Mössbauer study of intercalation modified compounds R_2Fe_{17} (R=Y, Sm)

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Mössbauer studies were carried out at 77 K in two series of R_2Fe_{17} compounds with a magnetic (Sm) and nonmagnetic (Y) rare-earth, intercalated with H, C, and N. The increase in hyperfine field is largest at the $12j(18f)$ sites for $R_2Fe_{17}H_{3.7}$ and $R_2Fe_{17}N_{2.3}$. While the lattice expansion in $R_2Fe_{17}C_2$ is similar to that in the nitrides and hydrides, the small change in hyperfine fields at the $12j(18f)$ and $12k(18h)$ sites indicates that the presence of neighboring carbon largely cancels the moment increase associated with the volume increase. For R_2Fe_{17} carbonitrides, a single, sharp magnetic transition indicates a uniform compound. However, Mössbauer spectra suggest the existence of both C-rich and N-rich precipitates in the carbonitrides whose average hyperfine fields and isomer shifts scale with the nitrogen to carbon ratio.

I. INTRODUCTION

Several light elements (notably H, C, and N) can be inserted into rare-earth iron compounds by means of gas–solid reaction. The intercalants occupy interstitial sites and the resulting metastable compounds retain the structure of the parent alloy while frequently exhibiting greatly enhanced magnetic properties.[1-9] It is interesting to study such changes on an atomic scale. Several ^{57}Fe Mössbauer studies have been reported on these modified R_2Fe_{17} (R =rare-earth) compounds.[3,10,11] However, up to now, no work has been reported on the Mössbauer study of the R_2Fe_{17} carbonitrides with different nitrogen-to-carbon ratios. The present work reports on such a study of two series of R_2Fe_{17} carbonitrides with R=Y and Sm. For comparison, the data of R_2Fe_{17} hydrides, carbides and nitrides are presented as well.

II. EXPERIMENTAL METHODS

Polycrystalline R_2Fe_{17} compounds were prepared by arc melting appropriate amounts of R and Fe, followed by vacuum annealing at 900 °C for two weeks. Sm_2Fe_{17} specimens contained a few percent of α-Fe. The gas–solid reaction was carried out by annealing the powdered specimens in a thermopiezic analyzer (TPA)[12] in a gas pressure of approximately one bar at 773 K for up to 120 min. The gases used were H_2, N_2, CH_4, C_2H_2, and C_2H_4. The R_2Fe_{17} carbonitrides were prepared either by annealing the powdered specimens in a mixture of N_2 and CH_4, or by a sequential annealing, i.e., annealing the powdered specimens in N_2 for up to 120 min, followed by in C_2H_2 for up to 20 min. The contents of H, C, and N were determined either by gas pressure change or by mass change. T_c was measured by making use of a thermomagnetic analyzer (Perkin–Elmer TGA-7) in a small field gradient. Mössbauer absorbers of 30 mg/cm^2 were made from powdered specimens. ^{57}Fe Mössbauer spectra were collected at 77 K using a conventional constant acceleration spectrometer with a 25 mCi ^{57}Co Rh source and was calibrated at room temperature with an α-Fe foil. The spectra were least-square fitted with the hyperfine field (B_{hf}), isomer shift (IS) and quadrupole splitting (QS) as variables. Compounds for R=Y (Sm) have the hexagonal Th_2Ni_{17} (rhombohedral Th_2Zn_{17}) structure. The spectra of Sm_2Fe_{17} carbide, nitride, and carbonitrides, which have easy-axis anisotropies, were fitted to four independent Lorentzian sextets, with an overall intensity ratio of 6:9:18:18 for the $6c$, $9d$, $18f$, and $18h$ subspectra; whereas those of the other modified R_2Fe_{17} compounds with easy-plane anisotropies were fitted to eight independent Lorentzian sextets, with further splittings of 1:2 for $6g(9d)$, 2:2:2 for $12j(18f)$ and 2:4 for $12k(18h)$. Up to 15 percent of α-Fe was included in the fits for most specimens. For some R_2Fe_{17} carbides and carbonitrides, a small contribution, up to 8 percent, due to Fe_3C formed during carbiding, was also included. In addition, 1%–2% of a paramagnetic doublet of uncertain origin was introduced in some spectra. The linewidths (half width at half maximum) were fixed at 0.17 mm/s. The order $4f(6c)>6g(9d)>12j(18f)>12k(18h)$ in B_{hf} was used to assign the components of the spectra to the iron sites.[3,10] The spectrum areas are used to calculate the overall average hyperfine field $\langle B_{hf}\rangle$, isomer shift $\langle IS\rangle$ and quadrupole splitting $\langle QS\rangle$.

III. RESULTS AND DISCUSSION

Figure 1 shows the Mössbauer spectra of R_2Fe_{17} and their intercalation modified compounds obtained at 77 K, with the fits shown as solid curves. The sharp absorption peaks show the good quality of the specimens. The spectra of $R_2Fe_{17}C_2$ are quite different from those obtained at 15 K reported earlier,[10] where the R_2Fe_{17} carbides were prepared in C_4H_{10}. These differences cannot be due to the different hydrocarbon gas used to prepare the specimens, because in the present work, R_2Fe_{17} carbides, prepared at 773 K in CH_4, C_2H_4, and C_2H_2 show essentially identical spectra. Since both 15 and 77 K are far below the T_c of more than 680 K, the difference in specimen temperatures is also unlikely to be the main reason for the different spectra. This discrepancy is probably related to different levels of the impurities in the specimens; however, further work is necessary to clarify this point.

The hyperfine fields obtained from the least-square fitting are listed in Table I. For comparison, B_{hf}, reduced to the corresponding values of R_2Fe_{17}, are plotted in Fig. 2.

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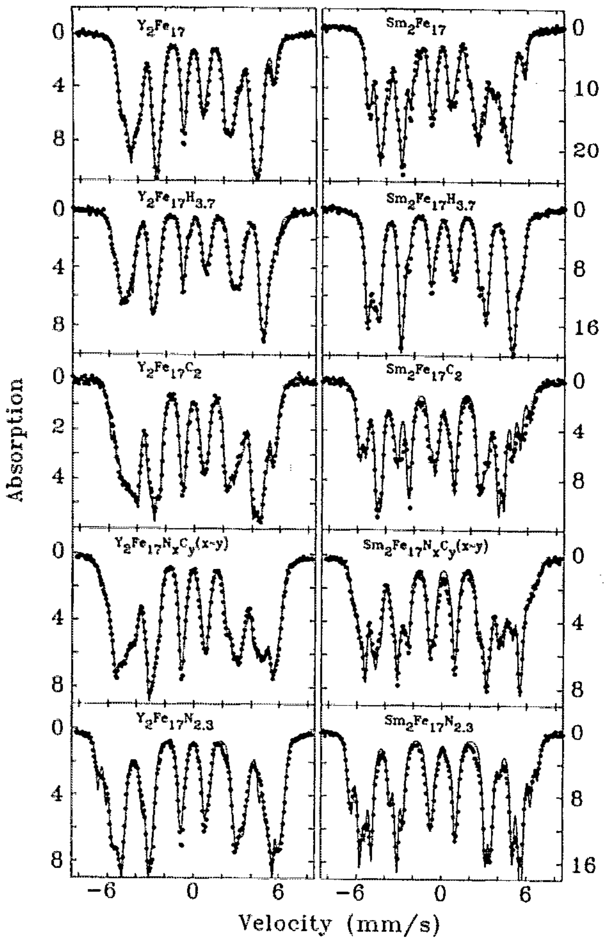

FIG. 1. ^{57}Fe Mössbauer spectra of R_2Fe_{17} compounds with and without interstitial H, C, and N at 77 K; the solid curves show the fits to the data.

For $R_2Fe_{17}N_{2.3}$, the B_{hf} of all sites are affected by interstitial nitrogen, with the $12j(18f)$ increasing the most. Similar effects are also observed for $R_2Fe_{17}H_{3.7}$. In contrast, for $R_2Fe_{17}C_2$, the B_{hf} of all Fe sites are not strongly affected, with the $12k(18h)$ increasing the least. It appears that the effects of Fe—C bonding substantially reduce the gain associated with the lattice expansion, resulting in a very small increase in $\langle B_{hf}\rangle$ for both R=Y and Sm.

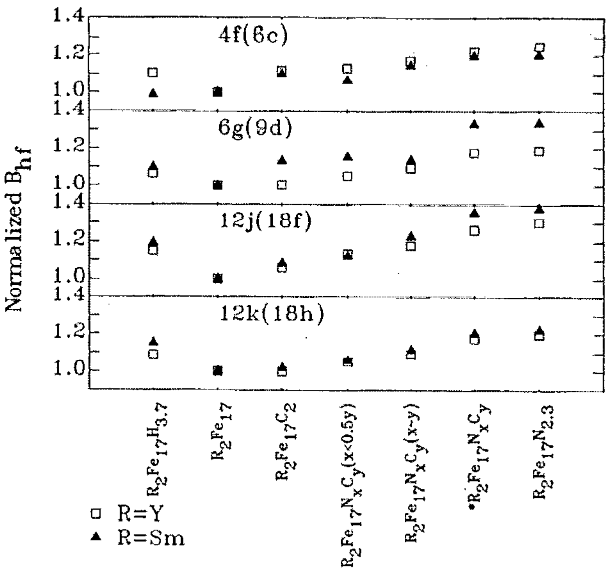

FIG. 2. Hyperfine fields at 77 K on different sites, normalized to the values of R_2Fe_{17}. The specimen marked with * was prepared by sequential annealing.

For R_2Fe_{17} carbonitrides, the interstitial carbon and nitrogen do not produce two different T_c, corresponding to the pure carbide and nitride phases, respectively. Figure 3 shows a sharp, single magnetic transition observed in a Y_2Fe_{17} carbonitride, indicating a uniform magnetic material. The Mössbauer spectra shown in Fig. 1 of carbonitrides, however, show the characteristic absorption peaks of both carbides and nitrides (e.g., ~4 mm/s and ~6 mm/s for R=Sm), and cannot be fitted to eight Lorentzian sextets. Instead, they can be fitted to sixteen Lorentzian sextets, which are the superposition of slightly modified spectra ($|\Delta B_{hf}| \leqslant 0.7$ T) of both carbides and nitrides. It seems that C-rich and N-rich precipitates exist in the carbonitrides. The two distinct sets of spectra suggest the size of these precipitates to be of at least 100 unit cells,

TABLE I. Hyperfine fields and isomer shifts of modified R_2Fe_{17} at 77 K.

	$6c(4f)$ (T)	$9d(6g)$ (T)	$18f(12j)$ (T)	$18h(12k)$ (T)	$\langle B_{hf}\rangle$ (T)	$\langle IS\rangle$ (mm/s)
$Sm_2Fe_{17}H_{3.7}$	34.0	32.1	30.7	29.1	30.8	0.112
Sm_2Fe_{17}	34.5	29.3	25.8	25.3	27.3	0.017
$Sm_2Fe_{17}C_2$	37.6	33.2	27.9	25.7	29.2	0.026
$Sm_2Fe_{17}N_xC_y(x<0.5y)$	36.7	33.7	28.9	26.7	29.9	0.074
$Sm_2Fe_{17}N_xC_y(x\sim y)$	39.5	33.2	31.6	28.2	31.6	0.117
$Sm_2Fe_{17}N_xC_y$(sequential)	41.2	38.9	34.9	30.4	34.8	0.145
$Sm_2Fe_{17}N_{2.3}$	41.4	39.1	35.5	30.9	35.2	0.145
$Y_2Fe_{17}H_{3.7}$	35.5	31.6	30.8	28.5	30.7	0.097
Y_2Fe_{17}	32.1	29.7	26.8	26.2	27.7	0.006
$Y_2Fe_{17}C_2$	35.9	29.8	28.4	25.9	28.6	0.043
$Y_2Fe_{17}N_xC_y(x<0.5y)$	36.3	31.3	30.4	27.5	30.2	0.076
$Y_2Fe_{17}N_xC_y(x\sim y)$	37.6	32.5	31.6	28.7	31.4	0.067
$Y_2Fe_{17}N_xC_y$(sequential)	39.2	34.9	33.8	30.8	33.6	0.087
$Y_2Fe_{17}N_{2.3}$	40.1	35.3	34.9	31.4	34.3	0.084

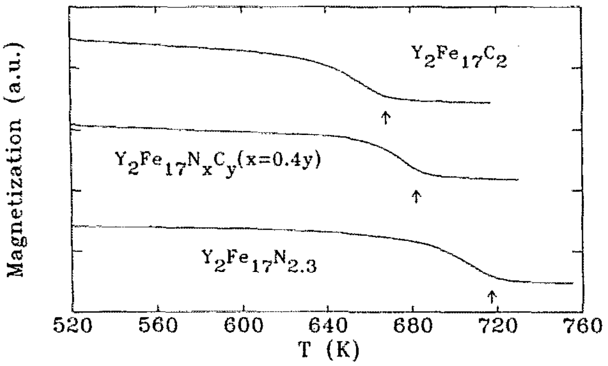

FIG. 3. Thermomagnetic scans of Y_2Fe_{17} compounds intercalated with N and/or C, showing a single T_c for each specimen.

since the number of the Fe atoms in the transition regions must be negligible. These precipitates, however, produce a single, sharp T_c transition, showing a homogeneous volume expansion in order to reduce the strain and stress. This can be understood from the stress–strain analysis of Coey *et al.*[13] for $Sm_2Fe_{17}N_x$, where it is shown how a nitrided surface can cause the N-poor core to expand and give a single T_c for the whole particle.

The nitrogen-to-carbon ratios of the R_2Fe_{17} carbonitrides, estimated by the spectrum area ratios, are at least twice the values expected from the gas pressure ratio, $P(N_2)/P(CH_4)$ used during preparation, indicating a preferential absorption of nitrogen for the specimens prepared in the gas mixture of N_2 and CH_4. Figure 2 shows the area weighted average B_{hf} of different Fe sites, which scale up with the nitrogen-to-carbon ratio of the carbonitrides. A similar trend is also observed for $\langle B_{hf}\rangle$. As is shown in Fig. 4, $\langle B_{hf}\rangle$ is proportional to the nitrogen content of the carbonitrides.

The $\langle IS\rangle$ and $\langle QS\rangle$ are plotted in Fig. 4. For both R=Y and Sm, the $\langle IS\rangle$ of $R_2Fe_{17}N_{2.3}$ increases much more than that of $R_2Fe_{17}C_2$. This suggests either an interband $3d \leftrightarrow 4s$ charge transfer occuring in the opposite sense in nitrides and carbides, or a greater $4s \rightarrow 2p$ interatomic charge transfer in the nitrides, on account of its greater electronegativity.[10] The $\langle QS\rangle$ are relatively independent of the type of interstitials for R=Y. For R=Sm, however, a discontinuity, observed in $\langle QS\rangle$, reflects a transition from easy-plane anisotropy to easy-axis anisotropy.

In conclusion, while interstitial modification of R_2Fe_{17} by carbon leads to lattice expansions and T_c increases similar to those in the nitrides and hydrides, the presence of carbon largely cancels the associated moment increase, particularly at the $12j(18f)$ and $12k(18h)$ sites which have carbon nearest neighbors. R_2Fe_{17} carbonitrides are magnetically uniform compounds, in spite of the existence of C-rich and N-rich precipitates. Both $\langle B_{hf}\rangle$ and $\langle IS\rangle$ scale with the nitrogen content of the R_2Fe_{17} carbonitrides.

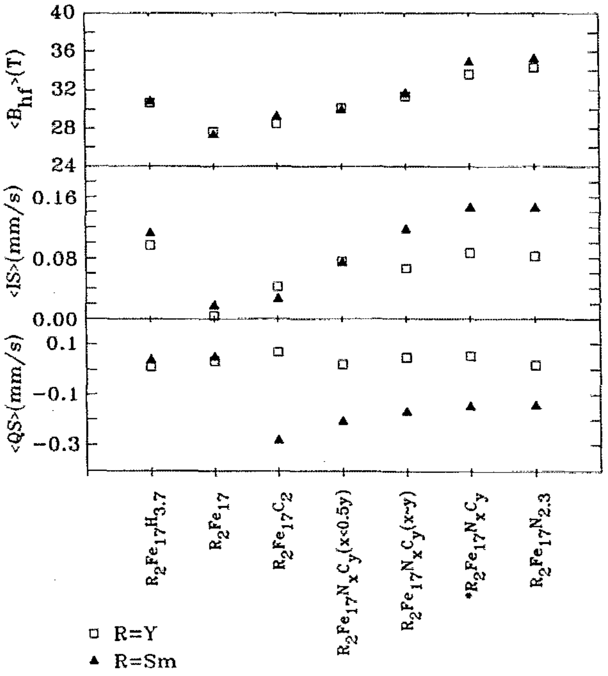

FIG. 4. Average hyperfine fields, isomer shifts, and quadrupole splittings of various modified R_2Fe_{17} compounds at 77 K. The specimen marked with * was prepared by sequential annealing.

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