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Mayot, Hervé; Isnard, Olivier; Grandjean, Fernande; and Long, Gary J., "A structural, magnetic, and Mössbauer spectral study of the Dy Co$_{4-x}$Fe$_x$B compounds, with x=0-3" (2008). Faculty Research & Creative Works. Paper 39.
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A structural, magnetic, and Mössbauer spectral study of the DyCo$_{4-x}$Fe$_{x}$B compounds, with x=0–3

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(Received 31 January 2008; accepted 13 March 2008; published online 14 May 2008)

The DyCo$_{4-x}$Fe$_{x}$B compounds, with x=0, 1, 1.5, 2, 2.5, and 3, have been investigated by x-ray diffraction, magnetic measurements, and iron-57 Mössbauer spectroscopy. The substitution of cobalt by iron induces both an anisotropic increase in the unit-cell volume and a large increase in the Curie temperature. The 4.2 K magnetization decreases with increasing iron content. The Mössbauer spectra of the DyCo$_{4-x}$Fe$_{x}$B compounds with x=1, 1.5, and 2 reveal rather small iron hyperfine fields of approximately 16 T and large quadrupole interactions of +1.0 and −1.0 mm/s, for the 6i and 2c sites, respectively. The relative areas of the 6i and 2c spectral components indicate a strong preferential substitution of iron on the 2c site. In DyCo$_{4-x}$FeB approximately 70% of the iron occupies the 2c site; a strong increase in the a lattice parameter and in the Curie temperature is observed between DyCo$_{3}$B and DyCo$_{2}$FeB and smaller increases are observed for x>1. The compensation temperature of the DyCo$_{4-x}$Fe$_{x}$B compounds decreases from 350 to 270 K between x=0 and 3, respectively, as a result of the iron induced increase in the transition metal magnetization. © 2008 American Institute of Physics. [DOI: 10.1063/1.2927499]

I. INTRODUCTION

Over the past few years there have been several studies devoted to rare-earth R, transition-metal M based compounds which also contain metalloids. Some of these metalloids containing compounds are pseudobinary compounds, such as the RM$_{3}$, Ga$_{5}$, and RM$_{5}$, Si$_{4}$ compounds, and some are true ternary compounds, such as the RM$_{5}$, B$_{2}$ compounds, also referred to as R$_{n+1}$Co$_{3n}$Fe$_{2n}$, in which boron is required to stabilize the compound’s crystal structure. Since the initial work of Kuzma et al., many RM$_{3}$B compounds, where R is yttrium or a rare earth and M is cobalt and iron, have been synthesized and studied in detail. These compounds crystallize in the hexagonal P6$_{3}$/mmc space group and exhibit either axial or basal magnetic anisotropy, an anisotropy that is influenced by temperature and/or composition. The boron occupies only one-half of the 2c site in the parent RCo$_{5}$ structure and, as a consequence, occupies the 2d site in the RCo$_{5}$B-type structure. The cobalt 3g site in the parent RCo$_{5}$ structure, with two RCo$_{2}$ neighboring planes, becomes the 6i site in the RCo$_{5}$B structure with one RCo$_{2}$ and one RB$_{2}$ neighboring planes. Finally, the cobalt 2c site in the RCo$_{5}$B structure is similar to the cobalt 2c site in the parent RCo$_{5}$ structure.

The study of the RCo$_{4-x}$Fe$_{x}$B compounds, in which R is yttrium or various different rare-earth elements, has shown that x can range, in some cases, from 0 to 4. The interest in these compounds lies in the sensitivity of their magnetic anisotropy to the nature of the rare earth, composition, and/or temperature and in the existence of a compensation temperature that can be controlled by the nature of the rare earth and the transition metal. These compounds are also interesting because they appear in the ternary phase diagram of the rare earth, iron, and boron, a phase diagram that also contains the important R$_{x}$Fe$_{14}$B compounds. Hence, it is of value to understand the macroscopic and microscopic properties of the RCo$_{4-x}$Fe$_{x}$B compounds.

The structural, magnetic, and Mössbauer spectral properties of the yttrium and light rare-earth RCo$_{4-x}$Fe$_{x}$B compounds have been studied by various authors. Herein, the DyCo$_{4-x}$Fe$_{x}$B compounds, with x=0, 1, 1.5, 2, 2.5, and 3, have been investigated by x-ray diffraction, magnetic measurements, and Mössbauer spectroscopy. Among the heavy rare earths, dysprosium was chosen because its size is similar to that of yttrium and, hence, the replacement of nonmagnetic yttrium by magnetic dysprosium permits a study of the influence of a magnetic rare earth without influence from size differences. Further, with the heavy rare earths, a larger amount of cobalt can be substituted by iron than with the light rare earths.

II. EXPERIMENTAL

The polycrystalline DyCo$_{4-x}$Fe$_{x}$B compounds, with x =0, 1, 1.5, 2, 2.5, and 3, have been prepared by melting the starting materials of 99.9% or higher purity in an arc furnace. The ingots were remelted in a high frequency furnace under an argon atmosphere for better homogeneity. Small pieces of the ingots were wrapped in tantalum foil, sealed in an evacuated silica tube, and annealed for two weeks at 1273 K. The phase purities of the samples before and after annealing were

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checked by powder x-ray diffraction by using copper Kα1 radiation with λ = 1.5406 Å. The samples were powdered and then sieved to a particle size of less than 50 μm. Oriented samples were prepared by solidifying, at room temperature, a mixture of epoxy resin and powdered sample in a magnetic field of 0.6 T.

The Curie temperatures have been determined by using a Faraday balance and a heating and cooling rate of 5 K/min. Magnetization measurements have been performed by using the extraction method in a continuous applied magnetic field up to 9 T. The spontaneous magnetizations Ms have been determined by extrapolation of the isothermal curves to zero applied field. The possible occurrence of anomalous magnetic behavior has been investigated by using a locally constructed ac susceptometer; the ac susceptibility measurements have been performed on powdered samples with frequencies ranging from 1 to 10 kHz.

The Mössbauer spectra of DyCo4−xB with 1, 1.5, and 2 have been measured at 85 and 295 K on a constant-acceleration spectrometer which utilized a rhodium matrix cobalt-57 source and was calibrated at room temperature with α-iron powder. The Mössbauer spectral absorbers contained approximately 25 mg/cm² of powdered sample which had been sieved to a 0.045 mm or smaller diameter particle size.

III. STRUCTURAL ANALYSIS

The analysis of the x-ray powder diffraction patterns confirms that the DyCo4−xB compounds are virtually single phase or contain a small amount of an FeCo alloy impurity. The CeCo4B-type structure8,17 of DyCo4B is preserved in the DyCo4−xB compounds for x values up to 3. An attempt to form DyFe4B led to the formation of a mixture of various phases including Dy2Fe14B. For comparison, the substitution of cobalt with iron has been successfully achieved in the RCo4−xB compounds for x values up to 3 when R is Y,16,18 for x values up to 1.5 when R is Nd,24–26 for x values up to somewhat less than approximately 3 when R is a light rare earth,24 and for x values up to 4 when R is a heavy rare earth, such as Er, Tm, or Lu.20–23,27–30 Hence, the substitution up to x values of 3 in the DyCo4−xB compounds is in agreement with those observed for the YCo4−xB compounds.

The lattice parameters obtained for the DyCo4−xB compounds are given in Table I and their compositional dependence is shown in Fig. 1. Surprisingly, the a lattice parameter increases from x = 0 to 1 and remains essentially constant upon further increase in x, whereas the c lattice parameter decreases from x = 0 to 1 and increases upon further increase in x. This surprising behavior indicates that a change in the substitutional pattern of cobalt by iron occurs for an x value of approximately 1. Similar behavior has been observed for the RCo4−xB compounds, where R is Y and Nd (Ref. 24) and has been related to the preferential substitution of cobalt by iron on the 2c crystallographic site. Because dysprosium has a very large thermal neutron absorp-

TABLE I. The lattice parameters, unit-cell volumes, and c/a ratios for the DyCo4−xB compounds.

<table>
<thead>
<tr>
<th>x</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.020(2)</td>
<td>6.885(7)</td>
<td>150.26</td>
<td>1.372</td>
</tr>
<tr>
<td>1</td>
<td>5.062(2)</td>
<td>6.859(5)</td>
<td>152.25</td>
<td>1.355</td>
</tr>
<tr>
<td>1.5</td>
<td>5.062(2)</td>
<td>6.887(2)</td>
<td>152.86</td>
<td>1.361</td>
</tr>
<tr>
<td>2</td>
<td>5.063(2)</td>
<td>6.913(2)</td>
<td>153.53</td>
<td>1.365</td>
</tr>
<tr>
<td>2.5</td>
<td>5.065(1)</td>
<td>6.939(1)</td>
<td>154.17</td>
<td>1.370</td>
</tr>
<tr>
<td>3</td>
<td>5.067(1)</td>
<td>6.9693(1)</td>
<td>154.96</td>
<td>1.375</td>
</tr>
</tbody>
</table>

FIG. 2. The powder x-ray diffraction pattern of DyCo3FeB obtained with an unoriented powder, bottom, and with a powder oriented in an applied magnetic field of 0.6 T perpendicular to the plane of the sample. The arrows indicate the presence of the (hk0) Bragg reflections.
tion cross section, the DyCo$_{4-x}$Fe$_x$B compounds have not been studied by neutron diffraction, and the preferential substitution of cobalt by iron will be discussed below on the basis of the iron-57 Mössbauer spectra. The compositional dependencies of the lattice parameters lead to a linear increase in the unit-cell volume with increasing $x$, as is shown in the inset in Fig. 1.

The 300 K x-ray diffraction pattern of DyCo$_3$FeB oriented in an external magnetic field of 0.5 T, applied perpendicular to the plane of the sample, shows only the (hk0) Bragg peaks, see Fig. 2. Hence, at 300 K the easy magnetization direction is perpendicular to the $c$-axis.

IV. MAGNETIC PROPERTIES

A. Magnetic ordering temperature

The magnetic ordering or Curie temperatures $T_C$ of the DyCo$_{4-x}$Fe$_x$B compounds, deduced from the thermomagnetic measurements, are given in Table II. As is shown in Fig. 3, the iron substitution between $x=0$ and 1 increases the Curie temperature by approximately 200 K, whereas further increases in $x$ do not further increase the Curie temperature which is nearly constant at approximately 665 K for $x$ above 1.5. Similar increases in the Curie temperature have been reported for the $\text{RCO}_{4-x}\text{Fe}_x\text{B}$ isotypic compounds$^{16,18,24}$ and have been explained, at least in part, by the increase in the transition metal sublattice magnetization and the concomitant unit-cell expansion. Finally, the $\text{RCO}_{4-x}\text{Fe}_x\text{B}$ compounds present a compositional dependence of the Curie temperature that is opposite to that observed for the binary $\text{RCo}_{4-x}\text{Fe}_x$ phases, in which cobalt substitution with iron reduces the Curie temperature.$^{31}$

B. Magnetization

The saturation magnetizations at 4.2 K are 5.6$\mu_B$/f.u. and 3.2$\mu_B$/f.u., for DyCo$_3$B and DyCoFe$_3$B, respectively. This decrease results from an increase in the transition metal sublattice magnetic moment with increasing iron content, a sublattice moment that is antiparallel to that of the dysprosium sublattice. The isothermal magnetization curves measured at 4.2 and 300 K for the DyCo$_{4-x}$Fe$_x$B compounds are shown in Fig. 4. At 4.2 K a large decrease in magnetization of nearly 50% is observed between $x=1$ and 2, whereas no further substantial decrease is observed between $x=2$ and 3. The 4.2 K saturation magnetizations are given in Table II for all the DyCo$_{4-x}$Fe$_x$B compounds. At room temperature, all compounds exhibit a substantially smaller magnetization than at 4.2 K, as a result of the existence of a compensation temperature close to 300 K, the temperature at which the two sublattice magnetizations cancel. The presence of this compensation is clearly shown in Fig. 5 for DyCo$_{2.5}$Fe$_{1.5}$B and DyCoFe$_3$B. The compensation temperatures and their compositional dependencies are given in Table II and are also shown in Fig. 3 as $T_{\text{comp}}/T_C$. The compensation temperature decreases with increasing iron content, in agreement with an
increased transition metal sublattice magnetization and the constant dysprosium sublattice magnetization. As is shown in Fig. 4, DyCo2FeB exhibits the smallest 300 K magnetization at all fields as a result of its 300 K compensation temperature. DyCo2Fe1.5B and DyCo1.5Fe2.5B exhibit virtually the same 300 K magnetization curve because, at this temperature, the dysprosium sublattice magnetization is larger and smaller, respectively, than the transition metal sublattice magnetization. In contrast, DyCo3FeB and DyCoFe3B exhibit a significant spontaneous magnetization of approximately 0.7 μB/f.u. because their compensation temperature is approximately 25 K above and below 300 K, respectively.

The temperature dependence of the magnetic susceptibilities of DyCo2Fe1.5B and DyCoFe2B is shown in Fig. 5. At low temperatures, the magnetization of the dysprosium sublattice dominates the antiferromagnetically coupled magnetization of the transition metal sublattice. The decrease of the magnetization with increasing temperature results from the fast thermal decrease of the magnetization of the dysprosium sublattice. At the compensation temperature Tcomp, the antiferromagnetically coupled transition metal and dysprosium sublattice magnetizations cancel. Above the compensation point, the transition metal sublattice magnetization dominates. Because the thermal decrease of the dysprosium magnetization is more pronounced than that of the transition metal magnetization, the net magnetization first increases and finally decreases as the Curie temperature is approached.

A systematic ac susceptibility investigation of all the DyCo4−xFe2xB compounds reveals that none of these compounds exhibits any magnetic spin reorientation between 4.2 and 300 K. Further, no spin reorientationlike anomaly has been observed in the thermomagnetic analysis. Hence, the easy magnetization direction remains in the basal plane of the unit cell between 4.2 and 300 K.

V. MÖSSBAUER SPECTRAL RESULTS

The 295 and 85 K Mössbauer spectra of the DyCo4−xFe2xB compounds, with x = 1, 1.5, and 2, are shown in Figs. 6(a) and 6(b), respectively. The small spectral absorption of approximately 0.25%, 0.5%, and 1.0% is surprising and results from the strong nonresonant scattering by dysprosium, a scattering that limits the ideal absorber thickness. Because of this small absorption, long counting times of several days have been required to obtained the spectra shown in Fig. 6. In addition to the main profile assigned to DyCo2FeB, the Mössbauer spectrum of DyCo3FeB exhibits a second component with a relative area of approximately 16 ± 7% with a hyperfine field similar to that of α-iron, a component that is assigned to an FeCo alloy impurity.

A comparison of the spectra in Fig. 6 to those of the YCo4−xFe2xB and GdCo4−xFe2xB compounds indicates that the magnetization and, hence, the iron magnetic moments and hyperfine fields are oriented in the basal plane of the hexagonal unit cell, in agreement with the conclusion drawn from the oriented powder x-ray diffraction results and the magnetic measurements. Because iron is present on both the 2c and 6i sites in the structure, at least two contributions are required to fit the Mössbauer spectra. The relative areas of these contributions have been initially constrained to the iron occupancies obtained from neutron diffraction studies of the YCo4−xFe2xB compounds. Further, because of the basal orientation of the iron magnetic moments and hence hyperfine fields, the 6i contribution is divided into two components with relative areas of 1:2, see below.

The simultaneous presence of both small hyperfine fields and large quadrupole interactions in the iron-57 Mössbauer spectra of the DyCo4−xFe2xB compounds prevents their analysis with a first-order perturbation of the Zeeman magnetic Hamiltonian by the quadrupole interaction. Hence, the exact solutions of the iron-57 ground and excited state Hamiltonians have been used to fit the Mössbauer spectra of the DyCo4−xFe2xB compounds. The resulting fits are shown as the lines and spectral components in Fig. 6; the corresponding spectral parameters, with their statistical errors, are given in Table III. The actual errors are probably twice as large as the statistical errors.
TABLE III. The Mössbauer spectral parameters of the DyCo$_{4-x}$Fe$_x$B compounds. The parameters are defined in the text and given with statistical error limits if they have been refined.

<table>
<thead>
<tr>
<th>x</th>
<th>$T$ (K)</th>
<th>Site</th>
<th>$\delta$ (mm/s)</th>
<th>$\varepsilon^2Qy/2$ (mm/s)</th>
<th>$H$ (T)</th>
<th>$\eta$</th>
<th>$\theta$ (deg)</th>
<th>$\phi$ (deg)</th>
<th>% area</th>
<th>$\Gamma$ (mm/s)</th>
<th>$\Delta\Gamma$</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>295</td>
<td>2c</td>
<td>−0.118(5)</td>
<td>−1.03(2)</td>
<td>15.86(5)</td>
<td>0</td>
<td>90</td>
<td>0</td>
<td>69(5)</td>
<td>0.28(2)</td>
<td>0.06(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6i$_1$</td>
<td>⋯</td>
<td>1.14(6)</td>
<td>15.5(3)</td>
<td>1</td>
<td>0</td>
<td>90</td>
<td>10(1)</td>
<td>0.50(7)</td>
<td>0.00</td>
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<tr>
<td></td>
<td></td>
<td>6i$_2$</td>
<td>−0.140(23)</td>
<td>−1.04(6)</td>
<td>14.2(2)</td>
<td>1</td>
<td>120</td>
<td>90</td>
<td>21(3)</td>
<td>0.50(7)</td>
<td>0.00</td>
</tr>
<tr>
<td>85</td>
<td>2c</td>
<td>−0.007(5)</td>
<td>−1.10(2)</td>
<td>17.44(5)</td>
<td>0</td>
<td>90</td>
<td>0</td>
<td>74(5)</td>
<td>0.32(2)</td>
<td>0.06(1)</td>
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<tr>
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<td>6i$_1$</td>
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<td>1.21(7)</td>
<td>15.3(2)</td>
<td>1</td>
<td>120</td>
<td>90</td>
<td>18(2)</td>
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<tr>
<td>1.5</td>
<td>295</td>
<td>2c</td>
<td>−0.120(2)</td>
<td>−0.96(1)</td>
<td>17.07(2)</td>
<td>0</td>
<td>90</td>
<td>0</td>
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<td></td>
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<td>0</td>
<td>90</td>
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<td>0.10(2)</td>
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<td>1.04(2)</td>
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<td>1</td>
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<td>90</td>
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<tr>
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<td>2c</td>
<td>−0.021(4)</td>
<td>−1.07(2)</td>
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<td></td>
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<td>1.03(2)</td>
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<td>1</td>
<td>0</td>
<td>90</td>
<td>13(1)</td>
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<tr>
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<td>1.03(2)</td>
<td>16.83(8)</td>
<td>1</td>
<td>120</td>
<td>90</td>
<td>26(2)</td>
<td>0.39(6)</td>
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<td>2c</td>
<td>−0.129(2)</td>
<td>−0.97(1)</td>
<td>18.1(2)</td>
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<td>90</td>
<td>0</td>
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<tr>
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<td>0.97(1)</td>
<td>17.69(8)</td>
<td>1</td>
<td>0</td>
<td>90</td>
<td>18.7(2)</td>
<td>0.85(2)</td>
<td>0.003(11)</td>
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<td>6i$_2$</td>
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<td>0.97(1)</td>
<td>16.38(5)</td>
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<td>37.5(4)</td>
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<td>−1.02(2)</td>
<td>19.5(5)</td>
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<td>0</td>
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<td>0.35(2)</td>
<td>0.08(8)</td>
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<tr>
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<td>18.3(2)</td>
<td>1</td>
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<td>90</td>
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<td>0.48(6)</td>
<td>0.08(3)</td>
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<td>17.5(9)</td>
<td>1</td>
<td>120</td>
<td>90</td>
<td>33(2)</td>
<td>0.48(6)</td>
<td>0.08(3)</td>
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</table>

The isomer shifts are given relative to room temperature α-iron powder.

In the fits, the asymmetric parameter $\eta$ of the 2c and 6i sites has been constrained to 0 and 1, respectively, in agreement with the point symmetry of these sites. Attempts to fit the $\eta$ value for the 6i site lead to at most insignificant changes from 1. The Euler angles $\theta$ and $\phi$ of the hyperfine field in the electric field gradient axes depend on the orientation of the iron magnetic moments in the unit cell. For a basal orientation of the iron magnetic moments, because the principal axis of the electric field gradient $V_z$ of the 6i site is along [100], the 6i site must be subdivided into two magnetically inequivalent sites, herein designated the 6i$_1$ and 6i$_2$ subsites, with relative populations of one and two, respectively. In this case, the angles $\theta$ and $\phi$ of the hyperfine field are $0^\circ$ and $90^\circ$ for the 6i$_1$ subsite and $120^\circ$ and $90^\circ$ for the 6i$_2$ subsite, respectively. The linewidths, isomer shifts, and quadrupole interactions of the 6i$_1$ and 6i$_2$ subsites have been constrained to be the same.

In addition to adjusting the above hyperfine parameters and the linewidth, an incremental linewidth has also been fitted in order to account for the distribution of cobalt and iron on the near neighbors of the 2c and 6i sites. This unitless incremental linewidth $\Delta \Gamma$ has been defined as $\Gamma'(v) = \Gamma + (v-\delta)\Delta \Gamma$, where $v$ is the velocity and $\delta$ is the isomer shift of a given spectral component. Finally, a texture parameter $y$ has been introduced into the fits as a factor multiplying the Clebsch–Gordan coefficient of the $\Delta m = 0$ transitions. In the case of a sextet this is essentially equivalent to a component area ratio of 3: y:1:1:1:y:3, where $y$ may vary from zero for a hyperfine field parallel to the $\gamma$-ray direction to four for a hyperfine field perpendicular to the $\gamma$-ray direction. Various attempts to fit this texture parameter lead to the conclusion that it did not significantly deviate from two. The fits presented in Fig. 6 and the parameters given in Table III correspond to $y=2$. The relative areas of the 2c and 6i components have been adjusted starting from the initial values given by the iron occupancies obtained from the neutron powder diffraction patterns of the YCo$_{4-x}$Fe$_x$B compounds.

The compositional dependence of the Mössbauer spectral parameters at both 85 and 295 K is shown in Fig. 7. The 2c and weight averaged 6i hyperfine fields increase with iron content both at 85 and 295 K, as is shown in Fig. 7(a), in agreement with the compositional dependence of the magnetization. The relatively small hyperfine fields on both sites of between 14 and 20 T result from a combination of the Fermi contact and orbital contributions to the hyperfine fields, contributions that have been discussed earlier. As previously observed for the RCo$_{4-x}$Fe$_x$B compounds, where $R$ is Y, Pr, Nd, Sm, and Gd, the 2c hyperfine field is larger than the weighted average 6i hyperfine field.

The compositional dependence of the 2c and 6i isomer shifts is shown in Fig. 7(b). At 85 K the 2c and 6i isomer shifts increase with increasing iron content, in agreement with the increase in unit-cell volume. The quadrupole interactions of the 2c and 6i sites are essentially independent of iron content, see Figure 7(c). Hence, it seems that the quadrupole interactions are not sensitive to either the replacement of cobalt by iron or the concurrent expansion of the lattice.

The compositional dependence of the iron 2c relative area is shown in Fig. 7(d) together with the iron 2c relative area as obtained from a neutron diffraction study of the isotopic YCo$_{4-x}$Fe$_x$B compounds. It is clear that in the DyCo$_{4-x}$Fe$_x$B compounds, iron shows a preferential occupation of the 2c site, a preference that is similar to that observed in the YCo$_{4-x}$Fe$_x$B compounds.

VI. CONCLUSIONS

The relative areas of the three components in the Mössbauer spectra of the DyCo$_{4-x}$Fe$_x$B compounds indicate that
iron preferentially substitutes for cobalt on the $2c$ crystallographic site. This preferential substitution explains the observed compositional dependence of the lattice parameters, a dependence that takes place in two steps between $x=0$ and 1 and for $x$ greater than 1. The compensation temperature of these compounds can be adjusted in a broad temperature range from approximately 270 to 350 K by varying $x$ in the DyCo$_{4-x}$Fe$_x$B compounds. A higher iron content increases the transition metal sublattice magnetization and consequently decreases the compensation temperature. The ordering temperature increases by 50% from 425 to 660 K between $x=0$ and 3. The large increase in ordering temperature from $x=0$ to 1 results almost exclusively from the preferential substitution of cobalt by iron on the $2c$ site. Hence, the exchange interactions in the $RCo_{4-x}Fe_xB$ compounds are largely determined by the transition metal $2c$ site. The dominant magnetic role of the $2c$ site is also apparent in its larger hyperfine field observed in the Mössbauer spectra, a larger field that is associated with a larger magnetic moment.

ACKNOWLEDGMENTS

The authors are very grateful to Dr. Raphaël P. Hermann for his help in developing the code to analyze the Mössbauer spectra. This work was partially supported by the Fonds National de la Recherche Scientifique, Belgium, through Grant Nos. 9.456595 and 1.5.064.05, by the “Commissariat Général aux Relations Internationales, Ministère de la Communauté Française de Belgique, Relations scientifiques avec la France,” Grant No. 2007/02242/S, and by the CNRS-cooperation Program No. PVB/ADK/FR/0084-22/03/2006-091-S.