Site distribution in heavily Sc^{3+}-, Zr^{4+}-, and Hf^{4+}- substituted yttrium iron garnet

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Mössbauer spectra of yttrium iron garnet containing large amounts of Sc^{3+}, Zr^{4+}, and Hf^{4+} substituted for Fe^{3+} ions (the last two with electrostatic compensation by Ca^{2+} ions) confirm the conclusions deduced from 0-K spontaneous magnetization that the Zr^{4+} and Hf^{4+} ions prefer octahedral sites exclusively. Very small amounts of Sc^{3+} ions enter tetrahedral sites: For a total of one Sc^{3+} ion per formula unit, 0.03 is tetrahedral; for a total of 1.5 Sc^{3+} ions per formula unit, 0.09 is tetrahedral. These results imply that in the region of the ferrimagnetic ground state, i.e., to 0.72 Sc^{3+} ion per formula unit, at *most* 0.02 is tetrahedral, but it could be that there is none because of the coincidence of the 0-K dependence of the spontaneous magnetization on the composition of the Zr^{4+}- and Sc^{3+}-substituted yttrium iron garnets in that region. Thus the model given by Geller *et al.* for the magnetic behavior of substituted iron garnets is corroborated by these results.

I. INTRODUCTION

It is now many years since the yttrium iron garnets containing the substituents Sc^{3+}, Zr^{4+}, and Hf^{4+} were synthesized and their thermomagnetic behavior studied. In the first study,[1] Gilleo and Geller accounted for the spontaneous magnetization versus temperature data on garnets containing a relatively low amount of the Sc^{3+} substituent by assuming that those Fe^{3+} ions that were linked only to the nearest-neighbor nonmagnetic ions did not contribute to the spontaneous magnetization.

Following this work, the Sn^{4+}-substituted yttrium iron garnet (YIG) system was studied[2] and Gilleo[3] modified the earlier model to account more clearly for the observations. This subsequent model eliminated from contribution to the spontaneous magnetization those Fe^{3+} ions that had at most one nearest Fe^{3+} ion neighbor. At first, this later Gilleo model was thought to account also for the Zr^{4+}-substituted YIG.[4] However, the fit near the maximum spontaneous magnetizations of both systems was quantitatively not completely satisfying. Subsequently, extensive work was done on the Si^{4+}- and Ge^{4+}-substituted YIG.[5] In these cases the differences of the 0-K spontaneous magnetizations and the values predicted by the Gilleo model were larger. Further detailed experiments proved[5] that the intrasublattice interactions must be taken into account. (This has also been done *quantitatively* by Dionne[6] in a semiempirical fashion for substitutions in the *ferrimagnetic ground state.*)

For a considerable time it has been accepted that the Sc^{3+} and Zr^{4+} ions prefer the octahedral sites in YIG exclusively.[7] However, more recently there have been indications[8] that the Sc^{3+} ion might, to some extent, go into tetrahedral sites. Fortunately, several of the specimens from the original work[5] (proving the importance of intrasublattice interactions) were still available.

It was decided to examine these specimens by means of Mössbauer spectroscopy. The results are reproducible and may be summarized briefly as follows: The Zr^{4+} and Hf^{4+} ions prefer the octahedral sites exclusively as deduced from the 0-K magnetization measurements. As to the Sc^{3+} ions, very small amounts enter tetrahedral sites; for $\{Y_3\}[Sc_{1.5-y}Fe_{0.5+y}](Sc_yFe_{3.0-y})O_{12}$, $y = 0.09$; for $\{Y_3\}[Sc_{1.0-y}Fe_{1.0+y}](Sc_yFe_{3.0-y})O_{12}$, $y = 0.03$. These results imply that in the ferrimagnetic ground state, $0 \leq y \leq 0.72$ as in $\{Y_3\}Sc_yFe_{5-y}O_{12}$, the amount of Sc^{3+} entering the tetrahedral sites is very low and does not affect the ideas promulgated in Ref. 5.

II. EXPERIMENTAL

A. Materials

The conditions under which the Sc^{3+}- and Zr^{4+}- (with Ca^{2+} for electrostatic compensation) substituted garnets were prepared are given in Ref. 5. The $\{YCa_2\}[Zr_2](Ga_{0.25}Fe_{2.75})O_{12}$ specimen is also the same as the one on which magnetic susceptibility measurements were made for Ref. 5 (see Fig. 9 of Ref. 5). The specimen $\{YCa_2\}[Hf_2](Fe_3)O_{12}$ may not be *precisely* single phase (see footnote 22 in Ref. 5); it is the same specimen originally discussed in Ref. 4.

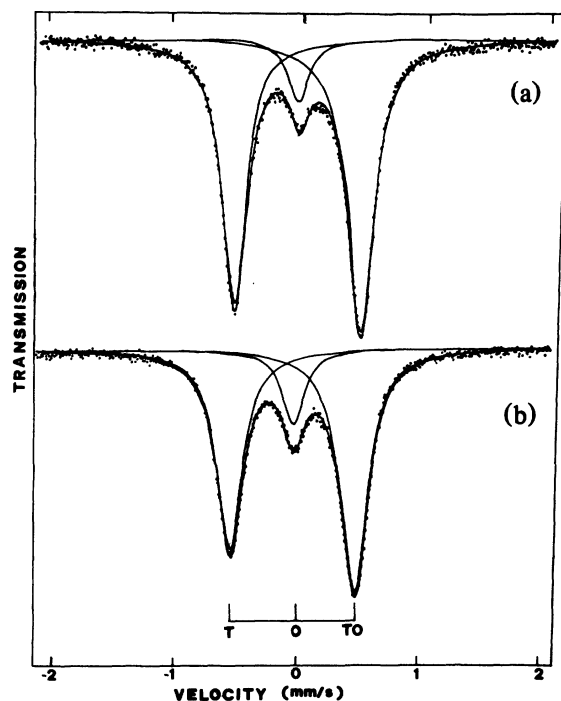FIG. 1. Mössbauer spectra at 300 K for Sc^{3+}-substituted yttrium iron garnets: (a) $\{Y_3\}[Sc_{0.97}Fe_{1.03}](Sc_{0.03}Fe_{2.97})O_{12}$; (b) $\{Y_3\}[Sc_{1.41}Fe_{0.59}](Sc_{0.09}Fe_{2.91})O_{12}$. The full line represents the fitting of the peak by Lorentzians.
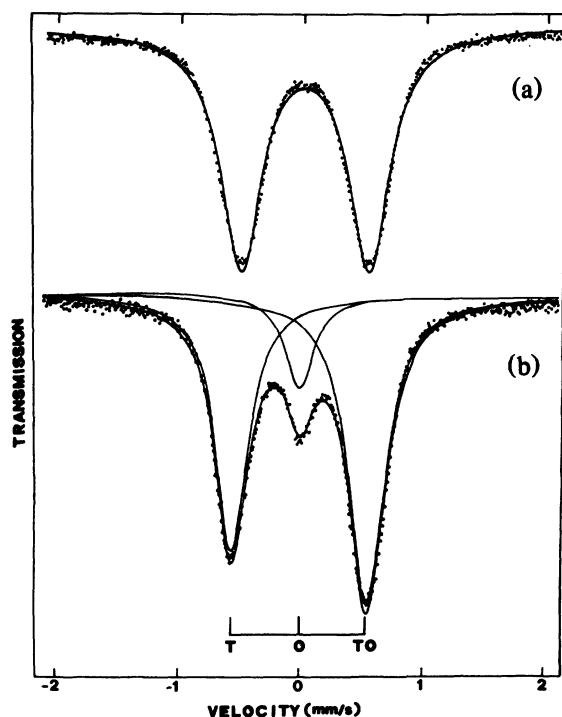

FIG. 2. Mössbauer spectra at 300 K for Zr^{4+}-substituted yttrium iron garnets: (a) $\{YCa_2\}[Zr_2](Ga_{0.25}Fe_{2.75})O_{12}$; (b) $\{Y_2Ca\}[ZrFe](Fe_3)O_{12}$.

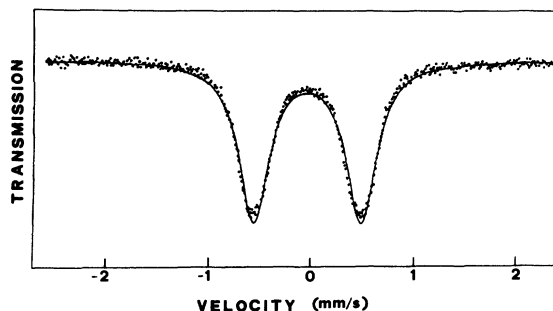

FIG. 3. Mössbauer spectrum at 300 K of $\{YCa_2\}[Hf_2](Fe_3)O_{12}$.

B. Mössbauer spectra

Mössbauer spectra were taken with an Elscint constant acceleration spectrometer; the source was ^{57}Co in Pd. For Mössbauer measurements the specimens were ground to fine powders. The powders were finally homogeneously mixed with fine powdered sugar. The absorber was the powdered specimen mixed with sugar held between two Be disks. To avoid intensity saturation effects the absorber densities were kept in a low range (between 4 and 6 mg/cm^2). All spectra were taken at room temperature and were least-squares fitted by three unconstrained Lorentzian peaks (see Figs. 1–3). The total amount of iron in the octahedral and tetrahedral sites was assumed proportional to the area of the corresponding peak in the spectrum; to this purpose only the resolved peaks were used. The area ratio between tetrahedral and octahedral peaks was multiplied by the appropiate recoilless-fraction ratio ($f_O/f_T = 0.94$ at room temperature[9]) to give the correct amount of iron in each site.

III. RESULTS

The fitted Mössbauer spectra taken at room temperature of $Y_3Sc_{1.0}Fe_{4.0}$ O_{12} and $Y_3Sc_{1.5}Fe_{3.5}$ O_{12} are shown in Fig. 1; those of $\{Y_2Ca\}[ZrFe](Fe_3)O_{12}$ and $\{YCa_2\}[Zr_2](Ga_{0.25}$ $Fe_{2.75})O_{12}$ in Fig. 2; and of $\{YCa_2\}[Hf_2](Fe_3)O_{12}$ in Fig. 3. According to the line fits, the distribution formulas for the Sc^{3+}-ion-substituted garnets should be written $\{Y_3\}[Sc_{0.97}Fe_{1.03}](Sc_{0.03}$ $Fe_{2.97})O_{12}$ and $\{Y_3\}[Sc_{1.41}Fe_{0.59}](Sc_{0.09}$ $Fe_{2.91})O_{12}$, respectively. The others are already correctly written, as can readily be seen from Figs. 2 and 3. The lines in the spectra of Figs. 2 and 3, for high Zr^{4+} or Hf^{4+} substitution are not Lorentzian, rather tending to be Gaussian. The lines in Fig. 1 for high Sc^{3+} substitutions still appear to be Lorentzian. The main difference in the materials that may give some clue to the reason for the difference in line shape is in the ions substituted for

the electrostatic compensation, namely, none for Sc^{3+} and partial substitution of Y^{3+} by Ca^{2+} for the tetravalent ions. Because the dodecahedral sites are close neighbors of the tetrahedral sites, the disorder on the latter probably cause an "extra" disorder on the oxygens about the Fe^{3+} ions on the tetrahedral sites.

The spectrum of $\{Y_{1.05}Ca_{1.95}\}[Zr_{1.95}Fe_{0.05}](Fe_3)O_{12}$ (not shown) contained a trace of the central octahedral peak. The ion distribution was determined from the difference of areas in the two major peaks, the result is 1.93 octahedral Zr^{4+} per formula unit, in very good agreement with the 1.95 value.

IV. DISCUSSION

Within very narrow limits the results corroborate the conclusions[4,5,7,10] that the Zr^{4+} and Hf^{4+} prefer the octahedral sites exclusively when substituted for Fe^{3+} ion in yttrium iron garnet. With respect to the Sc^{3+} substitutions, 3 at.% of the Sc^{3+} substitutes for tetrahedral Fe^{3+} when the *total* substitution for Fe^{3+} is one per formula unit. This implies that of 0.72 Sc^{3+} total substitution, at most 0.02 substitutes for tetrahedral Fe^{3+}, and of 0.60 Sc^{3+} total substitution, at most 0.015 substitutes for tetrahedral Fe^{3+}. The distribution formulas for these are then $\{Y_3\}$-$[Sc_{0.70}Fe_{1.30}](Sc_{0.02}Fe_{2.98})O_{12}$ and $\{Y_3\}[Sc_{0.585}Fe_{1.415}]$-$(Sc_{0.015}Fe_{2.985})O_{12}$, respectively. If these were ideal Néel ferrimagnets, the 0-K magnetization would be 8.40 and $7.85\mu_B$, respectively, as opposed to 8.60 and $8.00\mu_B$, if in both cases all the Sc^{3+} ions were in octahedral sites. The measured values are 7.65 and $7.44\mu_B$, respectively,[5] so that there is no doubt that

canting occurs in the ferrimagnetic ground state of the Sc^{3+}- ion-substituted garnets as originally proposed.[5] This, after all, must be the case, because $n_B(0 \text{ K})$ vs x superpose in the region $0 \leq x \leq 0.72$ for the Zr^{4+}- and Sc^{3+}-substituted yttrium iron garnets (see, e.g., Fig. 7 of Ref. 5).

Although the errors have not been determined statistically, the precision of these results must be high as is demonstrated by the following plausibility argument. The spectrum of $\{YCa_2\}[Zr_2](Ga_{0.25}Fe_{2.75})O_{12}$ [Fig, 2(a)] indicates that Zr^{4+} ions do not enter tetrahedral sites. This is further confirmed by the results on $\{Y_{1.05}Ca_{1.95}\}[Zr_{1.95}Fe_{0.05}](Fe_3)O_{12}$ in that a center peak still occurs in its spectrum, and the calculation described earlier gave agreement within 1% of the expected ionic distribution. It is reasonable to expect from these results that in the specimen that contains one Zr^{4+} per formula unit, no Zr^{4+} ion will be in tetrahedral sites. The results for this specimen, based on the spectrum shown in Fig. 2(b) and on the recoilless-fraction ratio $f_O/f_T = 0.94$, gave exact agreement with the hypothesis. Inasmuch as the same technique was used to determine the Sc^{3+} ion distribution in the Sc^{3+}-substituted YIG's as for the Zr^{4+}-substituted specimens, the precision must be the same for both. Because the results for the latter are highly reliable, the results for the former must be also.

ACKNOWLEDGMENTS

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