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# Neutron-diffraction and Mössbauer effect study of the $Tb_2Fe_{17-x}Al_x$ solid solutions

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The magnetic properties of a series of  $Tb_2Fe_{17-x}Al_x$  solid solutions, with nominal  $x$  compositions of 0, 2, 3, 4, 5, 6, 7, and 8, have been studied by neutron diffraction and Mössbauer spectroscopy. Neutron-diffraction data indicate that the compounds all crystallize with the  $Th_2Zn_{17}$  structure and that the aluminum atoms are excluded from the  $9d$  site and show a distinct preference for the  $6c$  site only for an aluminum content greater than 6. The unit-cell volume increases by approximately 1% per aluminum atom substituted in the formula unit. The magnetic moment per formula unit, measured at 295 K, shows very little change for  $x$  less than or equal to 4, but decreases rapidly with increasing aluminum content for higher values of  $x$ . Mössbauer spectral results indicate that all the samples are ferromagnetically ordered at 85 K. However, at 295 K  $Tb_2Fe_9Al_8$  is paramagnetic and  $Tb_2Fe_{10}Al_7$  is either paramagnetic or has at most very small ferromagnetic moments. An analysis of the magnetic spectra with a basal magnetic model is successful for  $x$  values of 5 or less; however, at higher  $x$  values an axial model for the magnetization is required, indicating the presence of a spin reorientation with increasing aluminum content and decreasing temperature. The weighted average hyperfine field decreases approximately linearly by 21 kOe per substituted aluminum atom at 85 K and more rapidly at 295 K. As expected, the isomer shifts increase with increasing aluminum content as a result of interatomic charge transfer and intraatomic iron  $4s-3d$  electronic redistribution.

The discovery<sup>1</sup> that the addition of interstitial nitrogen could dramatically increase the Curie temperature of  $R_2Fe_{17}$  and, in some cases, change the magnetic anisotropy from basal to axial has led to a renewed interest in these compounds. The primary reason for the increased  $T_C$  is the expansion of the lattice caused by the interstitial nitrogen.<sup>2</sup> The lattice may also be expanded by partially substituting the iron by other elements,<sup>3</sup> and an investigation of such partially substituted compounds may lead to a better understanding of the magnetization process and consequently to solid solutions possessing better magnetic properties. In the  $R_2Fe_{14-x}Al_xB$  solid solutions,<sup>4,5</sup> aluminum causes both the coercive and the anisotropic fields to increase with only slight decreases in the magnetization and  $T_C$ . Partial substitution of iron atoms by aluminum in  $Ce_2Fe_{17}$ ,  $Y_2Fe_{17}$ ,  $Nd_2Fe_{17}$ ,  $Dy_2Fe_{17}$ , and  $Ho_2Fe_{17}$  causes the unit cell to expand and the  $T_C$  to increase with aluminum content at lower aluminum concentrations.<sup>3,6-8</sup> In  $Tb_2Fe_{14}B$  the terbium magnetic moments are aligned antiparallel<sup>9</sup> with the iron moments and a similar antiparallel magnetic structure is expected in  $Tb_2Fe_{17-x}Al_x$ . It has been reported<sup>10,11</sup> that  $Tb_2Fe_{17-x}Al_x$  crystallizes in the hexagonal  $Th_2Ni_{17}$  structure at aluminum concentrations up to an  $x$  of 3.8 and in the

rhombohedral  $Th_2Zn_{17}$  structure at higher concentrations. Furthermore, its  $T_C$  increases with increasing aluminum content at low aluminum concentrations.<sup>10</sup>

The  $Tb_2Fe_{17-x}Al_x$  samples were prepared from 99.9% pure elements by arc melting followed by annealing at 900 °C for more than 3 weeks. The phase purity of the samples was checked by x-ray diffraction which indicated that the  $Tb_2Fe_{17-x}Al_x$  samples with nominal  $x$  values of 2 and higher crystallized with the rhombohedral  $Th_2Zn_{17}$  structure. This limiting composition for the rhombohedral phase is considerably lower than that reported by Oesterreicher and Boller<sup>10-12</sup> and may be due to the higher annealing temperature used for the samples in our study.

The neutron-diffraction patterns were measured<sup>6</sup> and refined<sup>13,14</sup> by the same methods as reported earlier. The Mössbauer spectra were measured<sup>6</sup> and fit<sup>15-17</sup> as reported earlier. The spectra that indicated ferromagnetic ordering were fit with four or seven magnetic sextets corresponding to the four or seven magnetically inequivalent iron sites expected for an axial or basal orientation of the magnetization and the site point symmetry.

The Curie temperature of the  $Tb_2Fe_{17-x}Al_x$  solid solutions increases with increasing aluminum content at lower aluminum concentrations and reaches a maximum at an  $x \sim 3$ .<sup>18</sup> The results of the refinement of the 295 K neutron-diffraction patterns of these solid solutions are given in Table

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TABLE I. The lattice and positional parameters, site occupancies, and moments in  $Tb_2Fe_{17-x}Al_x$  as measured by neutron diffraction at 295 K.

Compound	$Tb_2Fe_{15}Al_2$	$Tb_2Fe_{14}Al_3$	$Tb_2Fe_{13}Al_4$	$Tb_2Fe_{12}Al_5$	$Tb_2Fe_{11}Al_6$	$Tb_2Fe_{10}Al_7$	$Tb_2Fe_9Al_8$
$x$ refined	1.98	3.14	4.08	5.10	6.06	7.16	8.12
$a$ (Å)	8.5768(2)	8.6011(2)	8.6212(1)	8.6625(1)	8.6942(1)	8.7482(1)	8.7874(1)
$c$ (Å)	12.5191(4)	12.5549(3)	12.5872(2)	12.6307(3)	12.6501(2)	12.6988(3)	12.7270(3)
$c/a$	1.460	1.460	1.460	1.458	1.455	1.452	1.448
$V$ (Å <sup>3</sup> )	797.5	804.4	810.2	821.3	828.1	841.6	851.1
Tb, 6c, $z$	0.3413(4)	0.3408(3)	0.3406(3)	0.3433(2)	0.3417(3)	0.3458(2)	0.3480(2)
Fe/Al, 6c, $z$	0.0958(3)	0.0957(2)	0.0941(2)	0.0962(2)	0.0993(1)	0.1002(3)	0.1028(4)
Fe/Al, 18f, $x$	0.2964(2)	0.2947(1)	0.2896(1)	0.2893(1)	0.2920(1)	0.2905(2)	0.2928(2)
Fe/Al, 18h, $x$	0.1676(1)	0.1684(1)	0.1690(1)	0.1697(1)	0.1681(1)	0.1683(1)	0.1677(1)
Fe/Al, 18h, $z$	0.4921(2)	0.4920(1)	0.4895(1)	0.4895(1)	0.4882(1)	0.4905(1)	0.4904(1)
%Al, 6c	14.4	21.0	24.6	32.9	41.3	72.4	94.0
%Al, 9d	0.0	0.0	0.0	0.0	0.0	0.0	0.0
%Al, 18f	9.8	18.8	23.4	31.4	41.4	57.6	68.8
%Al, 18h	18.4	26.6	36.4	42.6	45.8	37.6	35.2
$R$ factor	5.88	5.24	5.26	5.09	4.46	4.84	4.97
$R_w$ factor	6.80	6.10	5.95	6.17	5.46	5.73	5.78
$R_m$ factor	10.1	8.23	5.07	8.48	9.67	14.0	...
$\chi^2$	2.57	2.49	2.56	2.61	2.62	2.50	2.54
$\mu$ , Tb, 6c ( $\mu_B$ )	-4.5(1)	-4.3(1)	-4.1(1)	-4.1(1)	-3.5(1)	-0.6(1)	...
$\mu$ , Fe, 6c ( $\mu_B$ )	2.7(2)	3.0(1)	3.1(1)	3.3(1)	32.3(1)	0.6(1)	...
$\mu$ , Fe, 9d ( $\mu_B$ )	1.9(1)	1.9(1)	2.0(1)	1.8(1)	1.7(1)	0.6(1)	...
$\mu$ , Fe, 18f ( $\mu_B$ )	1.9(1)	2.0(1)	2.1(1)	2.0(1)	1.9(1)	0.6(1)	...
$\mu$ , Fe, 18h ( $\mu_B$ )	1.5(1)	1.8(1)	1.6(1)	1.6(1)	1.1(1)	0.6(1)	...
$\mu$ /cell ( $\mu_B$ )	56.7	57.6	55.5	46.2	34.5	14.1	...
$\mu$ /formula ( $\mu_B$ )	18.9	19.2	18.5	15.4	11.5	4.7	...
$\mu(z)/\mu(x)$	0.0	0.0	0.0	0.0	1.2	infinite	...

I. The lattice parameters increase approximately linearly with  $x$  as was found<sup>19</sup> to be the case for the related  $Nd_2Fe_{17-x}Al_x$  solid solutions, but the increase differs from the behavior found for the  $c$  lattice parameter in  $Tb_2Fe_{17-x}Ga_x$ , which increases up to an  $x$  of 6 and then remains constant at higher values. The unit-cell volume of  $Tb_2Fe_{17-x}Al_x$  increases linearly by 8.9 Å<sup>3</sup> per aluminum, a value which is similar to that of the gallium solid solutions.<sup>20</sup>

As is shown in Fig. 1, the aluminum completely avoids the 9d crystallographic site, the site expected to have the smallest Wigner-Seitz cell volume.<sup>19</sup> In contrast, at least up to an  $x$  of 6, the aluminum somewhat favors the 18h site and occupies the 6c and 18f sites almost randomly. At  $x$  values above 6 these trends change and aluminum highly favors the 6c and 18f sites. A rather similar occupation has been observed<sup>19</sup> in the  $Nd_2Fe_{17-x}Al_x$  solid solutions and explained on the basis of the differing near-neighbor environments of the different sites.

The compositional dependence of the magnetic moments derived from the neutron-diffraction<sup>9</sup> scattering is given in Table I, and shown in Fig. 2. As expected on the basis of the terbium crystal field,<sup>20</sup> the terbium magnetic moments are antiferromagnetically exchange coupled to the iron moments which are in the basal plane of the unit cell for  $x$  values of 5 and less. At larger  $x$  values a spin reorientation occurs such that, in  $Tb_2Fe_{10}Al_7$ , the magnetization is axial. Unfortunately,  $Tb_2Fe_9Al_8$  is paramagnetic, at least at 295 K. The iron moment on the 6c site increases gradually for  $x$  values up to 6, whereas the other iron moments remain approximately constant for  $x$  between 0 and 6.

The Mössbauer spectra of the  $Tb_2Fe_{17-x}Al_x$  solid solutions have been measured at 85 and 295 K. The spectra were initially fit with either four or seven broadened magnetic sextets which represent the expected number of magnetic

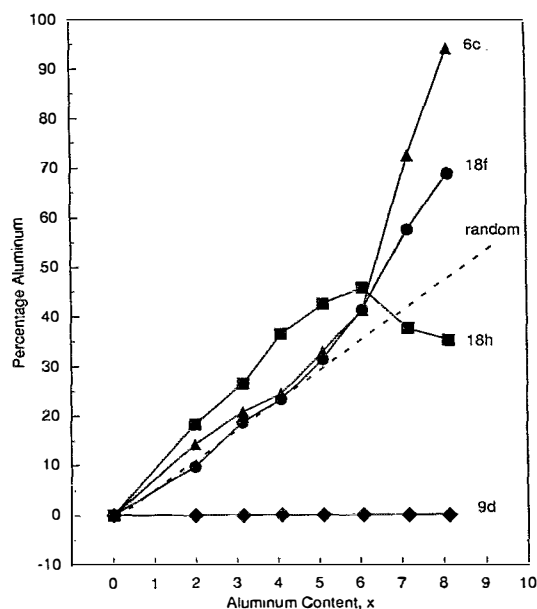


FIG. 1. The percentage of aluminum found by neutron diffraction on each of the four crystallographic iron sites in the  $Tb_2Fe_{17-x}Al_x$  solid solutions. The dashed line represents random occupation by aluminum.

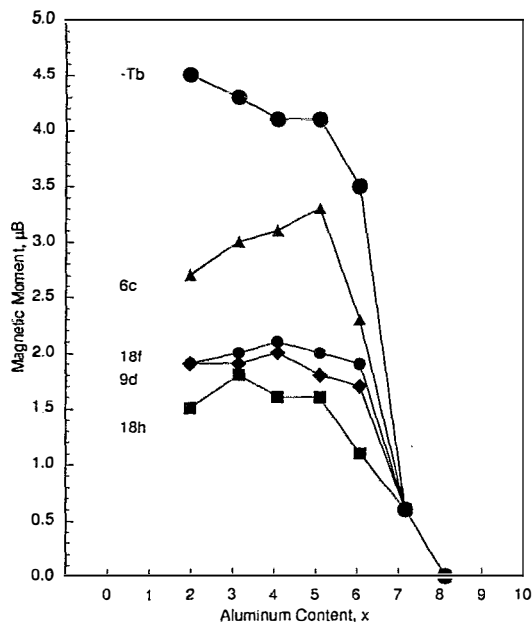


FIG. 2. The iron and terbium magnetic moments at 295 K in the  $Tb_2Fe_{17-x}Al_x$  solid solutions. The terbium moments are aligned antiparallel to the iron moments.

sextets in the axially or basally magnetized  $R_2Fe_{17}$  materials.<sup>15,21</sup> In agreement with the neutron-diffraction results, it was found that all the 295 K magnetic Mössbauer spectra could only be fit with the basal magnetization model, except for  $Tb_2Fe_{11}Al_6$ , for which a better fit with the simpler axial model was obtained. The low-temperature spectra for the samples with  $x$  values of 6, 7, and 8 were successfully fit with an axial model. This spin reorientation is also apparent in the quadrupole shift changes with increasing  $x$  and decreasing temperature. The fitting model, which does not take into account the near-neighbor environment of each iron site, is quite successful in reproducing the observed spectral absorption, but some problems with intensity do occur. A more detailed analysis of these spectra in terms of a binomial distribution of the near-neighbor aluminum environments will be reported elsewhere.<sup>22</sup> Because of the approximations involved in the spectral fits, only the weighted average hyperfine parameters are discussed herein.

The weighted average isomer shifts increase linearly with increasing aluminum content with variations of 0.0257 and 0.0185 mm/s per aluminum at 295 and 85 K, respectively. These increases are typical of those found upon the substitution of either aluminum<sup>19</sup> or gallium<sup>20</sup> for iron to form  $R_2Fe_{17}$  solid solutions. The increase may be attributed to an interatomic charge transfer between the iron and aluminum and a subsequent  $3d-4s$  intraatomic iron electronic redistribution.<sup>23-25</sup> The weighted average hyperfine fields at 295 and 85 K, as a function of aluminum content, are shown in Fig. 4. As expected the hyperfine field at 85 K decreases almost linearly by 21 kOe per aluminum atom with the increasing replacement of magnetic iron with diamagnetic aluminum and the decrease is even more rapid at 295 K; however, the observed hyperfine fields are higher than those observed in the  $Nd_2Fe_{17-x}Al_x$  solid solutions, even though the unit-cell volumes of the former are smaller.

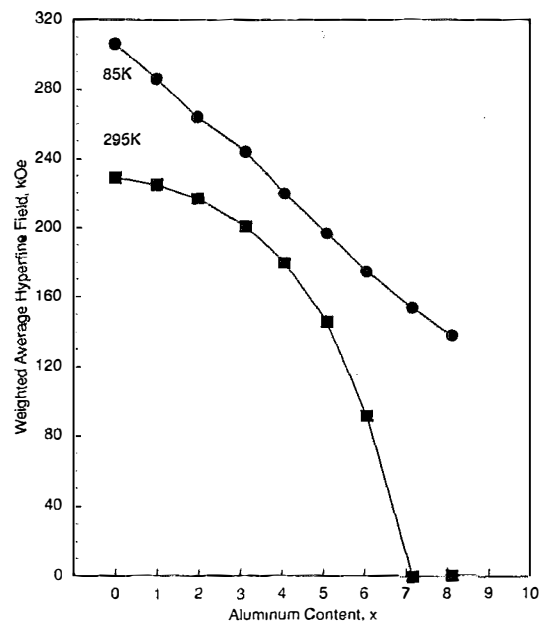


FIG. 3. The area weighted average hyperfine fields in the  $Tb_2Fe_{17-x}Al_x$  solid solutions.

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