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Comparative Mössbauer effect study of several R_2Fe_{17} and $R_2Fe_{17}N_x$ compounds

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The Mössbauer spectra of Sm_2Fe_{17} and Ho_2Fe_{17} and their nitrides have been measured between 295 and 85 K and analyzed with a model which is consistent with our earlier work on R_2Fe_{17} and $R_2Fe_{17}N_x$ compounds, where R is Pr, Nd, and Th. This model is completely consistent throughout these rare-earth compounds and is in agreement with the crystallographic changes occurring upon nitrogenation and with the prediction of band structure calculations. The dramatic increase in Curie temperature in the nitrides results from the expansion of the crystallographic lattice, an expansion which is mainly centered on the $9d$ and $18h$ iron sites as is indicated by the increase of their Wigner–Seitz cell volumes upon nitrogenation. The $9d$ and $18h$ sites show a larger enhancement of their hyperfine fields as compared to the $6c$ and $18f$ sites as a result of improved ferromagnetic exchange between these sites and their near neighbors because of the lattice expansion and the consequent reduced iron $3d$ -iron $3d$ overlap.

The R_2Fe_{17} compounds, where R is Pr, Nd, Sm, and Th, crystallize in the rhombohedral Th_2Zn_{17} structure¹ in which iron occupies four inequivalent crystallographic sites. Coey *et al.*^{2,3} have shown that nitrogenation of these compounds induces a large lattice expansion and an $\sim 400^\circ$ increase in Curie temperature. We have recently analyzed the Mössbauer spectra of Nd_2Fe_{17} , Pr_2Fe_{17} , and Th_2Fe_{17} , and their nitrides with a model^{4–6} based on the Wigner–Seitz cell volume. In this paper, we extend this analysis to Sm_2Fe_{17} and Ho_2Fe_{17} and their nitrides, and show that this model is consistent throughout the rare earths studied and is in agreement with both the crystallographic changes occurring upon nitrogenation and band structure calculations.^{7–10}

The samples were prepared¹¹ and their spectra were measured and fit⁴ as described previously. Between 2% and 7% of α -iron was found in the spectra of the R_2Fe_{17} compounds and between 5% and 20% of a nitrated iron phase was found in the $R_2Fe_{17}N_x$ compounds. The isomer shifts are given relative to α -iron and the estimated errors are at most ± 0.5 kOe for the hyperfine fields, ± 0.005 mm/s for the isomer shifts, and ± 0.01 mm/s for the quadrupole shifts.

Figure 1 shows the 85 K Mössbauer spectra of $R_2Fe_{17}N_x$, where R is Pr, Nd, Sm, and Ho. More extensive Mössbauer spectra have been published elsewhere.^{4–6} Because the magnetization³ is oriented along [001] in $Sm_2Fe_{17}N_x$, in the basal plane along [100] in Sm_2Fe_{17} , Nd_2Fe_{17} , Ho_2Fe_{17} , $Nd_2Fe_{17}N_x$, and $Ho_2Fe_{17}N_x$, along [010] in Pr_2Fe_{17} , $Pr_2Fe_{17}N_x$, and Th_2Fe_{17} , or along a general direction in $Th_2Fe_{17}N_x$, the Mössbauer spectra are analyzed with four, seven, or ten sextets representing the resulting inequivalent magnetic sites. In order to both reduce the number of adjustable parameters and to obtain a physically meaningful fit, we used the following constraints which are more restrictive than those used by other authors.^{2,3,12–14} One line-width was used for all lines in a given spectrum, the relative areas of the magnetically inequivalent iron sites were constrained equal to their relative crystallographic and magnetic

degeneracies, and the isomer shifts were constrained equal for the two or three magnetically inequivalent sites originating from the same crystallographic site. The linewidths of all the spectra discussed in this paper are in the range of 0.25–0.28 mm/s. As a result of these narrow linewidths we observe more highly resolved spectra, an improvement which permits a more detailed spectral analysis, but places tighter restrictions on the model and the resulting hyperfine parameters.

In order to check the validity of our analysis for $Sm_2Fe_{17}N_x$, which shows uniaxial anisotropy, and to extend our work through the rare-earth series, we have extended earlier work^{12–14} on Sm_2Fe_{17} and $Sm_2Fe_{17}N_x$ and analyzed the data as discussed^{4–6} for the other R_2Fe_{17} compounds. The experimental results are similar to the earlier work but show linewidths of ~ 0.26 mm/s, a value which is substantially smaller than the values found by Hu and Coey¹⁴ for Sm_2Fe_{17} , or by Chen *et al.*¹³ for Sm_2Fe_{17} and $Sm_2Fe_{17}N_x$. The 85 K spectrum of $Sm_2Fe_{17}N_x$ is shown in Fig. 1 and the hyperfine parameters of Sm_2Fe_{17} and $Sm_2Fe_{17}N_x$, obtained at several temperatures, are given in Tables I and II.

The assignment of the sextets to the different crystallographic sites is based first upon the relative areas and then, for the $18f$ and $18h$ sextets, is based upon their isomer shifts, hyperfine fields, and Wigner–Seitz cell volumes. In general, the larger the Wigner–Seitz cell volume of a site, the larger its isomer shift. Further, the larger the number of iron near neighbors for a site, the larger its hyperfine field. Figure 2 shows the 85 K isomer shifts in Sm_2Fe_{17} and $Sm_2Fe_{17}N_x$ versus the Wigner–Seitz cell volumes for the four crystallographic sites.^{1,15–17} This figure illustrates both the above-mentioned correlation and the effect of nitrogenation upon the isomer shifts. All four isomer shifts increase upon nitrogenation, the $6c$ and $9d$ because of the lattice and Wigner–Seitz cell expansion, the $18f$ because of the presence of a nitrogen near neighbor, and the $18h$ because of both the Wigner–Seitz cell expansion and the presence of a nitrogen

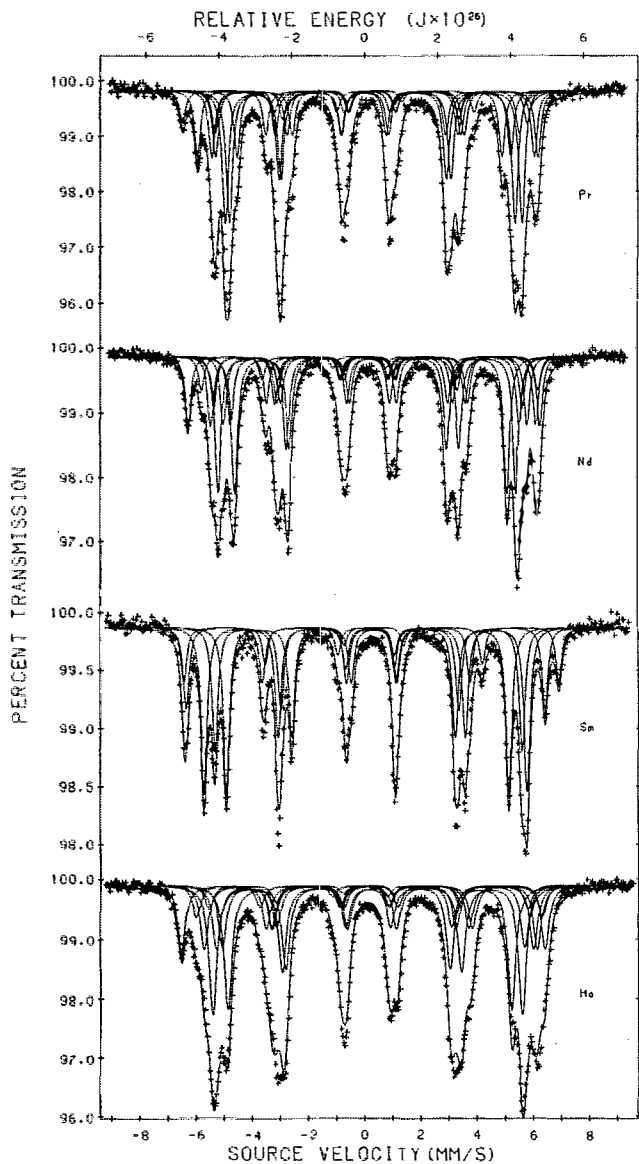


FIG. 1. The Mössbauer effect spectra of several $R_2Fe_{17}N_x$ compounds obtained at 85 K.

TABLE I. Mössbauer spectral hyperfine parameters for Sm_2Fe_{17} .

	T, K	$6c$	$9d_6$	$9d_3$	$18f_{12}$	$18f_6$	$18h_{12}$	$18h_6$	Wt. ave.
H_i (kOe)	85	354	304	288	286	324	275	281	298
	150	335	287	272	269	303	261	265	288
	225	307	257	246	244	277	238	238	255
	295	262	214	219	206	236	202	195	216
δ_i^a (mm/s)	85	0.245	-0.080	-0.080	0.050	0.050	0.060	0.060	0.054
	150	0.205	-0.115	-0.115	0.000	0.000	0.020	0.020	0.011
	225	0.160	-0.150	-0.150	-0.050	-0.050	-0.040	-0.040	-0.055
	295	0.090	-0.180	-0.180	-0.100	-0.100	-0.090	-0.090	-0.088
QS, ^b (mm/s)	85	-0.13	-0.34	0.06	0.42	-0.09	-0.33	0.69	...
	150	-0.11	-0.28	0.04	0.42	-0.08	-0.35	0.66	...
	225	-0.10	-0.18	0.04	0.42	-0.08	-0.39	0.63	...
	295	-0.08	-0.13	0.04	0.42	-0.05	-0.36	0.46	...

^aRelative to room temperature α -iron.

^bThe QS values are the quadrupole shift except for $6c$ site for which it is the quadrupole splitting for a θ value of 90° .

TABLE II. Mössbauer spectral hyperfine parameters for $Sm_2Fe_{17}N_{2.6}$.

	T, K	$6c$	$9d$	$18f$	$18h$	Wt. ave.
H_i (kOe)	85	413	395	355	311	353
	155	411	395	354	310	352
	225	407	392	349	306	348
	295	394	378	337	297	337
δ_i^a (mm/s)	85	0.285	0.045	0.144	0.215	0.168
	155	0.255	0.030	0.130	0.210	0.155
	225	0.230	-0.010	0.100	0.180	0.124
	295	0.160	-0.070	0.040	0.120	0.063
QS, ^b (mm/s)	85	-0.09	-0.02	0.44	-0.21	...
	155	-0.09	-0.02	0.44	-0.21	...
	225	-0.09	-0.02	0.41	-0.21	...
	295	-0.07	-0.02	0.35	-0.21	...

^aRelative to room temperature α -iron.

^bThe QS values are the quadrupole shift except for $6c$ site for which it is the quadrupole splitting for a θ value of 0° .

near neighbor. Very similar plots have been obtained for the other rare-earth compounds.⁴⁻⁶ Figure 3 shows the 85 K isomer shifts in R_2Fe_{17} and $R_2Fe_{17}N_x$. The smooth variation of the isomer shifts, and their increase upon nitrogenation, for the different rare-earth compounds strongly support the model and our assignment of the sextets.

Figure 4 shows the 85 K weighted average hyperfine fields in R_2Fe_{17} and $R_2Fe_{17}N_x$ for the different rare-earth compounds and reveals small variations with the rare-earth atom. $Sm_2Fe_{17}N_x$ shows the largest field because of its uniaxial anisotropy. Th_2Fe_{17} shows the largest increase upon nitrogenation, in agreement with the large observed increases in its magnetic moment and unit cell volume. Pr_2Fe_{17} , Nd_2Fe_{17} , and Ho_2Fe_{17} show very similar increases of 40–50 kOe in their weighted average hyperfine fields upon nitrogenation.

Our model⁴⁻⁶ for the analysis of the Mössbauer spectra of R_2Fe_{17} and $R_2Fe_{17}N_x$ is in excellent agreement with all available crystallographic data on these compounds and the resulting hyperfine parameters show both a smooth variation with the rare earth and the expected variation with temperature. Finally, the dramatic increase in Curie temperature in the nitrides results from the expansion of the crystallographic

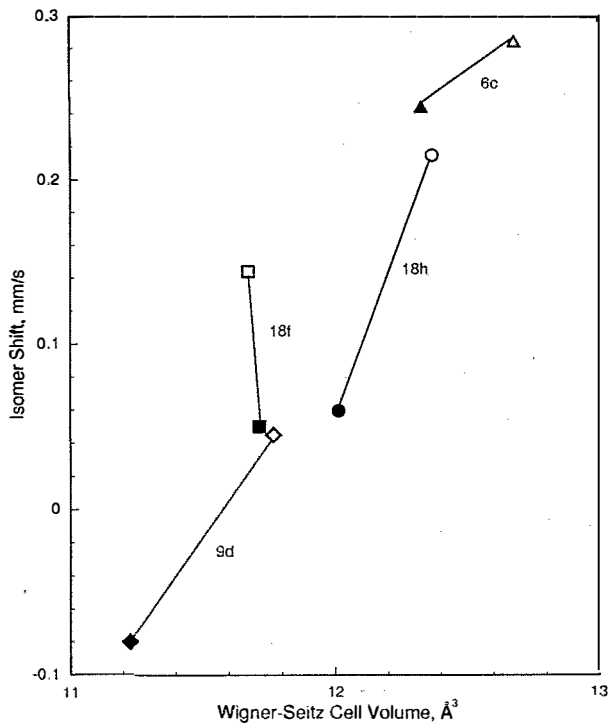


FIG. 2. The correlation between the Wigner-Seitz cell volume and the 85 K isomer shift for each site in going from $\text{Sm}_2\text{Fe}_{17}$ (closed symbols) to $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ (open symbols).

lattice, an expansion which is mainly centered on the $9d$ and $18h$ iron sites as indicated by the increase of their Wigner-Seitz cell volumes upon nitrogenation. In agreement with the predictions of band structure calculations,^{8,10} the $9d$ and $18h$ sites show a larger enhancement of their hyperfine fields and magnetic moments as compared to the $6c$ and $18f$ sites because of improved ferromagnetic exchange between these sites and their near neighbors. Indeed, all the distances between the $9d$ and $18h$ sites and their iron near neighbors increase upon nitrogenation, an increase which results in a reduced iron $3d$ -iron $3d$ overlap and hence improved ferro-

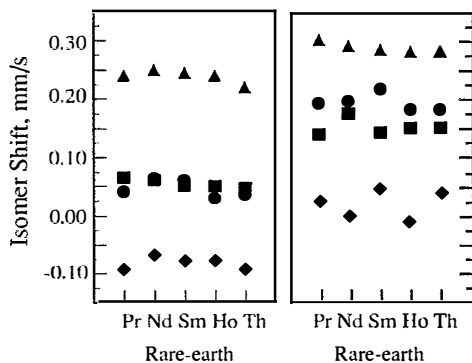


FIG. 3. Isomer shifts obtained at 85 K for the four crystallographic sites in R_2Fe_{17} (left) and $\text{R}_2\text{Fe}_{17}\text{N}_x$ (right) as a function of rare earth for the iron $6c$ site, \blacktriangle , for the iron $9d$ site, \blacklozenge , for the iron $18f$ site, \blacksquare , and for the iron $18h$ site, \bullet .

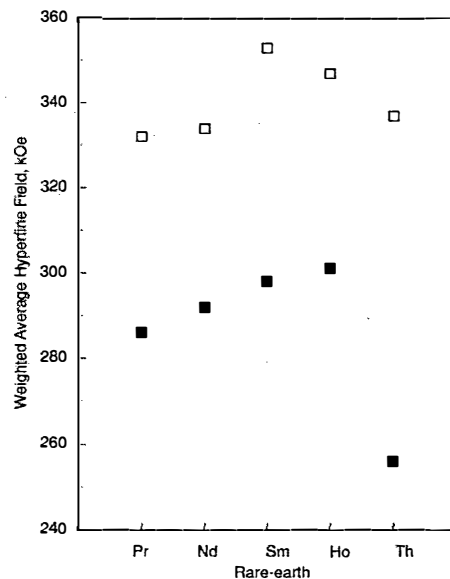


FIG. 4. The 85 K weighted average hyperfine fields in R_2Fe_{17} (solid symbols) and $\text{R}_2\text{Fe}_{17}\text{N}_x$ (open symbols) as a function of rare earth.

magnetic coupling. In contrast, the distances between the $6c$ and $18f$ sites and their near neighbors either increase or decrease upon nitrogenation, changes which yield a smaller improvement in the ferromagnetic exchange coupling for these two sites.

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