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Lamb-Mössbauer Factor of Sodium Ferrocyanide*

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Using a set of commercially prepared sodium ferrocyanide absorbers enriched to 91.2% Fe^{57} the Lamb-Mössbauer factor was measured to be 0.28 ± 0.03 . The thickness of Fe^{57} for these absorbers was measured using x-ray absorption techniques and was found to be considerably smaller than that advertised by the manufacturer even after correcting for the size of the ferrocyanide particles in the absorbers.

We have been using sodium ferrocyanide, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$, absorbers in nuclear gamma-ray resonance experiments^{1,2} because they give relatively narrow unsplit absorption lines. In order to better interpret our results we desired to know the Lamb-Mössbauer absorption factor f_a for this material but the only measurement in the literature³ was incorrectly analyzed. In this earlier work, the ratio of the peak resonant absorption at 300°K to that at 80°K was measured to be 0.60 ± 0.10 for a 0.25 mg/cm^2 sodium ferrocyanide absorber. Assuming $\theta_D \gg T$ and a formula for resonant absorption in the limit of infinitely thin absorbers, they calculated $\theta_D = 340 \pm 40^\circ\text{K}$ corresponding to $f_a = 0.54 \pm 0.14$. θ_D is not greatly larger than room temperature nor is the thickness of the absorber completely negligible. If one uses a more correct expression⁴ for $f_a(T)$ and a value for resonant absorption for absorbers of finite thickness⁵ a value of $\theta_D = 175 \pm 20^\circ\text{K}$ and $f_a = 0.26 \pm 0.08$ is obtained which is considerably different from the value reported by Ruby *et al.*³ For this calculation we assumed $1.5 < \Gamma_s/\Gamma_0 < 2.5$ and $1.0 < \Gamma_a/\Gamma_0 < 1.5$, where Γ_a and Γ_s are the absorber and source linewidths and Γ_0 the natural linewidth determined from the lifetime of the 14 keV state of Fe^{57} . Because of this discrepancy we decided to remeasure f_a for sodium ferrocyanide.

THEORY OF THE MEASUREMENT

For single line sources and absorbers, a simultaneous measurement of both linewidth and absorption areas, using a given source with several combinations of absorbers of various thicknesses, is sufficient to yield not only f_a but also Γ_a and Γ_s . The background corrected absorption area A , is related to the absorber thickness $t_a = n_a \sigma_0 f_a$ by the formula⁶

$$A = (\pi/2) f_s \Gamma_a L(t_a), \quad (1)$$

where f_s is the source Lamb-Mössbauer factor, n_a is the surface density of resonant nuclei, σ_0 is the resonant absorption cross section, and $L(t_a)$ is a saturation function given expressly in the Appendix. If A is measured for several absorbers of a given material but with different thicknesses, f_s is known, and if a relation between the various t_a is known, the value of Γ_a and

the respective t_a 's for each absorber can be varied (subject to the constraints on the t_a imposed by the known relation between them) until the data gives a least squares best fit to Eq. (1). The Lamb-Mössbauer factor for the absorber material is then determined from a measurement of the densities n_a of the absorbers assuming σ_0 is known. A measurement of the resonant linewidth for the same set of absorbers can collaborate the above measurement of f_a . For absorbers with $t_a \leq 5$ the measured linewidth is given by⁵

$$\Gamma_m = \Gamma_a + \Gamma_s + 0.27 \Gamma_0 n_a \sigma_0 f_a. \quad (2)$$

If σ_0 , Γ_0 , and the n_a for each absorber are known one can graph Γ_m vs n_a and determine f_a from the slope and $\Gamma_a + \Gamma_s$ from the intercept. Then using Γ_a determined by the area measurement one obtains Γ_s .

This analysis assumes the absorber is of uniform thickness which is a good assumption for metal foils but for crystals distributed in a plastic matrix one must consider the effects of inhomogeneity (see the appendix) if the crystals are not of sufficiently small dimensions.

EXPERIMENTAL TECHNIQUES AND RESULTS

The experiment was performed at room temperature with an inexpensive single-line source of 0.25-mCi Co^{57} in a copper foil matrix and a high quality 20-mCi Co^{57} source in a platinum foil matrix. The absorbers were sodium ferrocyanide in a lucite disk, enriched to 91.2% Fe^{57} , and purchased from New England Nuclear Corporation, with quoted thicknesses of 0.1, 2, and 2.0 mg/cm^2 Fe^{57} . The resonant spectra was taken using a constant acceleration Doppler spectrometer and the forward and return spectra each accumulated in 100 channels of a multichannel analyzer. These spectra were analyzed by a least squares fit to a Lorentzian line from which the area and linewidths were determined. A background correction⁷ was made on the measured areas by determining the count rate in the 14-keV gate with and without a 0.0125-cm-thick sheet of brass covering the detector window before and after each spectrum was collected.

Three different sets of measurements were made using the three absorbers, 0.1, 2, and 2.0, and combinations,

(0.1+2) and (2+2.0). Two of these runs used the copper source and the third used the platinum source. The thicknesses t_a for each absorber and Γ_a was determined by a least squares fit of the five measured areas to Eq. (1) using the constraints $t_a(0.1)+t_a(2)=t_a(0.1+2)$ and $t_a(2)+t_a(2.0)=t_a(2+2.0)$. We let f_s be 0.715 and 0.723, respectively, for the Cu and Pt sources⁸ and used a variable metric minimization technique⁹ on a digital computer to calculate the results. The background corrections ranged from 32% to 39% in the worst geometry to 5% to 11% for the best. All the measurements agreed to within one mean deviation for the calculated values of t_a giving credence to the background correction procedure. The results are given in Table I.

Because of the difference between the absorbers labeled 2 and 2.0 mg/cm² we realized that we must determine the actual amount of Fe⁵⁷ in each absorber. The total iron content was determined by x-ray absorption techniques and the 91.2% enrichment of Fe⁵⁷, quoted by the manufacturer, was assumed to be correct. The x-ray transmission was measured for each absorber at wavelengths on each side of the iron K_{α} absorption edge. The transmission measurements were at $\lambda_1=1.7367 \text{ \AA}$ and $\lambda_2=1.7494 \text{ \AA}$, where the absorption edge is $\lambda_k=1.7433 \text{ \AA}$. This data was analyzed considering both first- and second-order reflections from a flat LiF crystal used in a GE diffractometer. With I_{10} as the measured x-ray transmitted intensity

$$I_{10}=I_1 \exp(-\mu_1 n - \nu_1 m) + I_1' \exp(-\mu_1' n - \nu_1' m), \quad (3)$$

where I_1 and I_1' are the first- and second-order x-ray intensities incident on the absorber at λ_1 , μ_1 and μ_1' are the mass absorption coefficients of iron, ν_1 and ν_1' the average absorption coefficients of all other atoms in the absorber at the first- and second-order wavelengths, respectively, and m is the average thickness of atoms other than iron. There is a similar equation for the measurement at λ_2 . The values of μ_1 , μ_2 , μ_1' , and μ_2' are 413, 49.4, 67.2, and 68.6 cm²/gm, respectively.¹⁰ I_1 , I_2 , I_1' , and I_2' were determined from Eq. (3) for the iron

TABLE I. Mössbauer absorption results.

Absorber	Measured thickness (t_a) (dimensionless)		Corrected thickness ^a	
	Cu source	Pt source	Cu source	Pt source
0.1	0.40±0.05	0.35±0.06	0.44±0.06	0.38±0.07
2	2.6±0.4	2.7±0.2	2.7±0.5	2.9±0.2
2.0	5.6±1.0	6.4±0.5	5.7±1.0	6.5±0.5
Γ_a/Γ_0	1.6±0.2	1.5±0.1	absorber linewidth	

^a Corrected for finite crystalline particle size as discussed in the appendix.

TABLE II. X-ray results.

Absorber	Thickness (mg/cm ²)	Corrected thickness (mg/cm ²)
0.1	0.05±0.02	0.03±0.02
2	0.38±0.02	0.47±0.04
2.0	0.92±0.03	1.10±0.07

foil of measured thickness taking $m=0$. By examining tables of absorption coefficients, we estimated $\nu_1/\nu_2=(\lambda_1/\lambda_2)^3$ and $\nu_i'=\nu_i/6$, and then calculated n and $\nu_1 m$ for each sample by a self consistent method using Eq. (3). The results are given in Table II. The measurement of the 1.9 gm/cm² enriched iron foil gave 1.95 gm/cm² of total iron and 1.78±0.05 gm/cm² of Fe⁵⁷ assuming a 91.2% enrichment.

The above analysis assumed that the absorbers were uniformly distributed with Fe⁵⁷. One of the referees pointed out that it is difficult to attain a homogeneous enough absorber to eliminate effects of thickness fluctuations. Even though the x-ray measurement revealed no inhomogeneities, yet on a more microscopic scale there may be thickness fluctuations due to the finite size of the sodium ferrocyanide crystals embedded in the clear plastic. Such an inhomogeneity could cause an error in the value calculated for f_a because the experimental t_a and n_a are averages over different non-linear functions of Mössbauer and x-ray absorption, respectively. A correction for such fluctuations was made by measuring the particle size of the sodium ferrocyanide crystals in a metalurgical microscope and using the statistical analysis developed in the appendix. From this analysis, averages

$$\langle t_a \rangle = \int t_a(dS/a) \quad \text{and} \quad \langle n_a \rangle = \int n_a(dS/a),$$

are calculated where dS is a differential surface element and a is the total surface area. These are both linear averages over the absorber so we then calculate f_a from $f_a = \langle t_a \rangle / \sigma_0 \langle n_a \rangle$. By this method $f_a = 0.26 \pm 0.02$.

It is somewhat difficult to know how a fluctuation in thickness will alter the measured linewidth but since Γ_m is approximately linearly related to n_a it seems that one should graph Γ_m vs the linear average $\langle n_a \rangle$. (See Fig. 1). From the slope of the straight line the value of f_a is 0.30±0.02. The $n_a=0$ intercept along with Γ_a from the area measurement yields Γ_s for the sources. The values of f_a , Γ_s , and Γ_a are given in Table III.

DISCUSSION AND CONCLUSIONS

The Lamb-Mössbauer factor for sodium ferrocyanide is 0.28±0.03 as a best value considering all our measurements. This corresponds to $\theta = 179 \pm 8^\circ \text{K}$. This is in

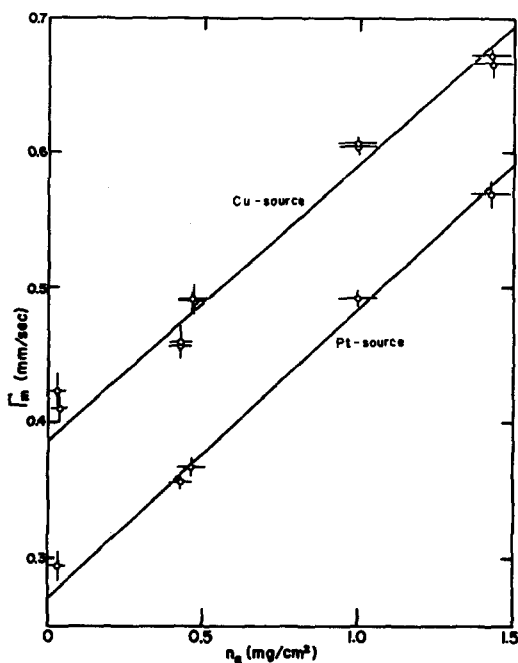


FIG. 1. Measured linewidth versus absorber thickness. Solid lines are least-squares-fit straight lines.

excellent agreement with our analysis of the results of Ruby *et al.*³ No particular care was taken in the Cu source preparation so that its linewidth is about what might be expected. The Pt source linewidth agrees with the 0.25 mm/sec measured by the supplier with a thin absorber.¹¹ The absorber linewidth is larger than one would like but is probably typical of commercially prepared sodium ferrocyanide absorbers. We do not understand why the amount of Fe⁵⁷ in the absorbers is so far below that specified by the manufacturer.

As a point of reference it should be pointed out that we had a 47% effect using the absorber which measured 1.10 mg/cm² of Fe⁵⁷. The χ^2 of the least squares fit of the Mössbauer spectrum to a single Lorentzian line increased from 1.2 to 2.3 times the expected value as the absorber thickness was increased. Part of the problem may be due to the 0.4% nonlinearity of the Doppler spectrometer but one more likely must interpret this increase as a departure from Lorentzian lineshape for the thicker absorbers. The original analysis which considered uniform absorber thickness gave an $f_a = 0.27$ from the area measurement and 0.33 from the linewidth measurement. We did not understand this discrepancy. The analysis which accounts for finite size of the absorbing crystals, however, greatly reduces this discrepancy such that the two types of measurements agree within experimental accuracy. This helps to verify the statistical calculation discussed in the appendix. There still remains uncertainties in the analysis due to the variation in the size of the sodium ferro-

cyanide crystals. The uncertainties quoted span an uncertainty in the average particle diameter of a factor of six.

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APPENDIX

Let us divide the absorber into N columns each of diameter d , where d is the diameter of the sodium ferrocyanide crystals. Let η be the average number of crystals per column

$$\eta = 3 \langle n_a \rangle / 2\alpha\rho d, \quad (\text{A1})$$

where $\langle n_a \rangle$ is the average mass surface density of Fe⁵⁷, ρ is the mass volume density of sodium ferrocyanide, and α is the atomic weight of Fe⁵⁷ times the fraction of iron, which is Fe⁵⁷, divided by the molecular weight of Na₄Fe(CN)₆·10H₂O. $\alpha = 0.129$ in this experiment. Let ρ_j be the probability that a given column contains j crystals. The Poisson distribution then gives

$$\rho_j = \eta^j e^{-\eta} / j!. \quad (\text{A2})$$

With t_a , the Mössbauer thickness for a uniform absorber, we let

$$A(t_a) = \sum_j \rho_j A(t_j), \quad (\text{A3})$$

where A is the background corrected absorption area and $t_j = \langle t_a \rangle j / \eta$, t_j is the thickness of a column containing j crystals, and $\langle t_a \rangle$ is the thickness of a column of η crystals. [Note, if all columns had η crystals $A(t_a) = A(\langle t_a \rangle)$. A is given by a saturation function⁶ $A = (\pi/2) f_a \Gamma_a L(t)$, where

$$L(t) = \sum_s (-1)^{s+1} [(2s-3)!! t^s / s! (2s-2)!!]. \quad (\text{A4})$$

Thus given $L(t_a)$ for each absorber we solved the following equation for $\langle t_a \rangle$ using a HP 9100B calculator:

$$L(t_a) = \sum_j \rho_j (-1)^{s+1} [(2s-3)!! \langle t_a \rangle^s j^s / s! (2s-2)!! \eta^s]. \quad (\text{A5})$$

These results are given in Table I.

Proceeding in a similar fashion for the x-ray measure-

TABLE III. Results from linewidth measurement.

	Cu source	Pt source
f_a	0.29 ± 0.02	0.31 ± 0.02
Γ_s / Γ_0	2.4 ± 0.2	1.3 ± 0.1

ments, we solved the following two simultaneous equations for $\langle n_a \rangle$ and $\nu_1 m$ using a digital computer.

$$I_{10} = I_1 \exp(-\nu_1 m) \sum_j \rho_j \exp(-\sigma_1 \langle n_a \rangle j / \eta) \\ + I_1' \exp(-\nu_1 m / 6) \sum_j \rho_j \exp(-\sigma_1' \langle n_a \rangle j / \eta)$$

and

$$I_{20} = I_2 \exp[-\nu_1 m (\lambda_2 / \lambda_1)^3] \sum_j \rho_j \exp(-\sigma_2 \langle n_a \rangle j / \eta) \\ + I_2' \exp\{-\frac{1}{6} [\nu_1 m (\lambda_2 / \lambda_1)^3]\} \sum_j \rho_j \exp(-\sigma_2' \langle n_a \rangle j / \eta).$$

(A6)

The results are given in Table II.

To obtain η one must first know $\langle n^a \rangle$ [see Eq. (A1)] which is originally not known, so one proceeds by first assuming $\langle n_a \rangle = n_a$; solves Eq. (A6) and then uses this new $\langle n_a \rangle$ to get a new η etc., until the process converges.

The sodium ferrocyanide crystals ranged in size from

0.2 to 20 μ . The average volume of these crystals would correspond to a crystal of 4- μ diameter which is the value used in the above calculation.

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Resistivity and Density of Ge Films Obliquely Deposited in Vacuum

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Ge films were made at 5×10^{-6} Torr by an oblique deposition. Resistivity and its change due to oxygen exposure were measured for different deposition angles. Resistivity anisotropy and its change caused by oxygen exposure were also measured. They increased with the deposition angle. The mass of the film was measured by a microbalance and its density was calculated. The density of the film was less than that of bulk and became smaller with an increase of the deposition angle. These phenomena are explained by the self-shadowing effect.

I. INTRODUCTION

Characteristic properties such as photovoltaic effect,¹⁻⁵ magnetic anisotropy,^{6,7} anisotropic resistance,^{6,8} and optical anisotropy^{6,9,10} have been known in films obliquely deposited in vacuum. Little has been known about the effect of gas adsorption on changes in resistivity and density with the deposition angle.

In this paper, change in resistivity of Ge film with deposition angle was measured in vacuum and oxygen. Density of the film was measured in air for different deposition angles. The experimental results are discussed on the basis of the self-shadowing effect.⁶

II. EXPERIMENTAL METHOD

Single crystal of intrinsic Ge was evaporated from a tungsten conical basket onto a glass substrate ($18 \times 18 \times 0.2$ mm³) at an oblique angle of incidence. Vacuum was maintained at about 5×10^{-6} Torr during the deposition and the rate of deposition was approximately 10 Å/sec. The substrate was not intentionally heated.

Figure 1 shows a schematic illustration of an oblique deposition. Deposition angle θ is defined there. Resistivity measured along the direction parallel to the incidence plane of vapor beam shall be called "parallel" resistivity, and is expressed as ρ_{\parallel} . In the perpendicular direction, "perpendicular" resistivity, ρ_{\perp} .