Recoilless-Fraction Ratios for Fe^{57} in Octahedral and Tetrahedral Sites of a Spinel and a Garnet*

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We have determined the ratio of recoilless fractions, f_B'/f_A', of Fe^{57} nuclei in octahedral (B) and tetrahedral (A) sites in Fe_3O_4 and in yttrium iron garnet (YIG), using the Mössbauer effect, by measuring the area ratios as a function of temperature. We find $f_B'/f_A'=0.99\pm0.01$ at $0°K$ and $f_B'/f_A'=0.94\pm0.02$ at room temperature. Since, in the Debye approximation, a difference in recoillesss fractions implies a difference in the Debye temperatures, we have defined two Debye temperatures for such materials corresponding to Fe ions in A and B sites. These Debye temperatures have been determined independently and are consistent with the ratio of recoilless fractions. The Debye temperatures are, however, considerably lower than those found by specific-heat measurements. Possible explanations for this difference are discussed.

INTRODUCTION

A SPINEL and a garnet are usually represented by the chemical formulas $(R)[Q_2]O_4$ and $\{P\}[Q_2](R_3)O_{12}$, respectively. Here the round brackets refer to ions in tetrahedral, the square brackets to ions in octahedral, and the curly brackets to ions in dodecahedral sites. For convenience, we will use the same notation for spinels and garnets, viz., A will refer to tetrahedral sites and B to octahedral sites. If the A and B sites are at least partially occupied by ions possessing a magnetic moment, these materials may show a ferrimagnetic behavior. The rare-earth ions in the simple garnets usually occupy the dodecahedral sites. The dominant magnetic interaction is the antiferromagnetic A-B superexchange interaction. Consequently, the magnetic properties of these compounds[1-4] are determined by the kind of cations in the A and B sites and how these ions are distributed among these sites.

The conventional technique of x-ray analysis[5] is not suitable for a determination of the cation distribution in these materials if the cations are nearby in the Periodic Table. More recently, the Mössbauer-effect technique has become a tool for measuring the cation distribution among crystallographically inequivalent sites.[6-14] This distribution can be determined from the ratio of the areas under the recoilless resonant absorption peaks for Fe^{57} nuclei in A and B sites, provided the recoil-free fractions f_A' and f_B' are known. These two recoil-free fractions are not necessarily equal, as has been pointed out by van Loef[15] and by Grant et al.[16]

To determine f_A' and f_B', we have recorded spectra of $(Fe)[Fe_2]O_4$ and $\{Y_3\}[Fe_2](Fe_3)O_{12}$. These materials are suitable for such a study because (a) over a wide range of temperature, the hyperfine fields differ sufficiently for an accurate determination to be made of the areas under the peaks due to Fe^{57} nuclei in A and B sites, and (b) the distribution of the iron cations among A and B sites is known for pure and stoichiometric samples.

EXPERIMENTAL

The absorption spectra have been obtained for powdered samples of Fe_3O_4 and YIG using a 7-m Ci source of Co^{57} in a Cr matrix. The absorbers were crushed single crystals of the mineral magnetite and synthetically grown single crystals of YIG. The stoichiometry of the magnetite sample was better than 1%.[17] The spectra are recorded using a Nuclear Data 1024-channel analyzer, model 2200. Clock pulses from the analyzer drive a scalar, and a digital-to-analog converter then generates a stepwise voltage with a saw-tooth waveform. This voltage serves as the reference for the transducer-driving electronics.[18] The

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furnace and temperature-control electronics have been described previously.[19]

RESULTS

Several absorption spectra of Fe_3O_4 have been recorded in the temperature range 300–800°K with absorber thicknesses of 25, 15, and 8 mg/cm². Some of these results have been published in a previous paper on the relation between the hyperfine magnetic fields and sublattice magnetizations in Fe_3O_4.[19] All the spectra have been corrected for some absorption in the middle of the spectrum due to iron impurities in the beryllium window of the proportional counter and in the aluminum-radiation shields of the furnace. The correction required was determined by recording spectra over the whole temperature range without any absorber. The shape of the base line was determined in the same way. The spectrum obtained at 298°K for Fe_3O_4 is shown in Fig. 1. Below 119°K ferrous and ferric ions occupy the B sites. Above this temperature a rapid electron hopping[20–23] removes the difference between Fe^{2+} and Fe^{3+} ions and consequently all the nuclei in the B sites feel the same field. Therefore, only two different spectra due to Fe in A and B sites are observed. The ratio of the areas I_A/I_B under the peaks assigned to the A and B sites can easily be determined from the spectra recorded between 300 and 800°K. For a thin absorber, this area ratio would be 0.50 if $f_A' = f_B'$. Above 800°K a considerable overlap of the peaks impedes an accurate determination of the area ratio. The areas I_A and I_B, as well as the ratio I_A/I_B, were determined by doing a least-squares fit to the spectrum, assuming Lorentzian line shapes on a
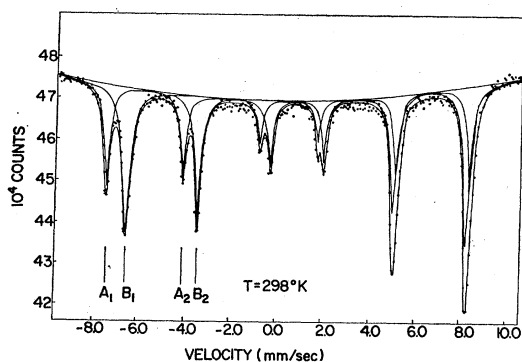

FIG. 1. Mössbauer spectra of Fe_3O_4 at 298°K. A and B indicate the peak positions of the absorption lines from Fe^{57} in A and B sites. The solid lines drawn show both the envelope and the individual lines as obtained from a fit to the spectrum by the method of least squares.

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parabolic base line. Only the lines marked A_1, A_2, B_1, and B_2 in Fig. 1 were used.

Spectra of Fe^{57} in YIG were obtained in the temperature range 300–775°K and for absorber thicknesses of 37, 34, and 17 mg/cm². The spectra obtained at 296 and 560°K are shown in Fig. 2. Below the ferrimagnetic Néel temperature the spectrum is complicated by the presence of two B-site lines. The A-site line is, however, well resolved from both of the B-site lines for lines 1, 5, and 6 as seen in Fig. 2(a). The two B-site lines are due to two possible angles between the principal axis of
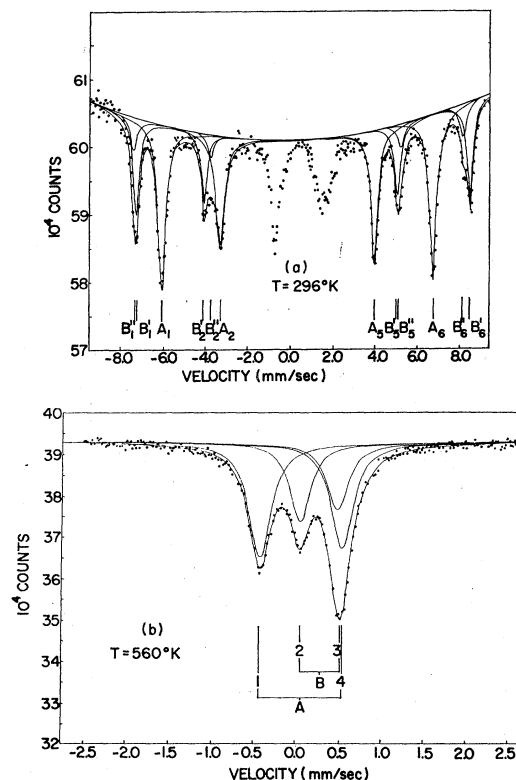

FIG. 2. Mössbauer spectra of YIG at (a) 296 and (b) 560°K. Absorber thickness is 17 mg/cm². A and B indicate the peak positions of the absorption lines from Fe^{57} in A and B sites. The solid lines drawn show both the envelope and individual lines as obtained from a fit to the spectrum by the method of least squares.

the electric field gradient and the magnetic field. The area ratio of the two B-site lines B' and B'' is expected to be 3:1.[24,25]

A least-squares fit was done to all spectra for lines 1, 2, 5, and 6. The fit was first done by imposing the constraint that the area ratio $I_B':I_B''$ was 3:1. The parameters obtained from this fit were used as initial guesses for a fit without constraints. The area ratio $I_A/(I_B'+I_B'')$ was insignificantly different for these two fits. From here on, we will use I_B as the total area of the octahedral line determined from $I_B = I_B' + I_B''$.

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The area ratio I_A/I_B is expected to be 1.50 for a thin absorber if $f_A'=f_B'$. Above T_{FN} there is only one spectrum due to Fe^{57} in B sites. The whole spectrum consists of two quadrupole split doublets, one for the A site and one for the B site. These spectra were fitted to the sum of four Lorentzians on a parabolic base line, which are identified with the two sites as shown in Fig. 2(b). It will be noticed that the peaks marked 3 and 4 in Fig. 2(b) have a slightly lower intensity than the peaks marked 1 and 2. This is due to the large amount of overlap of peaks 3 and 4 which increases the effective thickness of the absorber. This fact can be used to check the thickness corrections discussed below.

Corrections for the finite thicknesses of the absorber can be made by using the following relation given by Shirley et al.[26]:

$$P_{\text{expt}}\Gamma_{\text{expt}}=n\sigma_m ff'\Gamma(1-0.24\tau), \quad \text{for } \tau<4. \quad (1)$$

Here P_{expt} is the fractional absorption at the peak position, Γ_{expt} is the measured full width at half-height, and n gives the number of the Fe^{57} nuclei per cm^2 on a particular site and in the correct hyperfine state. The total cross section for recoil-free absorption is denoted by σ_m, and f and f' are the recoilless fractions for the source and absorber, respectively. For all the recorded spectra, the condition $\tau<4$ was fulfilled, where

$$\tau=nf'\sigma_m\Gamma/\Gamma'. \quad (2)$$

In (2), Γ is the natural linewidth, and Γ' is the absorber linewidth, which was chosen so that

$$\Gamma_{\text{expt}}=(\Gamma'+\Gamma_s')(1+0.135\tau), \quad (3)$$

and Γ_s' was adjusted to be consistent with all our data. Then, in a particular absorption spectrum, the ratio of the area I_1 to area I_2 of two lines denoted by 1 and 2, respectively, is given by

$$\frac{I_1}{I_2}=\frac{n_1}{n_2}\frac{f_1'}{f_2'}\frac{1-0.24\tau_1}{1-0.24\tau_2} \quad (4a)$$

and

$$\frac{n_1}{n_2}\frac{f_1'}{f_2'}=\frac{I_1}{I_2}\frac{1-0.24\tau_2}{1-0.24\tau_1}. \quad (4b)$$

Now $I_1/(1-0.24\tau_1)$ and $I_2/(1-0.24\tau_2)$ can be considered as the corrected areas under the peaks from which the ratio f_1'/f_2' can be determined. These corrections have been made for octahedral and tetrahedral peaks in the spectra of Fe$_3$O$_4$ and YIG if it turned out to be necessary. The thickness corrections required for the area ratio was at most 3% for the 37-mg/cm^2 YIG absorber for temperatures above the ferrimagnetic Néel temperature. Since f_A' and f_B' vary only slowly with temperature, the temperature dependence of the correction is small but was taken into account using values of f_A' and f_B' as determined from the measured
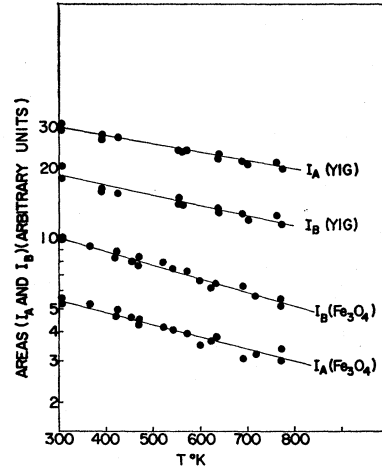
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FIG. 3. Areas of the A- and B-site spectra for Fe$_3$O$_4$ and YIG plotted on a logarithmic scale versus temperature. The solid lines are fits to the data as obtained by the method of least squares.

Debye temperatures. The final results are shown in Fig. 3. Here the corrected relative areas of the octahedral and the tetrahedral peaks are plotted on a logarithmic scale as a function of the temperature.

DISCUSSION

In the Debye approximation for lattice vibrations the recoil-free fraction f' can be written as[27]

$$f'=e^{-2w}=e^{-6E_rT/k\Theta^2}, \quad \text{for } T>\tfrac{1}{2}\Theta. \quad (5)$$

Here E_r is the recoil energy, k is the Boltzmann constant, Θ denotes the Debye temperature, and T is the absolute temperature. Actually spinels and garnets have structures which are too complicated for the Debye approximation. In order to correct in part for this, we introduce two Debye temperatures Θ_B and Θ_A for octahedral and tetrahedral sites, respectively. It is perhaps difficult to justify two Debye temperatures, but since this is the only variable in (5), we shall assume for data analysis that this can be done. A measure of the strength with which the ion is bound to its equilibrium position is given by Θ. In this way, we have made the model more realistic. Because I is proportional to f', the $\ln I$–versus–T curve should be a straight line for $T>\tfrac{1}{2}\Theta$; hence Θ_A and Θ_B can be determined from the slope of the straight line. The drawn lines in Fig. 3 are the least-squares fits to the data points. From this we find that the Debye temperatures are

$$\Theta_A=334\pm10°K, \quad \Theta_B=314\pm10°K, \quad \text{for Fe}_3\text{O}_4$$

and

$$\Theta_A=406\pm15°K, \quad \Theta_B=366\pm15°K, \quad \text{for YIG}.$$

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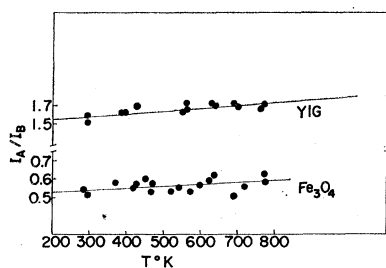
FIG. 4. Area ratio of the A- and B-site lines for Fe_3O_4 and YIG plotted versus temperature. The solid lines are fits to the data as obtained by the method of least squares.

The errors are calculated from the last-squares fit and do not take into account the possible inadequacy of the Debye model. These Debye temperatures are much lower than those obtained by specific-heat measurements. The values obtained from specific-heat data range from 570 to 660°K for Fe_3O_4[28,29] and from 454 to 599°K for YIG.[30-33] The Debye temperatures that we obtained are perhaps not suitable for comparison with those obtained from specific-heat data, because the latter were obtained at temperatures $T<300$°K, while ours were obtained at $T>300$°K. Another reason that this comparison is unsuitable is that with the Mössbauer effect we obtain information about the vibrational properties of the Fe^{57} nuclei, whereas the specific-heat data involve the vibrational properties of the whole lattice including the much heavier Y ions for YIG. Since it has been concluded that $Fe^{57}(A)$ and $Fe^{57}(B)$ have different vibrational properties, it is not inconceivable that these would be considerably different from the vibrational properties of the lattice as a whole.

In Fig. 4, we have plotted the corrected values of the area ratios I_A/I_B for both Fe_3O_4 and YIG. At high temperature and in the Debye approximation this area ratio can be written as

$$\frac{I_A}{I_B} = \frac{n_A}{n_B} \exp\left[-\frac{6E_rT}{k}\left(\frac{1}{\Theta_A^2} - \frac{1}{\Theta_B^2}\right)\right], \quad (6)$$

which can be approximated by

$$\frac{I_A}{I_B} \approx \frac{n_A}{n_B}\left[1 - \frac{6E_r}{k}\left(\frac{1}{\Theta_A^2} - \frac{1}{\Theta_B^2}\right)T\right]. \quad (7)$$

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The straight lines drawn in Fig. 4 are least-square fits to Eq. (7), and from this we find $n_A/n_B = 0.508 \pm 0.015$ and $1/\Theta_A^2 - 1/\Theta_B^2 = -(1.4 \pm 0.2) \times 10^{-6}$ for Fe_3O_4. For YIG, we get $n_A/n_B = 1.49 \pm 0.05$ and $1/\Theta_A^2 - 1/\Theta_B^2 = -(1.5 \pm 0.2) \times 10^{-6}$. The values of n_A/n_B are well within the experimental error of the known values for Fe_3O_4 (0.50) and for YIG (1.5). The values of $1/\Theta_A^2 - 1/\Theta_B^2$ are in good agreement with those calculated from the previously determined values of Θ_A and Θ_B. The two types of analysis, i.e., the determination of Θ_A and Θ_B from the areas and the determination of n_A/n_B and $1/\Theta_A^2 - 1/\Theta_B^2$, involve slightly different errors, especially for the cases where significant thickness corrections are required. The area ratio is of course much less sensitive to thickness corrections than the area is. It is gratifying to see that the two methods of analyzing the data give the same results.

At room temperature, the ratio of the recoilless fractions f_B'/f_A' determined from the intensity ratio is 0.94 ± 0.02 for Fe_3O_4 and 0.94 ± 0.02 for YIG. At 0°K the ratio of recoilless fractions can be calculated from

$$f_B'/f_A' = e^{-3E_r/2k}(1/\Theta_B - 1/\Theta_A). \quad (8)$$

By using the values determined for Θ_A and Θ_B, we get $f_B'/f_A' = 0.99 \pm 0.01$ for Fe_3O_4 and 0.99 ± 0.01 for YIG. In earlier work, f_B'/f_A' was found to be 0.85 at room temperature[15] and 0.96 ± 0.02 at 5°K,[16] for $BaFe_{12}O_{19}$ and $Ca_2Fe_2O_5$, respectively. These two materials have a different crystal structure and only ferric ions in octahedral and tetrahedral sites.

CONCLUSIONS

From Mössbauer spectra of Fe_3O_4 and YIG the relative intensities of the peaks ascribed to Fe^{57} nuclei in tetrahedral and octahedral ions have been determined. From these results, it has been shown that the recoil-free fractions of nuclei in the two sites are almost equal at 0°K. At room temperature, the recoil-free fraction f_B' of octahedrally situated nuclei is 6% lower than f_A' of tetrahedral nuclei. This means that the relative occupation numbers cannot simply be determined from Mössbauer spectra of these materials at room temperature. However, the information can be obtained by extrapolating from data taken at high temperatures over a wide temperature range.

ACKNOWLEDGMENT