Phys. Rev. 136, A1481 (1964).
[2] V. Ambegaokar and L. Tewordt, Phys. Rev. 134, A805 (1964); V. Ambegaokar and A. Griffin, *ibid.* 137, A1151 (1965); L. Kadanoff and P. Martin, *ibid.* 124, 670 (1961).