Neutron diffraction and Mössbauer studies of Ga site preference in $Nd_2Fe_{14}B$ and Fe internal-field assignments

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Neutron diffraction and Mössbauer spectroscopy were used in order to study gallium site preference and hyperfine fields at the six iron sites in $Nd_2(Fe_{1-x}Ga_x)_{14}B$ alloys ($x=0$–0.15). Ga atoms have a strong preference to substitute for the Fe(j_1) and then the Fe(c) atoms. The assignments of the 6 Fe sites and the corresponding hyperfine field are tentatively the following: 344 (j_2), 325 (k_2), 306 (j_1), 294 (k_1), 286 (c), and 261 (e) kOe.

$Nd_2Fe_{14}B$ compounds have been extensively studied during the last five years.[1] Such an alloy has extremely good permanent magnetic properties but its Curie temperature is not high enough. In order to improve the temperature coefficient, many kinds of substitution have been used. The addition of Co can improve the T_c but will decrease its coercive force H_c.[2] The addition of Al enhances the H_c but T_c drastically decreases.[3] The amorphous rare-earth–Ga–Fe alloys can have a very high H_c.[4] Both T_c and H_c increase for small added amounts of Ga.[5] For a good understanding of these results, it is necessary to know the detail of the Ga site preference in the Nd-Fe-B structure. We report here the results of neutron diffraction and Mössbauer studies and try to explain the Ga-content dependence of T_c by this analysis.

In the present work, all the samples of $Nd_2(Fe_{1-x}Ga_x)_{14}B$ ($x=0$, 0.025, 0.05, 0.075, 0.1, 0.125, and 0.15) were prepared by arc melting in argon from commercially available raw materials of high-purity ([Nd]=99.9%, [Fe]=99.9%, [B-Fe]=99.9%, and [Ga]=99.99%). Ingots were then annealed at 900 °C for 100 h under argon in order to homogenize. The samples were checked by Co $K\alpha$ x-ray diffraction and the data show the presence of only one phase having the $Nd_2Fe_{14}B$-type structure in the $Nd_2(Fe_{1-x}Ga_x)_{14}B$ alloy system for $0<x<0.15$.

The magnetic properties were investigated for all x,[5] but only part of the ingots were powdered using ball milling for neutron diffraction and Mössbauer studies. Cylinders of dimensions $\phi 5\times 10$ mm^3 for these powder samples were investigated with a triple-axis neutron spec-

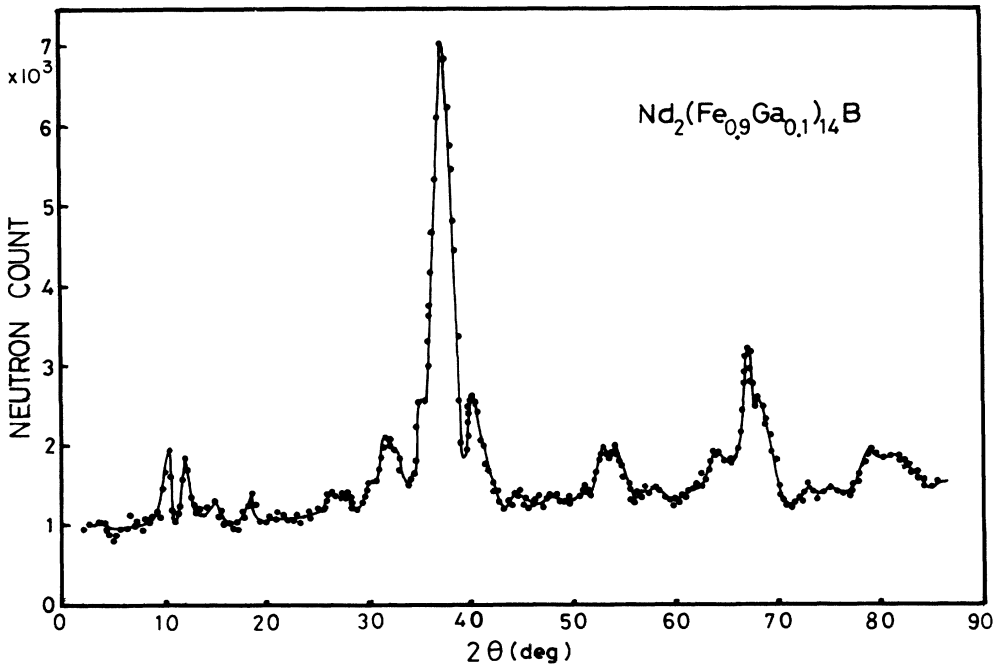

FIG. 1. Neutron-diffraction pattern for $Nd_2(Fe_{0.9}Ga_{0.1})_{14}B$.

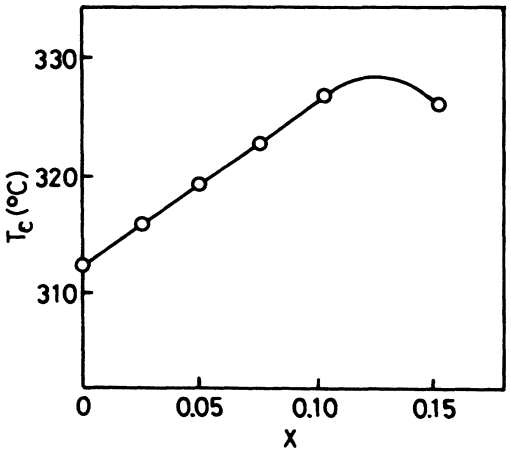

FIG. 2. Dependence of the Curie temperature T_c of $Nd_2(Fe_{1-x}Ga_x)_{14}B$ on the Ga concentration x.

trometer with $2\theta < 86$, wave length = 1.3 Å. The ^{57}Fe Mössbauer spectra were measured under room temperature using a constant acceleration spectrometer for $x=0$, 0.025, 0.05, 0.075, and 0.1.

The standard least-squares refinement procedure for powder neutron diffraction was used to fit our data. The adjustable parameters were as follows: parameters u, v, and w describe the half width of the Bragg reflection peak; x and y are the coordinates of the boron atoms; a substitution number of Ga into six Fe atom site; an overall temperature factor and an overall scale factor. During refinement, the number of Ga atoms in the unit cell was limited to 56. The total nuclear and magnetic R factor was 8%. The substitution number of Ga into k_1, k_2, j_1, j_2, c, and e for $x=0.1$ was calculated to be 0.00±0.07, 0.00±0.07, 0.74±0.08, 0.01±0.07, 0.66±0.08, and 0.01±0.08, respectively.

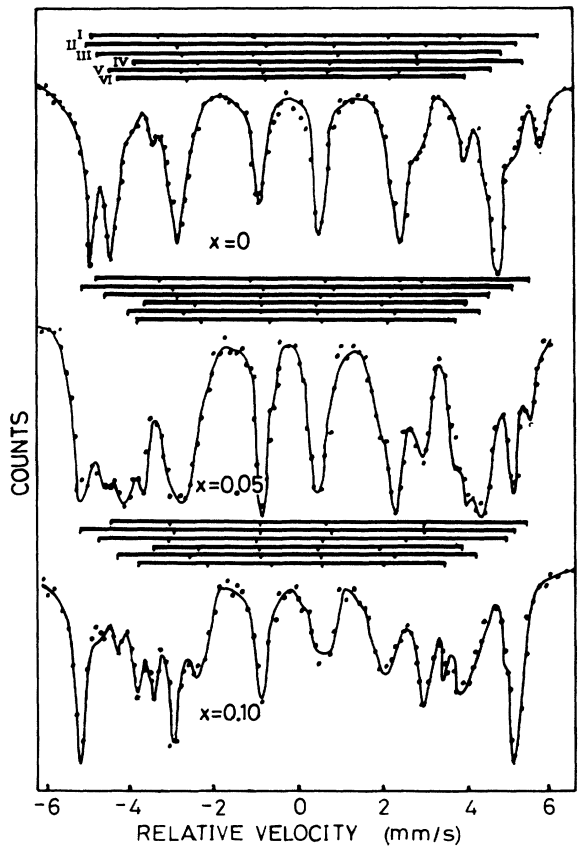

FIG. 3. Room temperature ^{57}Fe Mössbauer spectra of $Nd_2(Fe_{1-x}Ga_x)_{14}B$ ($x=0$, 0.05, and 0.1). The six derived subspectra are indicated also.

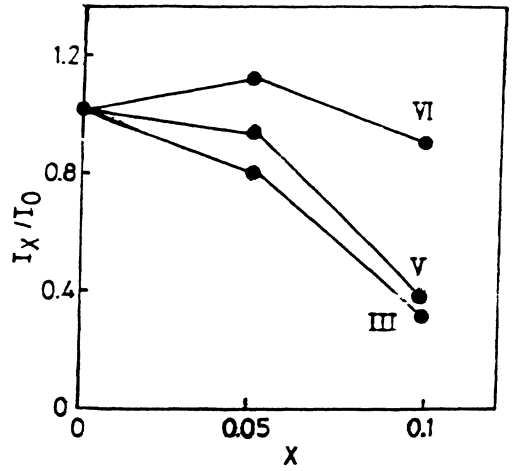

FIG. 4. Dependences of the relative peak amplitude I_x/I_0 of $Nd_2(Fe_{1-x}Ga_x)_{14}B$ Mössbauer spectra on the Ga concentration x.

Figure 1 shows the neutron-diffraction spectrum for $Nd_2(Fe_{1-x}Ga_x)_{14}B$ alloy at $x=0.1$. The result showed a strong preference for Ga atoms occupying the j_1 site and then the c site. About 74% of the j_1 sites and 66% of the c sites will be occupied by Ga atoms for $x=0.1$.

There are three coordination atoms for the j_1 site with negative exchange interaction since the interatomic distance are 2.377 and 2.402 A for j_1-k_2 and j_1-j_1 pairs, less than 2.44 A.[6] Obviously the preferential substitution of Ga into j_1 site will remove the negative exchange interaction and increase the Curie temperature T_c, as shown in Fig. 2. The total concentration of Ga should be $x=\frac{8}{56}=0.14$ when all of the j_1 sites are occupied by Ga atoms, but the composition for maximum T_c is around $x=0.13$. Other effects, such as the 87% c site occupied by Ga in this case, will remove some positive exchange interaction and decrease T_c.

Figure 3 shows the room-temperature Mössbauer spectra for $x=0$, 0.05, and 0.1 and also indicates the six derived subspectra. It is quite similar to other Mössbauer experiments,[7-10] but the assignments for the hyperfine-field values at the corresponding Fe sites analyzed by these authors were rather different except for the j_2 site. Most fittings were based on the population of the 6 Fe sites in the ratios 16:16:8:8:4:4 for k_1, k_2, j_1, j_2, c, and e, separately. As mentioned by Buschow,[11] this implies that the intensity alone may not be sufficient for such an assignment. In Ref. 7, the assignment is j_2, k_2, c, k_1, j_1, e but the assignment of j_2, k_2, j_1, k_1, c, and e based on NMR measurements seems more reasonable.[12] It agrees with the result of Pinkerton except that the c and e sites are

indistinguishable in his work.[9] The only difference between Refs. 7 and 12 is the order of c and j_1 sites. Fortunately Ga will prefer to occupy j_1 and then the c site, which is useful to confirm the order of c and j_1. The assignment for the hyperfine values analyzed by our Mössbauer measurement for $x=0$ is I (344 kOe), II (325 kOe), III (306 kOe), IV (294 kOe), V (286 kOe), VI (261 kOe). The highest one I(344 kOe) should be contributed by the j_2 site and II, IV with strong peak amplitude, must be the subspectra of k_2 and k_1 as mentioned by many authors. Figure 4 shows the variation of the relative peak amplitude I_x/I_0 of III, V, VI subspectra with Ga content x. The III subspectrum decreases with x and implies that Ga atoms are preferential to occupying this site. I_x/I_0 for subspectrum V decreases slowly when $x<0.05$ and then more rapidly up to $x=0.1$. It means that Ga atoms will occupy the III site for $x<0.05$ and then the V site also. For VI, I_x/I_0 changes only weakly in the whole range of $0<x<0.1$. Combining with the results of neutron diffraction, it is not difficult to identify that III, V, VI are related with j_1, c, and e sites separately. For j_1 and c sites at $x=0.1$, I_x/I_0 decrease about 70% and 62%, respectively. These values are quite compatible with the neutron-diffraction data. As a conclusion, the assignment from our neutron diffraction and Mössbauer studies is 344(j_2), 325(k_2), 306(j_1), 294(k_1), 286(c), and 261(e) kOe.

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