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A Mössbauer Spectral Study of Tb_2Fe_{17} and the $Tb_2Fe_{17-x}Si_x$ Solid Solutions

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The Mössbauer spectra of a series of rhombohedral $Tb_2Fe_{17-x}Si_x$ solid solutions, with x equal to 0, 1, 2, and 3, have been measured as a function of temperature. Although the spectra of Tb_2Fe_{17} change substantially upon cooling from 295 to 85 K, it has been possible to fit them with a consistent seven sextet model corresponding to a basal magnetization. The spectral analysis yields reasonable hyperfine parameters and the expected changes with temperature. The resulting weighted average effective iron recoil mass of 66 g/mol and the Mössbauer temperature of 395 K are typical of this type of intermetallic compound. In addition, the isomer shifts and the hyperfine fields observed for the crystallographically distinct iron sites in Tb_2Fe_{17} agree well with those expected from the differences in the Wigner–Seitz cell volumes and the near-neighbor environments of the four sites. The spectra of the silicon substituted solid solutions have been fit with the same model and similar hyperfine parameters, but with a binomial distribution of near-neighbor environments. The weighted average hyperfine field decreases slowly with increasing silicon content, whereas the isomer shift increases. © *1998 American Institute of Physics.* [S0021-8979(98)35611-X]

R_2Fe_{17} is a very common intermetallic phase whose magnetic properties can be modified by replacing part of the iron by a substitutional metal such as aluminum,[1–4] gallium,[5,6] or silicon.[7,8] Often the Curie temperatures increase up to a maximum at $x \approx 3$ in these $R_2Fe_{17-x}M_x$ solid solutions. Thus a systematic study of these compounds may lead to improved permanent magnet materials as a result of a better understanding of the influence of the substitutional metal.

Herein, we report on the magnetic properties of Tb_2Fe_{17} and its silicon substituted solid solutions, $Tb_2Fe_{17-x}Si_x$, with $x = 1$, 2, and 3, by Mössbauer spectroscopy between 85 and 295 K. We are interested in these solid solutions because their lattices contract with increasing x, contractions which are rather surprising because it has generally been believed that such contractions would lead to an increase in the antiferromagnetic coupling between some of the iron atoms. Such an increase should lead to a decrease in the Curie temperature in contrast to the observed increase with x. Thus a study of these compounds, which seem to be an exception to this general belief, may help to better understand the magnetic behavior of such substituted intermetallic compounds.

The $Tb_2Fe_{17-x}Si_x$ solid solutions, with $x = 0$, 1, 2, and 3, were prepared as described previously.[5] Powder x-ray diffraction results indicate that all of these compounds are virtually single phase and crystallize with the rhombohedral Th_2Zn_{17}-type structure. Three silicon atoms per formula unit are the most that can be introduced into Tb_2Fe_{17} and still yield a single phase solid solution.

The Mössbauer spectral absorbers contained 27 mg/cm² of powder[10] which had been sieved to a particle diameter of 0.045 mm or less. The Mössbauer spectra were measured on a constant acceleration spectrometer which utilized a rhodium matrix cobalt-57 source and was calibrated at room temperature with an α-iron foil.

A preliminary study[11] of the Mössbauer spectra of Tb_2Fe_{17} at 78 and 295 K has revealed a distinct difference in the shape of the spectra at these two temperatures. Further, the reported temperature dependence of the spectral hyperfine parameters was unusual. In order to better understand these changes, the Tb_2Fe_{17} Mössbauer spectra were remeasured at several temperatures between 85 and 295 K. Figure 1, which shows several of these spectra, reveals a continuous change in the shape of the spectrum upon cooling. At 85 K the spectrum shows a very distinct absorption at ca. −5.3 mm/s as well as two distinct shoulders at ca. −2.5 and 4.5 mm/s, absorptions which begin to converge with others above 175 K such that at 295 K there is little if any sign of these three spectral features.

Because the magnetization of Tb_2Fe_{17} is basal, we have fit its Mössbauer spectra with a seven sextet model[9] in which the hyperfine parameters are consistent with both the near-neighbor environment and the Wigner–Seitz cell volume of each iron site. The seven sextets correspond to the seven inequivalent magnetic sites,[9] $6c$, $9d_6$, $9d_3$, $18f_{12}$, $18f_6$, $18h_{12}$, and $18h_6$, respectively, and the isomer shifts for the crystallographically equivalent, but magnetically inequivalent, sites were constrained to be equal. Further, in this model the isomer shift increases with the cell volume of a crystallographic site because of a reduced s-electron density at the iron-57 nucleus. The results of these fits are given in Table I along with the 295 K Wigner–Seitz cell volume for each site.[12,13]
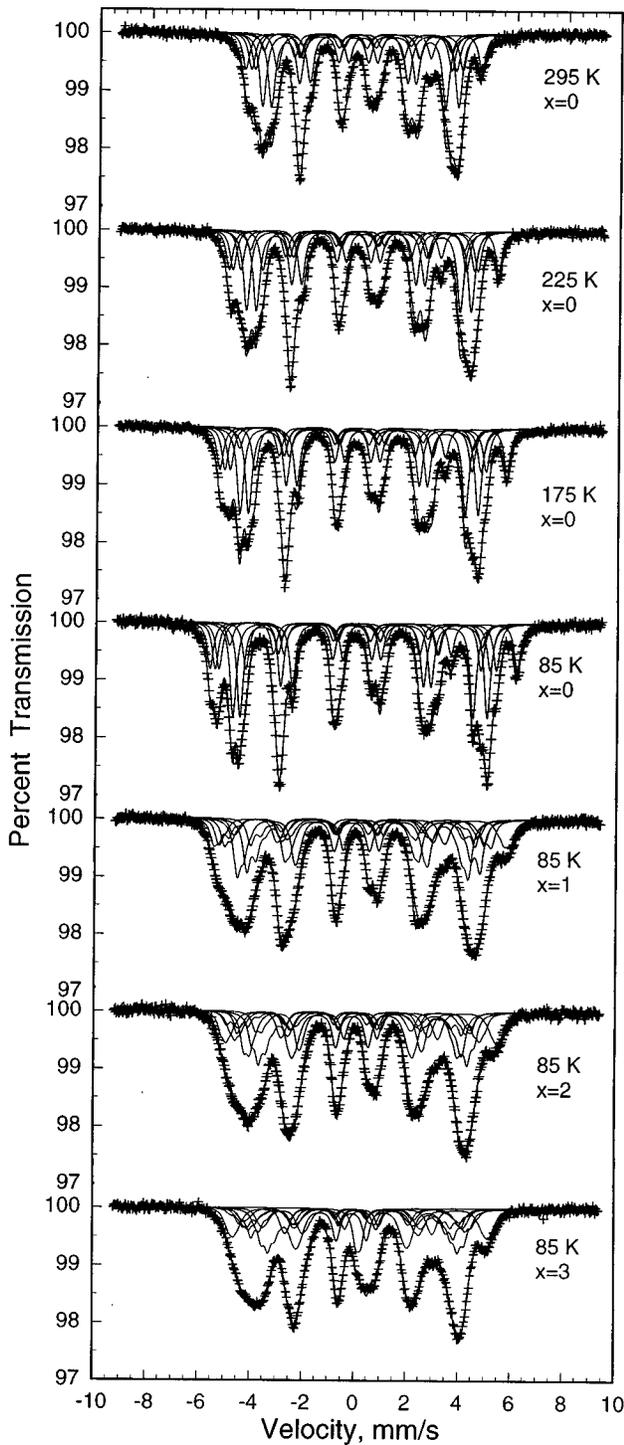
FIG. 1. The Mössbauer spectra of Tb_2Fe_{17} measured at 295, 225, 175, and 85 K, and the 85 K Mössbauer spectra of the $Tb_2Fe_{17-x}Si_x$ solid solutions with $x = 1$, 2, and 3.

As already observed[9] in many related R_2Fe_{17} compounds, the hyperfine fields increase with the number of iron near neighbors for each crystallographic site, see Fig. 2. As expected, the hyperfine fields decrease with increasing temperature and the quadrupole shifts are independent of temperature. The effective mass, M_{eff}, of each iron site can be calculated[14] from the temperature dependence of the isomer shift. Table I reveals that the $9d$ site has the largest, the $18f$ and $18h$ sites have similar intermediate, and the $6c$ site has
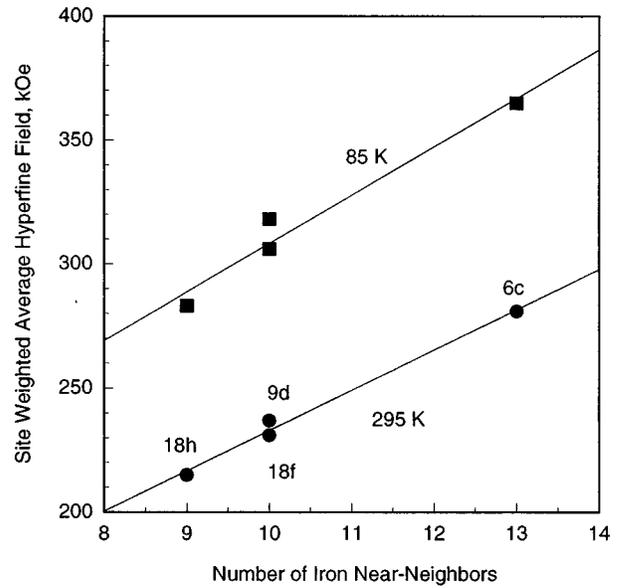
FIG. 2. The correlation between the Tb_2Fe_{17} site weighted average hyperfine fields and the number of iron near-neighbors.

the smallest effective masses. This indicates that the $9d$ site is more covalently bound than the other sites, as is expected for the site with the smallest Wigner–Seitz cell volume. The temperature dependence of the isomer shift and the logarithm of the spectral absorption area may be used to calculate[14] the Mössbauer temperature, θ_M, for each site. The resulting values, of ca. 400 K, see Table I, are typical for this type of intermetallic compound.[15]
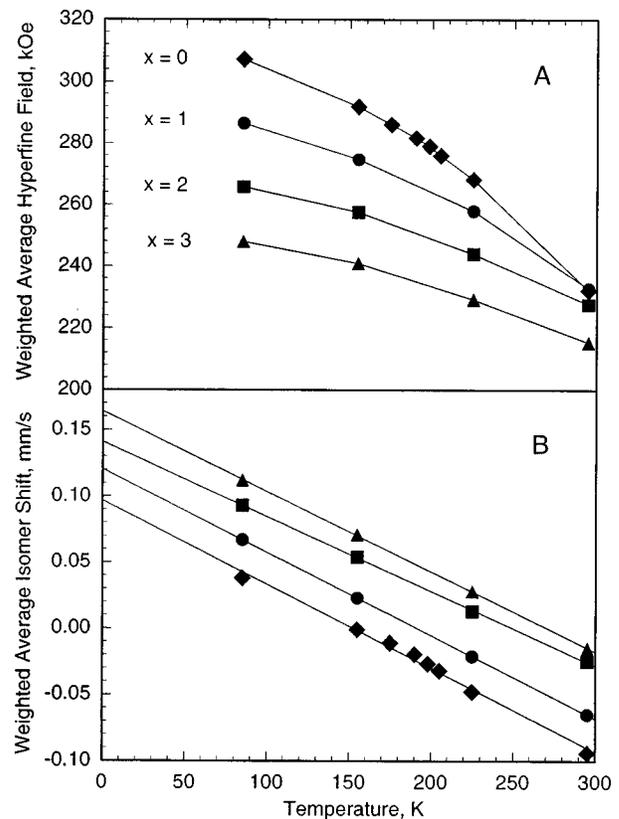

FIG. 3. The temperature dependence of the weighted average hyperfine fields, A, and the weighted average isomer shifts, B, for the $Tb_2Fe_{17-x}Si_x$ solid solutions with $x = 0$, ◆; 1, ●; 2, ■; and 3, ▲.

TABLE I. Mössbauer spectral hyperfine parameters[a] and Wigner–Seitz cell volumes for Tb_2Fe_{17}.

	T, K	$6c$	$9d_6$	$9d_3$	$18f_{12}$	$18f_6$	$18h_{12}$	$18h_6$	Wt. ave.
H, kOe	295	281	244	223	223	247	218	208	232
	85	365	327	300	294	330	285	279	307
δ, mm/s[b]	295	0.066	−0.180	−0.180	−0.084	−0.084	−0.113	−0.113	−0.094
	85	0.229	−0.063	−0.063	0.041	0.041	0.021	0.021	0.038
δ_0, mm/s[c]		0.304	0.082	0.082	0.095	0.095	0.080	0.080	0.112
$d\delta/dT$[c]		−7.55	−5.55	-	−6.15	-	−6.43	-	−6.36
M_{eff}, g/mol		55	74	-	67	-	64	-	66
θ_M, K		433	371	-	390	-	399	-	395
QS, mm/s	295	0.05	−0.21	0.04	0.45	−0.01	−0.33	0.45	0.06
	85	0.06	−0.20	0.04	0.45	−0.02	−0.33	0.45	0.06
V_{WS}, Å³ [d]	295	12.55	11.28	-	11.77	-	11.88	-	11.81

[a]The linewidth is 0.32 mm/s at 295 K and 0.29 mm/s at 85 K and $d(\ln \text{Area})/dT$ is -7.51×10^{-4} K^{-1}.
[b]Relative to room temperature α-iron foil.
[c]δ_0 is the zero Kelvin intercept and the slope, $d\delta/dT$, is $\times 10^{-4}$ (mm/s)/K.
[d]Calculated with the structural parameters given in Ref. 13 and BLOKJE, Ref. 12, with the 12 coordinate atomic radii of 1.80 and 1.26 Å for terbium and iron, respectively.

The Mössbauer spectra of $Tb_2Fe_{17-x}Si_x$, with $x=1$, 2, and 3, were measured between 85 and 295 K, and the 85 K spectra are shown in Fig. 1. These spectra are clearly much broader than those of Tb_2Fe_{17} and thus must be fit with a distribution of hyperfine fields resulting from the binomial distribution of silicon near neighbors, a fitting procedure which has been described in detail elsewhere.[8,11] To carry out these fits, the amount of silicon on each iron site must be known. Unfortunately, at this time, no neutron diffraction results are available for these compounds, and thus the silicon occupancies reported[8] for $Ce_2Fe_{17-x}Si_x$ were used herein. Indeed, earlier work[1–8] has shown that the M site occupancies are rather independent of the nature of the rare earth in $R_2Fe_{17-x}M_x$. Further, for low silicon content even less variation with the rare earth is expected. A single linewidth, between 0.29 mm/s at 85 K and 0.32 mm/s at 295 K, was used in the fits.

The resulting isomer shifts follow the sequence $9d < 18f \leqslant 18h < 6c$ as observed in Tb_2Fe_{17}. Figure 3 shows the temperature dependence of the average isomer shift for the four compounds studied herein. It is clear that the 85 K weighted average isomer shift increases with silicon content from 0.038 mm/s at $x=0$ to 0.112 mm/s at $x=3$. A similar variation was observed[7,8] in $Nd_2Fe_{17-x}Si_x$ and $Ce_2Fe_{17-x}Si_x$. Figure 3 shows the temperature dependence of the weighted average hyperfine field. The decrease in the hyperfine field, ΔH, due to each silicon near neighbor at a given site, is ca. 16 kOe, a value[7,8] which is typical of these solid solutions.[15]

The temperature dependence of the spectral hyperfine parameters, and their changes with x in $Tb_2Fe_{17-x}Si_x$, show an internal consistency in the series, agree well with previous results[1–8] obtained for similar $R_2Fe_{17-x}M_x$ solid solutions, and agree with the magnetization measurements,[13] measurements which indicate a maximum Curie temperature of 520 K for $Tb_2Fe_{14}Si_3$. This consistency will be discussed in detail in a future paper.[13]

In the experimental section, it was noted that a maximum of three silicon atoms per formula unit can be introduced into Tb_2Fe_{17}. In the fits of $Tb_2Fe_{14}Si_3$, a doublet with an isomer shift of 0.2 mm/s, a quadrupole splitting of 0.19 mm/s, and a relative area of 4%, had to be included at 85 K. Its parameters are consistent with the iron–silicon phase previously observed[7] in $Nd_2Fe_{17-x}Si_x$. Both the formation of this stable impurity phase and the contraction of the unit cell lattice with increasing x may explain why no more than three silicon atoms can be substituted into Tb_2Fe_{17}.

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