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ABSTRACT

The Mössbauer effect has been observed in the 21.7-keV transition in Eu^{151} . The absorption pattern is a single line, independent of temperature, as expected for an ion in which the ground level has $J=0$. A lower limit of 0.92×10^{-8} sec can be set on the lifetime of the isomeric state.

The 21.7-keV transition is thus about a factor of 100 slower than the single-particle estimate. The large discrepancy between the Debye temperatures required to fit the data at 77°K and 295°K is attributed to the influence of optical branches.

THE MÖSSBAUER EFFECT IN Eu^{151} ; POSSIBLE INFLUENCE OF OPTICAL BRANCHES *

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I. Introduction

Soon after the initial discovery of recoil-free γ -ray resonance by Mössbauer in 1958¹, the effect was observed in several nuclei. With the experimental realization of the very sharp 14.4 keV resonance in Fe^{57} ,² and particularly after the discovery of the nuclear Zeeman effect, it became clear that very few nuclei were qualified for detailed investigations of local fields. In fact the combined requirements of a reasonable lifetime for the isomeric state, an appropriate transition energy, and a low conversion coefficient, as well as other technical factors, have excluded all the Mössbauer nuclei save Fe^{57} and Sn^{119} from extensive application. While these two nuclei have been used in a great variety of chemical environments, there are many potential problems for which they are not suitable. In particular it was desirable to find a Mössbauer resonance in an element having the chemical properties of a rare earth. With this goal the present research was undertaken.

In this paper we discuss the spectroscopy associated with the 21.7 keV resonance in Eu^{151} , and some experimental problems, as well as reporting the resonance and some rather tentative quantitative results obtained with oxide sources and absorbers.

II. Electronic Spectroscopy of Trivalent Europium

Rare earth ions have electronic configurations of the form $4f^n$. In Russell-Saunders coupling these form terms spaced by $\sim 10^4 \text{ cm}^{-1}$ in energy. Spin-orbit splitting yields levels (in which J is essentially a good quantum number) spaced by $\sim 10^3 \text{ cm}^{-1}$. The relatively small perturbation of a typical crystalline field splits these levels into states spaced by a few tens of cm^{-1} . Only the states comprising the lowest level are appreciably populated at ordinary temperatures and therefore of interest for most Mössbauer absorption experiments. Still the great spectral complexity implied for a recoil-free absorption experiment on a system involving many Stark levels (as well as line broadening from paramagnetic relaxation) detracts considerably from the feasibility of such experiments. This complexity can be partially avoided by judicious use of low ambient temperature and/or systems with long spin-lattice relaxation times.

An alternative solution that can actually yield a single line of the natural width is also available; namely the use of an ion in which the lowest spin-orbit level is non-degenerate in a crystalline field (i.e., $J=0$). This is possible in Eu^{+3} , in which the lowest level is 7F_0 . Fortunately Eu^{151} has an isomeric nuclear level at 21.7 keV. This state is strongly populated in the decay of 140-day Gd^{151} and depopulates to the ground state via an M1 transition.^{3,4} The lifetime of the isomeric state is unknown, but a single particle estimate, using Moszkowski's formula,⁵ yields a theoretical total lifetime of 1.1×10^{-10} sec. Inasmuch as M1 transitions are usually slower than the single particle values, a natural linewidth of 10^{-5} eV or less seemed a priori attainable, and a considerably smaller width seemed probable.

III. Experimental

An "automatic" spectrometer was used. The absorber was driven sinusoidally by a "voice coil" transducer and the instantaneous velocity was sensed by a pickup transducer. The intensity vs. velocity spectrum was recorded in a 100-channel pulse height analyzer. The drive could be operated at liquid helium temperature without serious reduction of intensity (i.e., with a source-to-counter distance of seven centimeters).

The parent Gd^{151} was produced by a (p,n) reaction on enriched Eu^{151} oxide, from which it was separated by the usual ion-exchange techniques. Sources were prepared using both Nd_2O_3 and Eu_2O_3 enriched in Eu^{153} (to minimize self-absorption). All the absorbers were natural Eu_2O_3 .

The photon spectrum from Gd^{151} is singularly difficult. When a thin sodium iodide crystal is used the 21.7 keV peak lies between a very much more intense 41-keV x-ray and its 12-keV escape peak, and is not a prominent feature of the spectrum (Fig. 1). Some Mössbauer absorption spectra were taken with such a counter, but the observed effect was reduced by about a factor of three by the background in the 22 keV region. An argon filled proportional counter was also used, yielding the spectrum shown in Fig. 2. Here the 21.7 keV peak is well resolved, but the effect is still reduced by a factor of 3 or more if most of the peak is used, and the efficiency is low.

The best results were obtained by using a well-type sodium iodide crystal with a 0.001" aluminum cover. The photon beam was collimated to strike the bottom of the well, and the intensity of the escape peak was thus greatly reduced (Fig. 3). With this counter it was possible to use 50% of the 21.7 keV peak with the effect attenuated by only a factor of 1.1-1.4 (depending on absorber thickness) by background. The intensity of the background radiation from other γ -rays in the source was determined by absorption experiments with thin gold absorbers.

IV. Results

The purpose of this research was to observe and characterize the 21.7 keV resonance in Eu^{151} . No systematic study of the subtleties of source preparation was made, although the sources were prepared carefully by coprecipitation and subsequent dehydration of the hydroxides. Thus a narrower line or a slightly larger effect may be obtainable.

In every experiment the spectrum consisted of a single line at zero velocity (small shifts were actually observed, but they were almost certainly instrumental). The line has a Lorentz shape to within experimental error. The spectrum using the Nd_2O_3 source and a 9.59 mg cm^{-2} natural Eu_2O_3 absorber is shown in Fig. 4. The magnitude of the recoil-free absorption at zero relative velocity for the Eu_2O_3 source and natural Eu_2O_3 absorbers is shown in Figures 5 and 6 as a function of absorber thickness. These data, with other parameters, are tabulated in Table 1.

The narrowest line was obtained using the Nd_2O_3 source and a 4.80 mg cm^{-2} Eu_2O_3 absorber. The line width was $0.23 \pm 0.03 \text{ cm sec}^{-1}$ which immediately implies a mean life for the isomeric level in excess of 8.0×10^{-9} sec. This line width must be corrected for the effects of absorber thickness. In doing this we make the assumptions: (1) the total theoretical M1 conversion coefficient of 32 is used. The experimental value is 29 ± 4 . (2) the statistical factor $(2I_{\text{ex}} + 1)/(2I_{\text{g}} + 1)$ in the absorption cross section is taken as $4/3$. The spin of the excited state could be $3/2$, $5/2$, or $7/2$, and this factor could be as low as $2/3$ or as high as $4/3$. (3) the recoil-free fraction, f , in the absorber is taken as 0.36 (see Table 1). With these assumptions the quantity $x = n\sigma f$ is 1.15, and, using Visscher's formula,⁶ the line width correction factor is 1.15, and a lower limit of 0.92×10^{-8} sec may be set on the lifetime of the isomeric level. While this may be near the true lifetime, the possibility of unresolved quadrupole

hyperfine structure interactions caused by small crystal field effects^{7,8} leaves this an open question. A direct measurement of this lifetime by delayed coincidence techniques would be highly desirable.

V. Discussion

The magnitude of the effect is directly related to the recoil-free fraction when source and absorber are chemically identical, by the expression

$$\% \text{ effect} = 100 f \left[1 - e^{-\frac{x}{2}} I_0\left(\frac{x}{2}\right) \right], \quad x = n \sigma f \quad (1)$$

where $I_0\left(\frac{x}{2}\right) = J_0\left(\frac{ix}{2}\right)$, the zero-order Bessel function. We note that the theoretical curves in Figures 5 and 6 may be considered to be associated with recoil-free fractions of 0.54 at 77°K and 0.36 at 295°K, respectively, and that the shapes of the curves are independent of assumptions about the phonon spectrum. Indeed the very different Debye temperatures of 125°K and 185°K which are associated with these theoretical curves at the two temperatures show that the Debye model is not applicable to Eu_2O_3 . It has long been known from heat capacity data that the Debye model is not applicable to oxides and salts, and indeed it was never intended for such application.

In lattices of two or more unlike atoms optical branches have been predicted and in some cases clearly identified.⁹ Kagan has discussed the influence of optical branches on the recoil-free fraction¹⁰ and has concluded that this influence should be manifest in a larger recoil-free fraction at high temperatures than would be expected on the Debye model. We note that this behavior might be expected on simple physical grounds because an optical branch is essentially a high frequency branch of relatively narrow bandwidth. In a lattice consisting of atoms (or ions) of very different masses the optical branches should be particularly well defined, although possibly difficult to observe. Thus it seems reasonable to associate the great discrepancy between

the two Debye temperatures needed to fit our data at 77°K and 295°K with the influence of optical branches. We note in passing that the heat capacity data on rare earth oxides¹¹ do not follow a Debye curve but that these data can be approximated by Debye curves for θ in the range 100-200°K. Furthermore, our room temperature data can be fitted by a Debye temperature of 185°K which is lower than, but not grossly different from, the value of 230°K found by Ofer, et al.¹² for Dy₂O₃.

The spin assignment of 7/2 to the 21.7 kev level seems quite firm¹³ and it is thus unlikely that our data would require re-interpretation on this account. At any rate, a different spin would change the two "Debye temperatures" only slightly, and in the same direction, and would not change our conclusions about optical branches.

In summary, the Eu¹⁵¹ resonance should prove useful in experiments where a rare earth is required. The single fairly narrow line and large nuclear moments make the absorption spectrum rather sensitive to internal fields. In an odd-proton nucleus there is in addition a good chance of observing a sizable chemical shift, especially when s-electrons are involved.

Acknowledgements

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Footnote and References

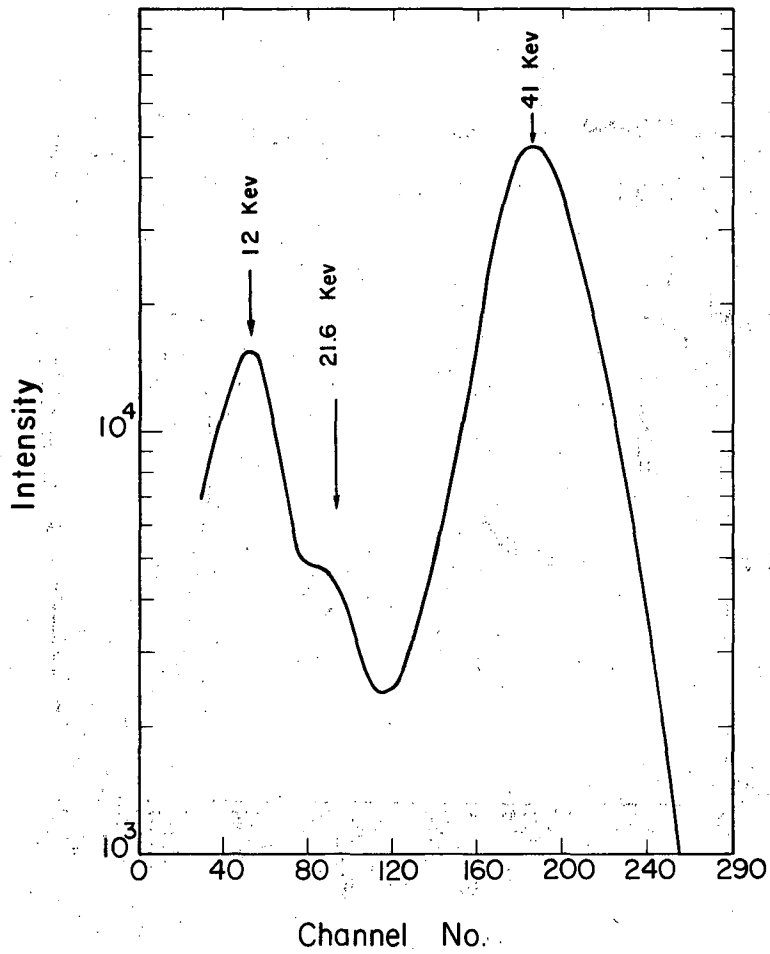
* Work done under the auspices of the U. S. Atomic Energy Commission.

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Table 1

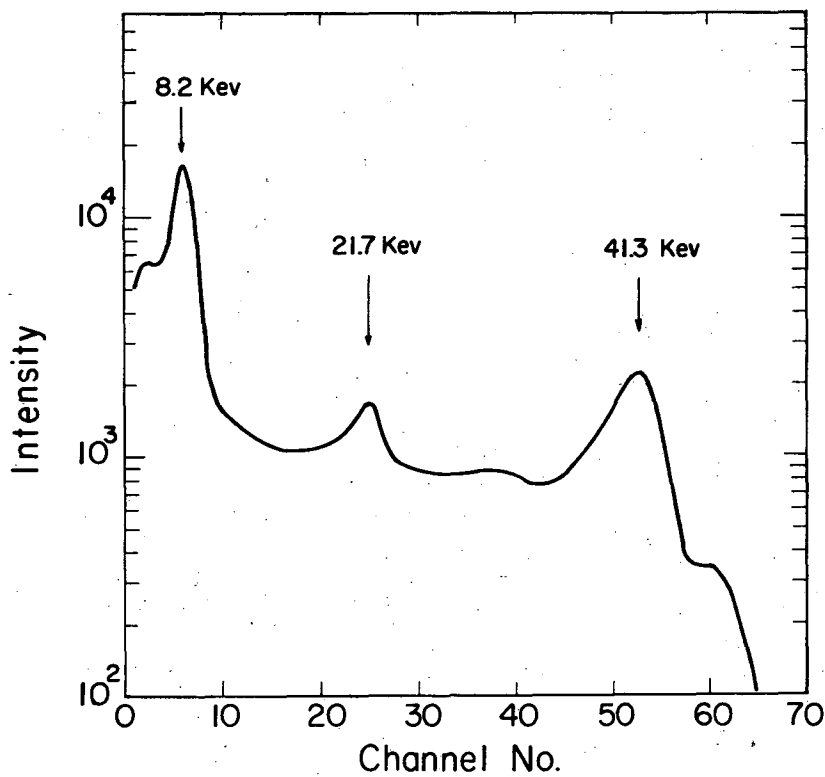
Percent absorption at zero velocity for Eu_2O_3 source and absorber

Temperature (°K)	Absorber thickness (mg/cm ² natural) Eu_2O_3	Percent Effect		Average recoil-free fraction
		uncorrected	corrected	
77	4.8	14.0	17.0	.54
"	10.8	24.6	26.3	
"	17.5	29.0	35.6	
"	31.2	29.1	40.5	
295	1.4	5.0	5.6	.36
"	4.8	8.4	10.1	
"	7.9	10.1	11.6	
"	9.6	14.0	16.5	
"	17.5	16.0	19.7	
"	23.3	17.7	22.1	
"	31.2	16.8	23.1	



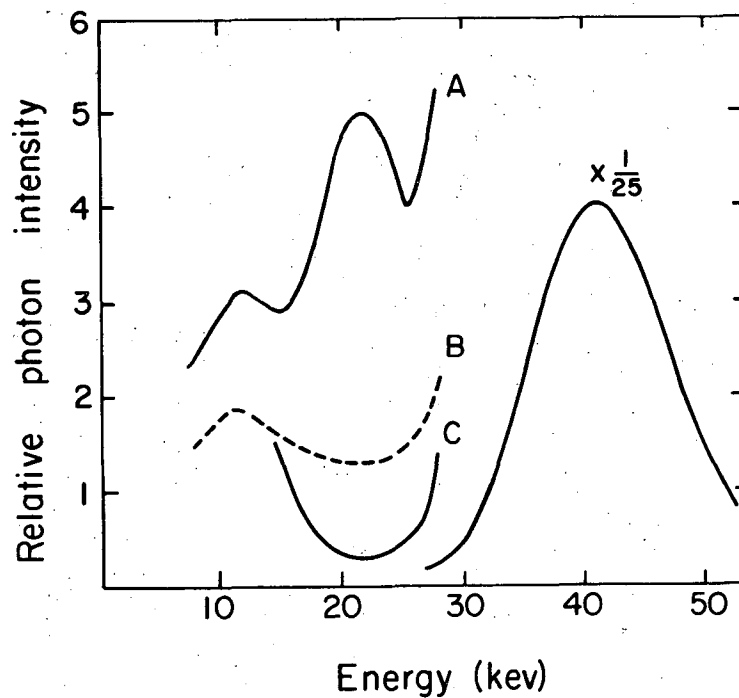
MU-26487

Fig. 1. Low energy gamma-ray spectrum of Gd^{151} obtained with a $1\frac{1}{2}'' \times \frac{1}{4}''$ NaI(Tl) scintillation counter. The 12 kev peak is the K x-ray escape peak; the 21.7 kev peak is the photo peak; the 41 kev peak is the K x-ray.



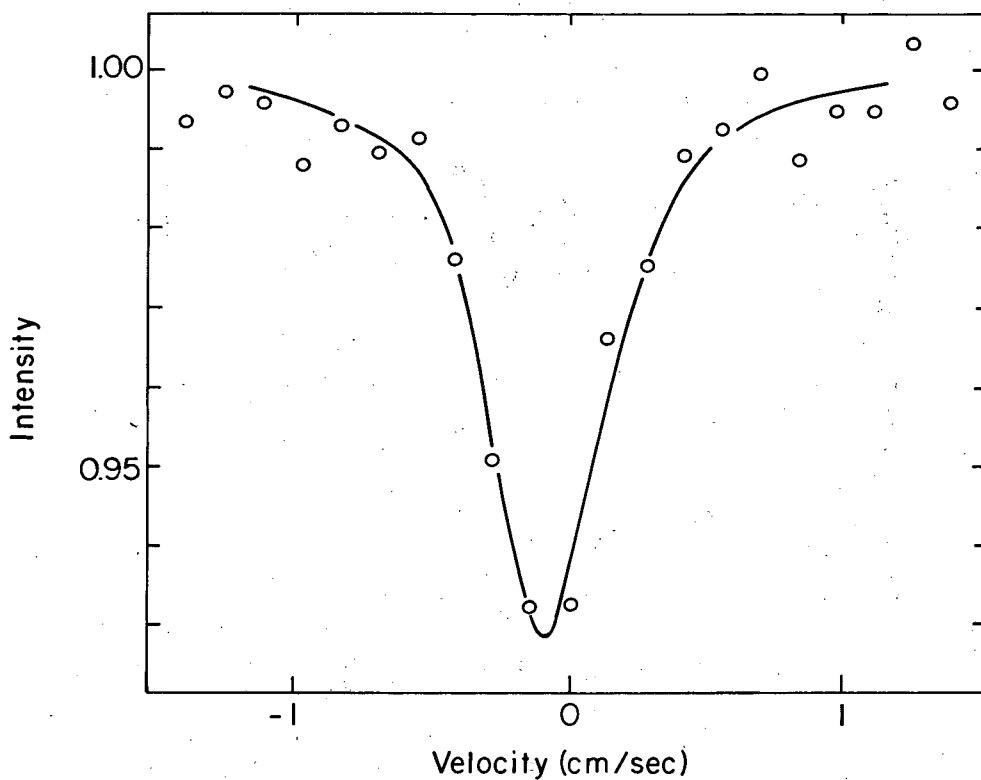
MU-26488

Fig 2. Low energy gamma-ray spectrum of Gd^{151} obtained by means of a proportional counter filled to a pressure of 2 atm. with a mixture of 90% argon - 10% methane. The 21.7-kev gamma ray is clearly resolved from the 41.3-kev Eu x-ray and exhibits a signal-to-noise ratio of about 1:3. The 8.2-kev radiation is due to x-rays from the material of the counter wall.



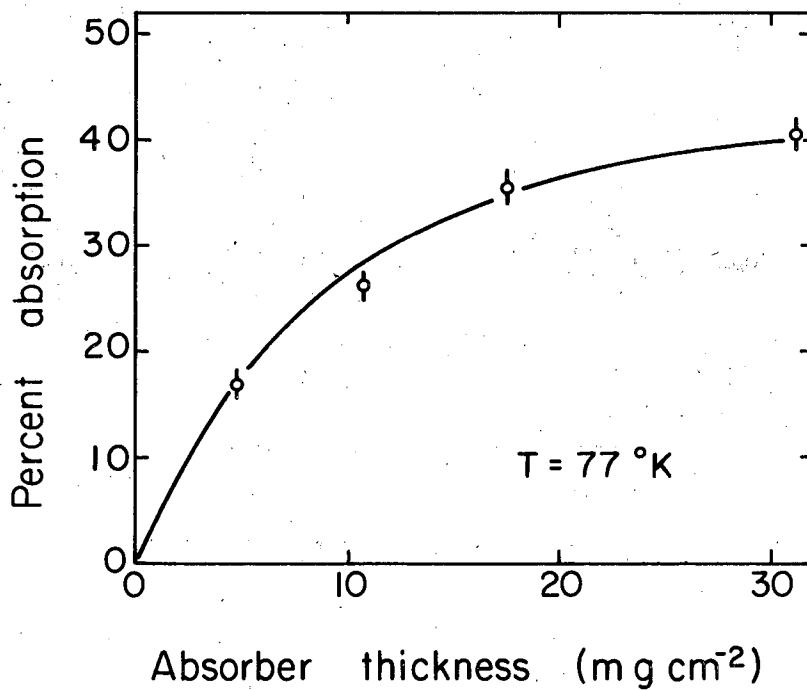
MU-26489

Fig. 3. Low energy γ -ray spectrum of Gd^{151} taken with a collimated beam and a well-type NaI scintillation counter. The peaks are the 21.7 keV γ -ray, the 41 keV x-ray, and its 12-keV escape peak. Curve A was taken with no absorber, and curve B with a 29.9 mg cm^{-2} gold absorber. Curve C represents the background which would be left if the 21.7 keV γ -ray were completely absorbed, based on curves A and B.



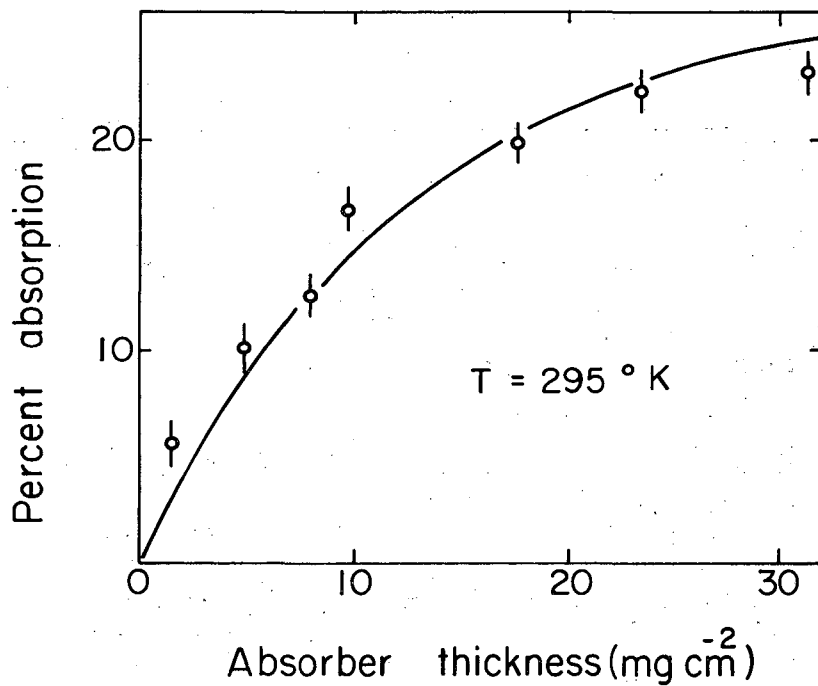
MU-26490

Fig. 4. Room temperature velocity spectrum of the 21.7 kev γ -ray in Eu^{151} , uncorrected for background, using a thin sodium iodide scintillation counter. Source is natural Nd_2O_3 , absorber is 9.6 mg cm^{-2} natural Eu_2O_3 .



MU-26491

Fig. 5. Absorption vs. absorber thickness for a source of Gd^{151} in Eu_2O_3 enriched in Eu^{153} , and an absorber of natural Eu_2O_3 , both at 77°K . The theoretical curve is for a Debye θ of 125°K , an excited state spin of $7/2$, and a total conversion coefficient of 32.



MU-26492

Fig. 6. Absorption vs. absorber thickness for a source of Gd^{151} in Eu_2O_3 enriched in Eu^{153} , and an absorber of natural Eu_2O_3 , both at 295°K . The well-type crystal was used, and background corrections of up to 38% were made to the raw data. The theoretical curve is for a Debye temperature of 185°K and an excited state spin of $7/2$.

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