Journal of Nanoparticle Research **4:** 221–224, 2002.

Determination of the recoilless fraction in iron oxide nanoparticles using the two-lattice method

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Received 31 July 2001; accepted in revised form 12 November 2001

Small to greater matters must give way.
(William Shakespeare)

Key words: magnetite, hematite, nanoparticles, Mössbauer spectroscopy, modeling

Abstract

We propose a two-lattice method for direct determination of the recoilless fraction using a single room-temperature transmission Mössbauer measurement. The method is first demonstrated for the case of iron and metallic glass two-foil system and is next generalized for the case of physical mixtures of two powders. We further apply this method to determine the recoilless fraction of hematite and magnetite particles. Finally, we provide direct measurement of the recoilless fraction in nanohematite and nanomagnetite with an average particle size of 19 nm. A list of values obtained for the recoilless fraction in various materials using the two-lattice method is given.

Introduction

The most important parameter in a Mössbauer effect experiment is the recoilless fraction $f = \exp(-k^2\langle x^2\rangle)$, where k is the wave vector of the gamma rays and $\langle x^2\rangle$ is the mean square vibrational amplitude of the resonant atom in the direction of observation. Knowledge of the recoilless fraction is thus of utmost importance, since it provides unique information on the lattice dynamics, phonon softening, crystallization processes and phase transformations occurring in solids incorporating the Mössbauer isotopes. However, direct determination of the recoilless fraction has been to date very difficult, since the only method available relied on the temperature dependence of the recoilless fraction and the determination of the Debye temperature from complicated equation plots.

Quantitatively, the Debye model of solids gives the following expression for the recoilless fraction (Gonser, 1975):

$$f = \exp\{-(3E_R/2k_B\theta_D)[1 + 4(T/\theta_D)^2 \times \int_0^{\theta_D/T} (x/e^x - 1)\,dx]\}. \quad (1)$$

Since the spectral area is proportional to the product $N(^{57}\mathrm{Fe})f(T)$, where $N(^{57}\mathrm{Fe})$ is the number of ^{57}Fe nuclei in the unit area of the absorber and $f(T)$ is the recoilless fraction (Barb, 1980) at temperature T, pairs of measurements at two different temperatures enable the reduction of θ_D from the ratio of the spectral areas and the ultimate derivation of the recoilless fraction. However, the errors implied by this approach are often recognized to be substantial (Nowik et al., 1993; Sorescu, in press).

We propose herewith a much simpler and accurate method to determine the recoilless fraction based on a single room-temperature transmission Mössbauer

measurement of a two-foil absorber. We apply the new method to determine the recoilless fraction in $Fe_{81}B_{13.5}Si_{3.5}C_2$ metallic glass. We further extend the applicability of the two-lattice method for the case of physical mixtures of powders.

Next, we apply the two-lattice method to determine the recoilless fraction of hematite and magnetite powders and compare them with the values of the corresponding nanoparticles. A significant reduction of the recoilless fraction with particle size is observed in both cases.

Experimental

The hematite and magnetite powders were prepared using the hydrothermal method and the average particle diameter was 1.05 and 1.07 μm, respectively. The hematite and magnetite nanoparticles were purchased from NanoTek and had an average particle diameter of 19 nm. Physical mixtures of hematite and magnetite particles and respectively, nanoparticles with iron powders were prepared. The iron particles had less than 10 μm in diameter. The metallic glass sample was provided by Allied Signal. The absorbers were placed in a conventional room-temperature transmission Mössbauer experiment using a ^{57}Co(Rh) source. The least-squares fitting of all spectra was performed with the NORMOS program.

Results and discussion

In our initial experiment, we apply the two-lattice methodology in order to determine the recoilless fraction of iron in Metglas 2605 SC ($Fe_{81}B_{13.5}Si_{3.5}C_2$), in the form of a 25 μm thick foil. Figure 1 shows the room-temperature transmission Mössbauer spectrum of the iron etalon superimposed over the metallic glass foil. The spectrum was fitted using a sextet corresponding to the iron sample and a magnetic hyperfine field distribution, representing the amorphous material. The area ratio derived from the spectral analysis corresponds to

$$A_{\mathrm{Fe}}/A_{\mathrm{mg}} = 59.59\%/40.41\% = 1.47. \qquad (2)$$

On the other hand, one has from chemical arguments:

$$\begin{aligned} A_{\mathrm{Fe}}/A_{\mathrm{mg}} &= (N_{\mathrm{Fe}} f_{\mathrm{Fe}})/(N_{\mathrm{mg}} f_{\mathrm{mg}}) \\ &= [\mu_{\mathrm{mg}}/(0.81\mu_{\mathrm{Fe}})](\rho_{\mathrm{Fe}}/\rho_{\mathrm{mg}})(f_{\mathrm{Fe}}/f_{\mathrm{mg}}) \\ &= \frac{56.85 \times 7.87 \times 0.7}{0.81 \times 55.847 \times 7.32 \times f_{\mathrm{mg}}} \\ &= 0.946/f_{\mathrm{mg}}. \end{aligned} \qquad (3)$$

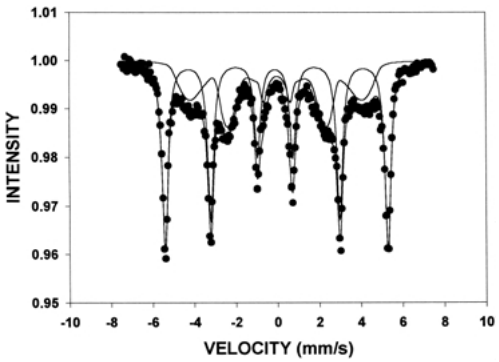

Figure 1. Room-temperature transmission Mössbauer spectrum of iron and Metglas 2605 SC in a two-foil arrangement.

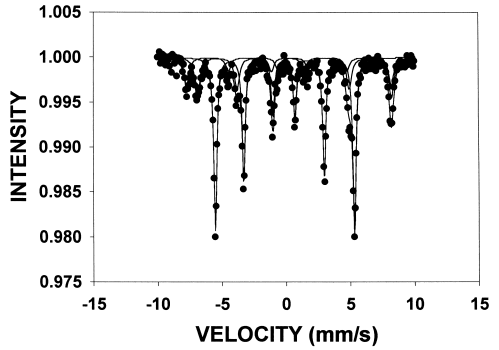

Figure 2. Room-temperature transmission Mössbauer spectrum of magnetite and iron powder mixture.

In this formula 'mg' stands for metallic glass. Consequently, this experiment leads to a value of $f_{\mathrm{mg}} = 0.64$ for the recoilless fraction in $Fe_{81}B_{13.5}Si_{3.5}C_2$ metallic glass at room temperature, with an estimated error of $\pm 3\%$. As expected, this value is less than the recoilless fraction in iron at room temperature, because the crystalline lattice of iron is more rigid as compared to that locally present in amorphous materials.

In what follows, we apply the two-lattice approach by considering the case of magnetite (Fe_3O_4) which was combined with a standard natural iron powder. The resulting room-temperature transmission Mössbauer spectrum of the two-phase absorber is shown in Figure 2. The spectrum was analyzed using three sextets, one for the iron etalon and two for the tetrahedral and respectively, octahedral sites of magnetite. The area ratio derived from the spectral analysis corresponds to

$$A_{\mathrm{Fe}}/A_{\mathrm{mag}} = 61.47\%/38.53\% = 1.59. \qquad (4)$$

On the other hand, one has from chemical arguments:

$$\begin{aligned} A_{\mathrm{Fe}}/A_{\mathrm{mag}} &= (N_{\mathrm{Fe}} f_{\mathrm{Fe}})/(N_{\mathrm{mag}} f_{\mathrm{mag}}) \\ &= [\mu_{\mathrm{mag}}/(3\mu_{\mathrm{Fe}})](\rho_{\mathrm{Fe}}/\rho_{\mathrm{mag}})(f_{\mathrm{Fe}}/f_{\mathrm{mag}}) \\ &= \frac{231.539 \times 7.87 \times 0.7}{3 \times 55.847 \times 5.26 \times f_{\mathrm{mag}}} \\ &= 1.44/f_{\mathrm{mag}}. \end{aligned} \tag{5}$$

In this formula 'mag' stands for magnetite. This leads to a value of $f_{\mathrm{mag}} = 0.9$ for the recoilless fraction in magnetite. Estimated errors are $\pm 3\%$.

The next case is that of hematite (Fe_2O_3) mixed with iron, both in powder form. The resulting room-temperature transmission Mössbauer spectrum of this physical mixture is presented in Figure 3. The spectrum was analyzed by considering two sextets, corresponding to the iron etalon and the hematite component, respectively.

The area ratio derived from the spectral analysis corresponds to:

$$A_{\mathrm{Fe}}/A_{\mathrm{he}} = 74.39\%/25.61\% = 2.9 \tag{6}$$

On the other hand, one has from chemical arguments:

$$\begin{aligned} A_{\mathrm{Fe}}/A_{\mathrm{he}} &= (N_{\mathrm{Fe}} f_{\mathrm{Fe}})/(N_{\mathrm{he}} f_{\mathrm{he}}) \\ &= [\mu_{\mathrm{he}}/(2\mu_{\mathrm{Fe}})](\rho_{\mathrm{Fe}}/\rho_{\mathrm{he}})(f_{\mathrm{Fe}}/f_{\mathrm{he}}) \\ &= \frac{159.692 \times 7.87 \times 0.7}{2 \times 55.847 \times 5.3 \times f_{\mathrm{he}}} \\ &= 1.48/f_{\mathrm{he}}. \end{aligned} \tag{7}$$

In this formula 'he' stands for hematite. This leads to a value of $f_{\mathrm{he}} = 0.51$ for the recoilless fraction in hematite. Estimated errors are $\pm 3\%$.

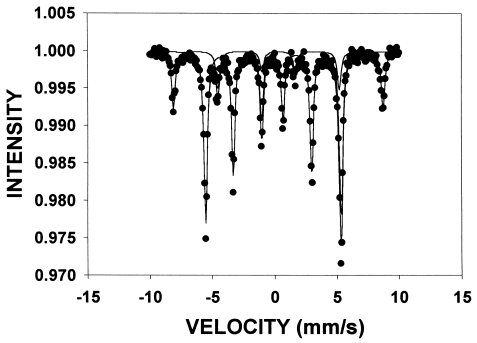

Figure 3. Room-temperature transmission Mössbauer spectrum of hematite with iron powder mixture.

Figure 4 shows the room-temperature transmission Mössbauer spectrum of nanohematite mixed with iron powder. The two-lattice fit of the spectrum was also applied in this case. The areal ratio obtained from the Mössbauer measurement was:

$$A_{\mathrm{Fe}}/A_{\mathrm{nh}} = 85.13\%/14.87\% = 5.73. \tag{8}$$

In this formula 'nh' stands for nanohematite. This leads to a value of $f_{\mathrm{nh}} = 0.25$ for the recoilless fraction in nanohematite. This value is considerably lower that that obtained for the f factor in hematite powder. Although a decrease in the recoilless fraction with particle size is probably expected for nanoparticles, due to their small masses, we emphasize that only the application of the two-lattice method enables one to directly measure this effect.

Figure 5 shows the room-temperature transmission Mössbauer spectrum of a physical mixture of nano-magnetite with iron. The three-subspectrum fit was applied in this case, similar to the theoretical treatment of magnetite. However, the signal-to-noise ratio in this

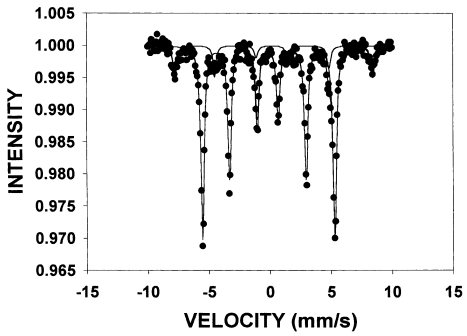

Figure 4. Room-temperature transmission Mössbauer spectrum of the nanohematite with iron physical mixture.

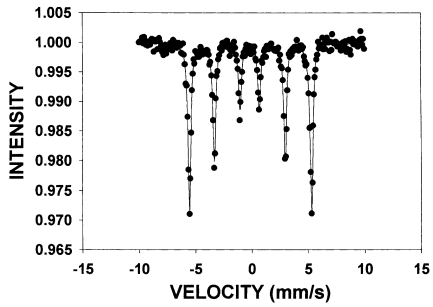

Figure 5. Room-temperature transmission Mössbauer spectrum of the nanomagnetite with iron physical mixture.

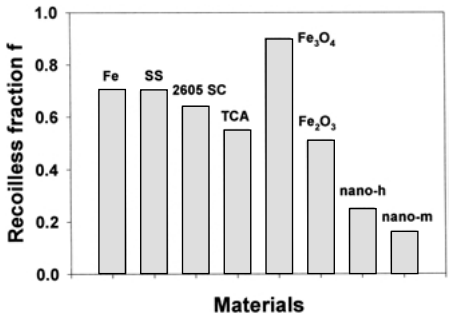

Figure 6. The recoilless fraction determined using the two-lattice method in various absorbers to date. Fe: iron foil; SS: stainless steel foil; 2605 SC: $Fe_{81}B_{13.5}Si_{3.5}C_2$; TCA: $Fe_{78}B_{13}Si_9$; magnetite; hematite; nanohematite; nanomagnetite.

case is at the limit of detection of the experimental method used, such that only an upper limit for the f value can be derived for nanomagnetite. The spectral analysis leads to the value:

$$A_{\mathrm{Fe}}/A_{\mathrm{nm}} = 94.89\%/5.11\% = 18.5. \qquad (9)$$

In this formula 'nm' stands for nanomagnetite. This result implies that the recoilless fraction in nanomagnetite is 0.16 at most. This finding is in agreement with our previous results on the hyperfine parameters of nanomagnetite (Sorescu, 2000). Estimated errors for nanoparticles recoilless factors are $\pm$ 3%.

Figure 6 summarizes the results obtained to date for the Debye–Waller f factor in various materials using the two-lattice method.

Conclusions

In conclusion, this two-lattice approach has the decisive advantage of avoiding the determination of the Debye temperature from complicated equation plots based on the temperature dependence of the recoilless fraction. Besides being simple and direct, it relies on a single room-temperature Mössbauer measurement and thus *minimizes* the experimental errors due to the *comparative* approach. The method can be further developed to determine the recoilless fraction in other systems, for instance in multilayers in which all films contain Mössbauer active nuclei. In particular, the accurate determination of the f factor in nanoparticles is another success of our method.

Acknowledgement

This work was supported by the National Science Foundation.

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