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B. Fultz and J. W. Morris, Jr.

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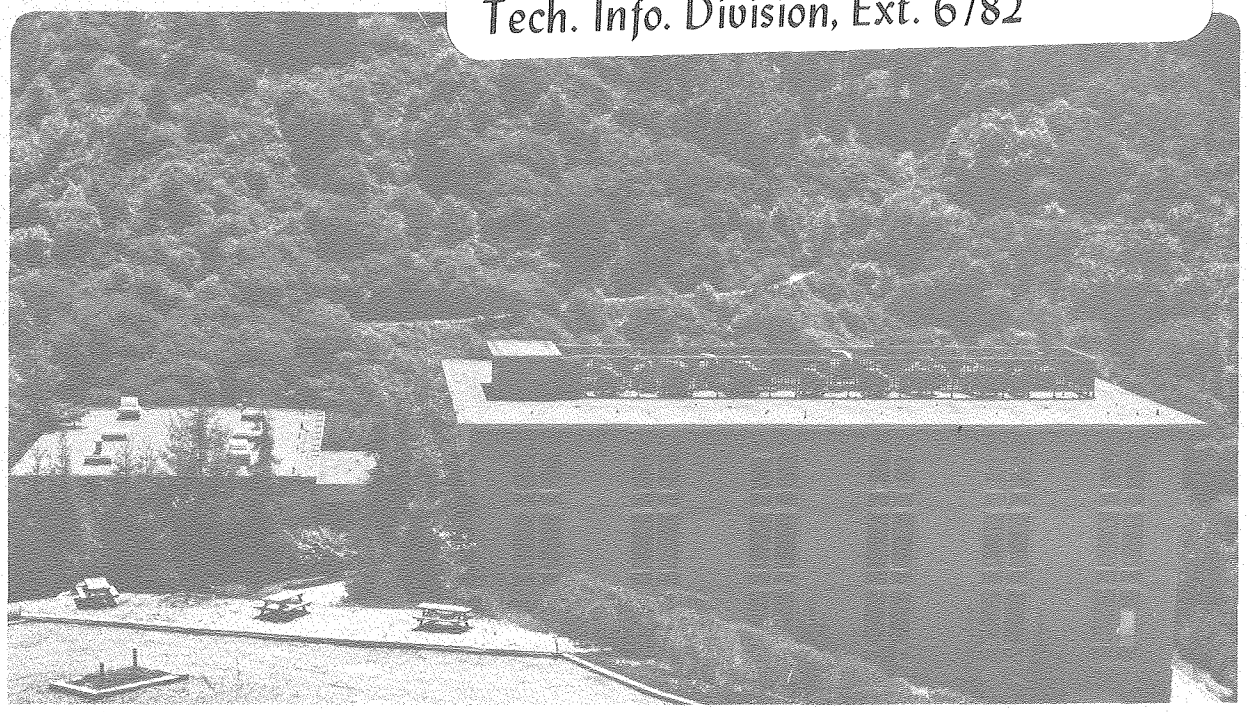

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THE THICKNESS DISTORTION OF Fe^{57} BACKSCATTER MÖSSBAUER SPECTRA

B. Fultz and J. W. Morris, Jr.

Department of Materials Science and Mineral Engineering and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA. 94720.

ABSTRACT

The thickness distortion of a backscatter 14.41 keV γ-ray Mössbauer spectrum is calculated for the case of isotropic γ-ray re-emission in the absorber, and a method of extracting the true absorber material resonant scattering cross section from experimental data is suggested and demonstrated. Some other features of backscatter and transmission Fe^{57} Mössbauer spectra are compared.

INTRODUCTION

Most Mössbauer spectra are obtained from transmission geometry experiments in which the measured γ-ray beam intensity is reduced when there is resonant scattering of the γ-rays passing through a thin absorber. The observed spectrum may not accurately represent the absorber material resonant scattering cross section, $\sigma_A(E)$, because the number of γ-rays with energies subject to strong resonant scattering will be substantially reduced after they have traversed much of the specimen thickness, so material near the exit surface of the absorber will see disproportionately fewer γ-rays which it can resonantly absorb. This thickness distortion and theoretical methods of its correction are well-known.[1-4]

Alternatively, Mössbauer spectra may be obtained from backscatter geometry experiments by counting radiations re-emitted by the specimen following resonant absorbtions. In this paper we shall only consider spectra obtained from backscattered 14.41 keV γ-rays. The internal conversion coefficient for the decay of the first excited state of Fe^{57}, α, is 8.3 so only about 11% of the recoilless absorptions will result in the re-emission of a 14.41 keV γ-ray. A limited detector collection angle will also reduce the intensity of a backscatter spectrum, and in fact, for a natural iron absorber at room temperature a backscatter spectrum will require nearly an order of magnitude of more counting time than that required for a transmission spectrum of comparable counting statistics. This disadvantage of the backscatter geometry is, however, counterbalanced by several advantages which, particularly following the recent development of high efficiency detectors,[5-8] make the backscatter geometry attractive for a variety of experiments.

The principle advantages of the backscatter geometry are these: (1) Sample preparation. While the transmission geometry requires a thin (frequently $\simeq$10 μm) absorber with flat and parallel surfaces in order to correct for thickness distortions, backscatter Mössbauer spectra can be obtained from bulk specimens having only one good surface which need not be strictly flat. However, the best ratios of peak intensity to background intensity are obtained when natural iron absorbers for room temperature backscatter experiments are $\simeq$200 μm thick so as to help reduce Compton scattering in the absorber of incident 122 keV γ-rays and hard x-rays from the source material. (2) Peak-to-background ratio. Using the new high efficiency detectors Mössbauer spectra from backscattered 14.41 keV γ-rays are readily obtained with a ratio of peak intensity to background intensity which is an order of magnitude better than for conventional transmission spectra. The necessary counting time for backscatter experiments with absorbers of low $f_A n_A \sigma_A(E)$ (where f_A is the recoil free fraction of the absorber and n_A is the number of Fe^{57} nuclei per cubic centimeter) may even be less than that required for transmission geometry experiments because of their inherently lower non-resonant background intensity. (3) Sample-to-sample comparison. As long as the absorbers are thicker than a practical lower limit ($\cong$200 μm for natural iron), virtually all incident 14.41 keV γ-rays will be scattered by the absorber. The thickness distortion for such thick polycrystalline absorbers of similar crystal structure and chemistry will be the same. This greatly facilitates the comparison of spectra generated from absorbers of different shapes and thicknesses.

While the thickness distortion of the absorber material resonant scattering cross section, $\sigma_A(E)$, is independent of sample thickness for thick absorbers, this distortion usually must be accounted for when quantitative information is to be extracted from a backscatter spectrum because the thickness distortion will only be negligible when $f_A n_A \sigma_A(E) << \mu$, where μ is the ordinary non-resonant mass attenuation coefficient for 14.41 keV x-rays. Although the thickness distortion for transmission geometry spectra has been worked out in detail,[1-4] we are aware of no comparable formulation for backscatter spectra. In the following we obtain the functional form of the thickness distortion for 14.41 keV backscatter γ-ray spectra, offer an approximation which permits straightforward and accurate data correction in many cases, and give an experimental example drawn from recent work on Fe-Ni-Cr alloys.

The Thickness Distortion

Assuming normal γ-ray incidence, the fraction of 14.41 keV γ-rays from a monochromatic source which are resonantly absorbed in an interval dt at the depth t below the absorber surface is:

$$A(\delta,t) = \frac{f\Gamma}{2\pi} e^{-\mu t} \int_{-\infty}^{\infty} \frac{1}{(E+\varepsilon+\delta)^2 + \frac{\Gamma^2}{4}} f_A n_A \sigma_A(E) e^{-f_A n_A \sigma_A(E) t} dE dt \quad . \qquad (1)$$

f is the probability of a recoilless γ-ray emission, Γ is the full width at half maximum (FWHM) of the source lineshape, ε is the isomer shift difference between the source and absorber materials, and $\delta = v/c(14.41\ \text{keV})$ is the Doppler shift energy of the source with respect to the absorber. We note that Eq. (1) above may be obtained from the normalized Eq. (1) in Ref. 1 by differentiating with respect to t and ignoring the non-resonant

part of the result. Of these γ-rays resonantly absorbed at the depth t, only $(1+\alpha)^{-1} e^{-\mu z}\, d\Omega/4\pi$ represents the fraction of re-emitted 14.41 keV γ-rays which will reach the absorber surface after traveling back the distance z (which may be larger than t) through the solid angle dΩ.

We next consider the contributions to the measured intensity (back-scattered into a detector subtending 2π steradians in front of the absorber), I(δ), from all depths t below the surface of a thick absorber. After considering the isotropic re-emission of 14.41 keV γ-rays into cones with slant height z, height t, and with verticies at each differential volume of re-emitting absorber we obtain:

$$I(\delta) = \int_{t=o}^{\infty} \int_{z=t}^{\infty} \frac{A(\delta,t)}{1+\alpha}\, e^{-\mu z}\, \frac{t}{z^2}\, dz dt \quad .$$

With Eq. (1) and after some manipulations we find:

$$I(\delta) = \frac{f\Gamma}{2\pi(1+\alpha)} \int_{-\infty}^{\infty} \frac{1}{(E+\varepsilon+\delta)^2 + \frac{\Gamma^2}{4}} \frac{f_A n_A \sigma_A(E)}{\left(2\mu+f_A n_A \sigma_A(E)\right)}\, dE +$$

$$- \frac{\mu f\Gamma}{2\pi(1+\alpha)} \int_{-\infty}^{\infty} \frac{f_A n_A \sigma_A(E)}{(E+\varepsilon+\delta)^2 + \frac{\Gamma^2}{4}} \frac{{}_2F_1\left(1,2;3;\ \frac{\mu+f_A n_A \sigma_A(E)}{2\mu+f_A n_A \sigma_A(E)}\right)}{2\left(2\mu+f_A n_A \sigma_A(E)\right)^2}\, dE. \quad (2)$$

The first integral represents the convolution of the absorber resonant scattering cross section with the monochromatic source lineshape weighted by the harmonic mean of the absorber material characteristic distances for resonant and non-resonant scatterings. This first integral is identical to the result obtained for the shape of a Mössbauer spectrum collected by counting only those 14.41 keV γ-rays which are backscattered

along a direction normal to the specimen surface. Those 14.41 keV γ-rays which originate at the depth t but travel to the surface along a path of length $z > t$ are subject to more absorptions. The $e^{-\mu z}$ dependence of this absorption probability will reduce the contribution to the measured spectrum from γ-rays re-emitted at large t, and this is expressed by the smaller second integral in Eq. (2). A spectrum collected with a detector which intercepts less than a 2π steradian collection angle (but still centered around the specimen normal) will be described by the first integral of Eq. (2) minus a correction smaller than the second integral of Eq. (2). Although it should be possible to devise procedures to fit this exact result to experimental data, in the next section we pursue a simpler, albeit approximate, relationship to extract $\sigma_A(E)$ from $I(\delta)$.

It does not seem worthwhile to consider the effect on $I(\delta)$ due to processes in which a resonantly scattered 14.41 keV γ-ray undergoes a second resonant absorption before leaving the absorber as a 14.41 keV γ-ray. The longer average distance traveled for two resonant scatterings and the factor $\frac{f_A^2}{1+\alpha}$ for the second absorption and re-emission will reduce the probability of such double scatterings 2 orders below that of the single scattering processes we have just considered.

A Data Correction Procedure

The power series definition of the hypergeometric function,

$$ {}_2F_1(1,2;3;\theta) = 1 + \sum_{k=0}^{\infty} \frac{2}{(3+k)} \theta^{k+1}, $$

was evaluated numerically and is graphed in Fig. 1. In many cases of practical interest, such as for natural ferromagnetic iron alloys at room temperature where θ only varies from 1/2 to ≈0.6, ${}_2F_1(1,2;3;\theta)$ can be replaced with an accurate linear approximation of ${}_2F_1(1,2;3;\theta) = 0.5452 + 2\theta$. With the additional approximation of

$$\theta = \frac{\mu + f_A n_A \sigma_A(E)}{2\mu + f_A n_A \sigma_A(E)} \simeq 1/2 + 1/4 \frac{f_A n_A \sigma_A(E)}{\mu}$$ we have:

$$I(\delta) \cong \frac{f\Gamma}{2\pi(1+\alpha)} \int_{-\infty}^{\infty} \frac{f_A n_A \sigma_A(E)}{(E+\varepsilon+\delta)^2 + \frac{\Gamma^2}{4}} \left(\frac{1}{2\mu + f_A n_A \sigma_A(E)}\right)\left(1 - \frac{.7726\mu + f_A n_A \sigma_A(E)/4}{2\mu + f_A n_A \sigma_A(E)}\right) dE \tag{3}$$

Our two approximations are quite good when $f_A n_A \sigma_A(E) << \mu$, and the maximum error in the integrand of Eq. (3) is less than $\sim$1% of the integrand until $f_A n_A \sigma_A(E) \simeq \mu$. The accuracy is more than adequate for most absorber materials which are not enriched in Fe^{57}.

The approximate form of Eq. (3) is particularly convenient for processing a backscatter spectrum to recover the true absorber material resonant scattering cross section, $\sigma_A(E)$, and a straightforward procedure for this is now suggested. The deconvolution of the lorentzian source lineshape from the measured spectrum gives a result, D(v), which is related to $\sigma_A(E)$ as:

$$\frac{D(v)}{k} = \frac{f_A n_A \sigma_A(E)}{2\mu + f_A n_A \sigma_A(E)} \left\{1 - \frac{.7726 + f_A n_A \sigma_A(E)/4}{2\mu + f_A n_A \sigma_A(E)}\right\} . \tag{4}$$

This relationship yields a quadratic equation for $\sigma_A(E)$ from which we extract the root:

$$\sigma_A(E)\left(\frac{f_A n_A}{\mu}\right) = \frac{2.4548 - 8\frac{D(v)}{k} - \sqrt{8.7232\frac{D(v)}{k} + 6.026}}{4\frac{D(v)}{k} - 3} . \tag{5}$$

$\sigma_A(E)$ may be described as a sum of single lorentizian lineshapes with identical FWHM's but different mean energies due to the different nuclear environments in the adsorber material. The sum of the maxima of these

component lorentizians is known to be $f_A(2.4 \times 10^{-18})cm^2$ when normalized to one Fe^{57} nucleus. A fit of lorentzian functions to the deconvolved experimental data, D(v), will show approximately how this $f_A(2.4 \times 10^{-18})cm^2$ total cross section is distributed among the component lorentzians. D(v) normalized in this way may be used as $\sigma_A(E)$ in Eq. (4) to approximately determine the scale factor, k, when we also know the absorber material constants μ and n_A. With this first approximation for k, $\sigma_A(E)$ can be recovered from D(v) with Eq. (5). This $\sigma_A(E)$ can then be used for a better approximation for k in Eq. (4), and a better $\sigma_A(E)$ may then be determined from D(v) with Eq. (5). Such an iterative procedure converges quickly when $\max\{f_A n_A \sigma_A(E)\} < \mu$.

The determination of the mean energies and individual maxima of the component lorentzians which make up $\sigma_A(E)$ is frequently a goal of an experimental study. When there is a low statistical counting error in the raw data, a lorentzian curve with a FWHM as large as that of the component lorentzians making up $\sigma_A(E)$ could be deconvolved from $\sigma_A(E)$ determined from Eqs. (4) and (5). The height of the resulting function at δ is proportional to the number of Fe^{57} nuclear environments in the absorber with resonant absorptions centered at the Doppler shift δ.

Example:

The -3/2 → -1/2 transition line for an unenriched ferromagnetic Fe - 8.5 w/o Ni - 0.2 w/o Cr absorber is shown in Fig. 2A. The Γ for our radiation source was determined to be 0.12 mm/sec. A computer generated lorentzian function with this FWHM was deconvolved (using a Gaussian rolloff of higher order Fourier components of the data) from the background corrected data to give the result shown in Fig. 2B.

Using the first approximation for k with $\max\{f_A n_A \sigma_A(E)\} = 300\ cm^{-1}$ and $\mu = 450\ cm^{-1}$ in Eq. (4) gives the result from Eq. (5) for $\sigma_A(E)$ shown in Fig. 2C. To more sharply reveal the intensities and mean energies of the nuclear environments contributing to $\sigma_A(E)$, a lorentzian function of FWHM = 0.08 mm/sec was deconvolved from the function of Fig. 2C to give the result shown in Fig. 2D.

Conclusion:

The thickness distortion of $\sigma_A(E)$ in a measured 14.41 keV backscatter γ-ray Mossbauer spectrum can be described (for the case of isotropic γ-ray re-emission in the absorber and a 2π steradian detector collection angle) in a clumsy exact way or in an approximate way convenient for data processing and with acceptable accuracy when $f_A n_A \sigma_A(E) < \mu$. Such an approximate procedure for extracting $\sigma_A(E)$ from experimental data is described and demonstrated. For absorber materials with large maxima of $f_A n_A \sigma_A(E)$ good counting statistics are more readily obtained with transmission rather than backscatter experiments. Nevertheless, advantages in specimen preparation and the consistency expected in the thickness distortions for different absorbers may in themselves make the 14.41 keV γ-ray backscatter technique an attractive choice for precision work in Fe^{57} Mössbauer spectrometry.

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FIGURE CAPTIONS

Figure 1. The Hypergeometric Function ${}_2F_1(1,2;3;\theta)$.

Figure 2. Backscatter 14.41 keV γ-ray Mössbauer Spectrum of Quenched Fe-8.5Ni-0.2Cr. a) raw data. b) source line shape deconvolved. c) thickness distortion corrected. d) absorption line width deconvolved.

Note the visibility of the resonance peak from Fe atoms with a Cr atom as a nearest neighbor. (Data channel interval $\simeq$.029 mm/sec).

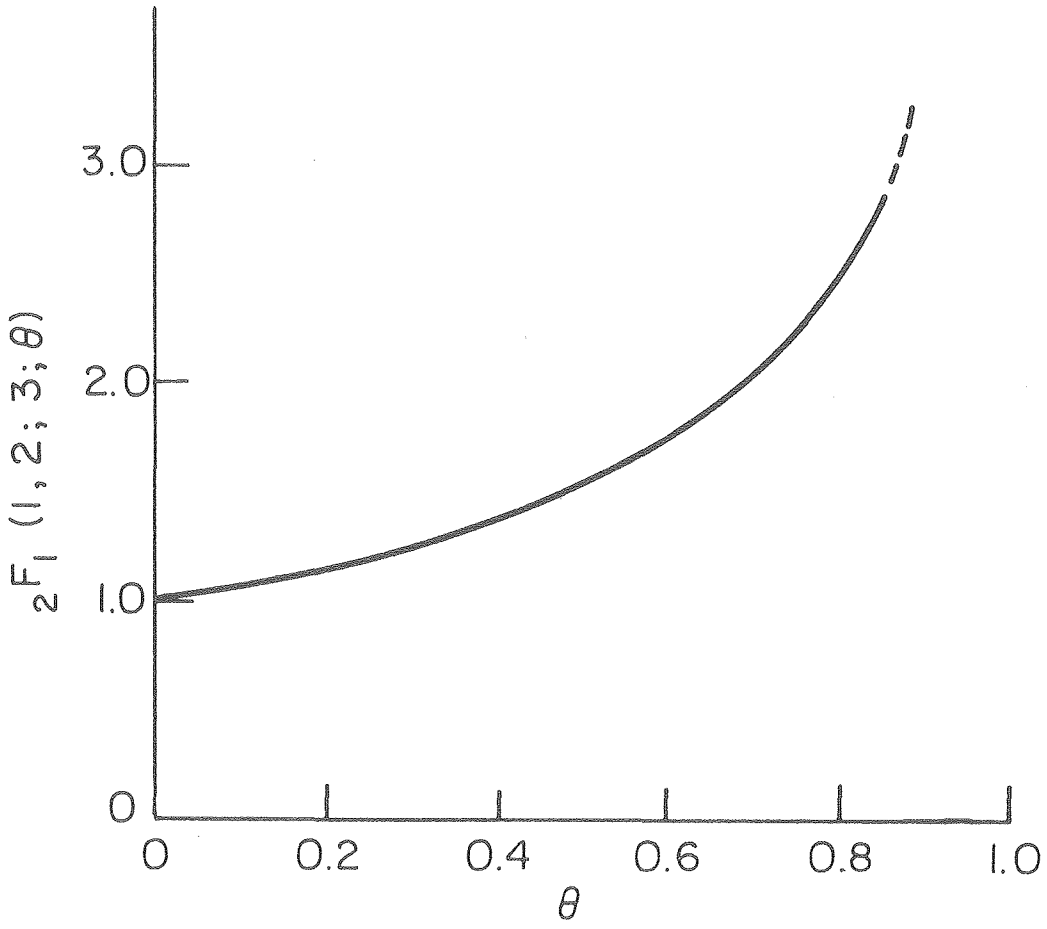

Figure 1

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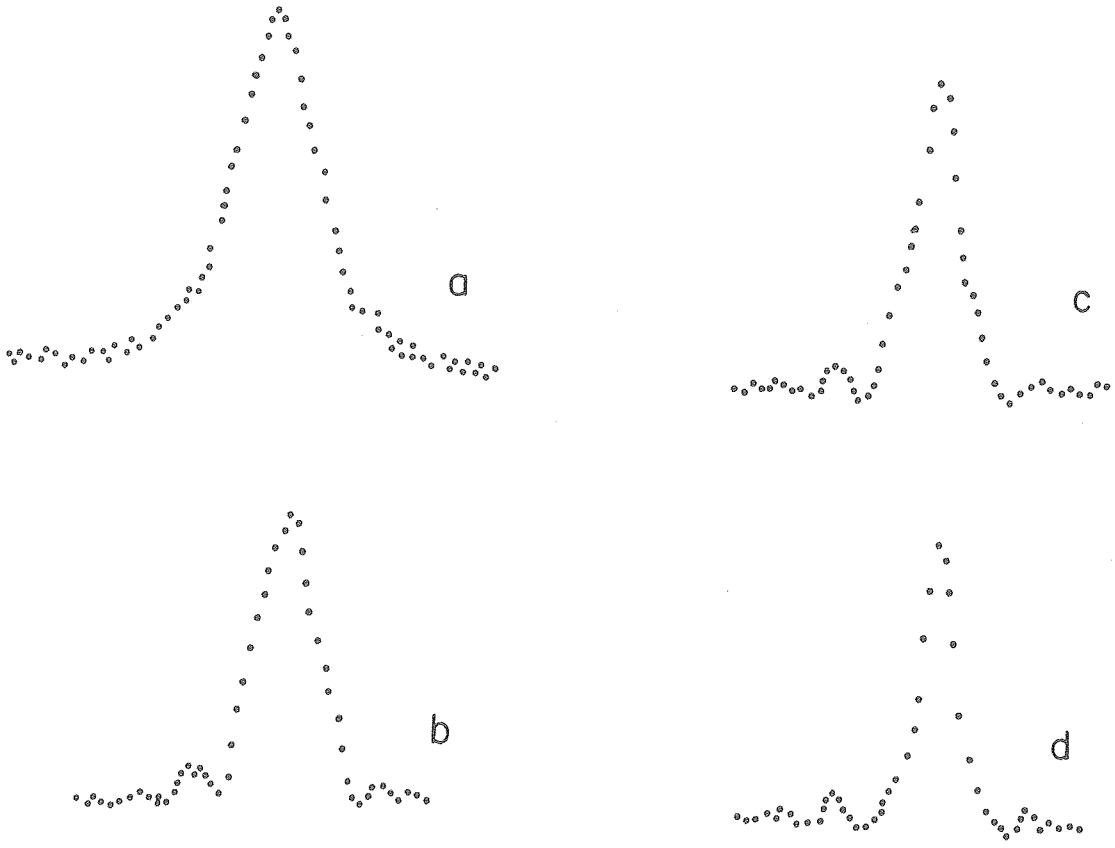

Figure 2.

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