# Structure and magnetic properties of rare-earth iron nitrides, carbides and carbonitrides (invited)

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Iron-rich rare-earth (R) compounds, such as  $R_2Fe_{17}$  do not show great potential for high-performance magnet materials due primarily to their low Curie temperatures ( $T_c \sim 300-400$  K). However, relatively large quantities of nitrogen or carbon atoms can be introduced into the structure, resulting in a dramatic enhancement of magnetic properties including  $T_c$  (>700 K). The N or C atoms cause a volume expansion of a few percent of the unit cell without changing the crystal structure. The large increase in  $T_c$  can be attributed to the volume dependence of the Fe-Fe exchange interactions. A large uniaxial anisotropy field develops for R=Sm upon nitriding/carbiding with an anisotropy field that is almost double the value for  $Nd_2Fe_{14}B$  at room temperature. Problems including the precipitation of soft magnetic phases (mainly  $\alpha$ -Fe) and the limited thermal stability of the nitrides have so far restricted the applications of these compounds. Here data are presented on combined carbide/nitride alloys prepared using a novel technique. These alloys exhibit many of the advantages of the pure compounds but with greater thermal stability and less interference from precipitated phases. A typical material,  $Sm_2Fe_{17}(N_xC_{1-x})_{3-\delta}$  has a  $T_c$  of 758 K and an anisotropy field ( $\mu_0H_A$ ) of 15 T at room temperature.

## I. INTRODUCTION

The discovery of Nd<sub>2</sub>Fe<sub>14</sub>B in 1983 has led to an extensive search for new high performance magnet materials. The important intrinsic magnetic properties for such a material are the Curie temperature  $T_c$ , the spontaneous magnetization  $M_{sp}$  and the uniaxial anisotropy field  $H_A$ . The main drawback of Nd-Fe-B-based magnets is the relatively low Curie temperature ( $T_c = 585$  K for Nd<sub>2</sub>Fe<sub>14</sub>B). The high temperature coefficient of the anisotropy field and hence the coercivity is also a major concern. The  $R_2Fe_{17}$ (R=rare earth) compounds have the highest  $M_s$  among all R-Fe compounds. They exist across the rare-earth series in two related crystallographic modifications. The light rare-earths (Ce to Tb) form the rhombohedral  $Th_2Zn_{17}$ structure and the heavy rare-earths (Dy to Lu) and Y form the hexagonal Th<sub>2</sub>Ni<sub>17</sub> structure. Both structures are derivatives of the hexagonal CaCu<sub>5</sub> structure. They are not, however, suitable as permanent magnet materials because of their low  $T_c$  values, e.g., the maximum  $T_c$ , corresponding to R = Gd, is only 476 K. In addition to their low  $T_{c}$ , all R<sub>2</sub>Fe<sub>17</sub> compounds have basal-plane anisotropy at room-temperature. The low  $T_c$  in these compounds is attributed to the short Fe-Fe distances associated with antiferromagnetic interactions. It has been shown<sup>1</sup> that rareearth intermetallics can absorb large quantities of hydrogen. The accompanying expansion of the unit cell may lead to changes in the magnetic properties in these compounds. Interstitial hydrogen atoms were introduced in some R<sub>2</sub>Fe<sub>17</sub> compounds by heating the alloys in an atmosphere of hydrogen.<sup>2</sup> A unit cell expansion of 2.9%

accompanied by an enhancement of 138 K in  $T_c$  was reported for Sm<sub>2</sub>Fe<sub>17</sub>H<sub>2</sub>. However, no increase in the magnetic anisotropy was observed.

An important discovery was made in 1990 when Coey and Sun<sup>3</sup> reported that heating  $R_2Fe_{17}$  (R=Y,Sm) compounds under an atmosphere of NH<sub>3</sub> or N<sub>2</sub> resulted in a 7% volume expansion. Dramatic enhancements of 370 K and 350 K in  $T_c$  were observed after nitriding for R=Yand R=Sm, respectively. This work was later extended to all other rare-earths with similar unit cell expansions and  $T_c$  enhancements.<sup>4</sup> Among all  $R_2Fe_{17}N_x$  ( $x\sim2.5$ ) compounds, uniaxial anisotropy was developed only for R=Sm (Ref. 3). The uniaxial anisotropy field for  $Sm_2Fe_{17}N_{2.3}$  was measured to be 14 T (Ref. 5) at room temperature ( $\mu_0H_a=8$  T for Nd<sub>2</sub>Fe<sub>14</sub>B), making it the most promising alloy for permanent magnet applications.

Efforts to introduce other small atoms into the  $R_2Fe_{17}$ structure gave mixed results. So far no positive results have been reported for  $R_2Fe_{17}$  borides. This may be due to the relatively large atomic size of boron compared to nitrogen. The small interstitial site may require large lattice deformation which costs elastic energy and can lead to disproportionation of the  $R_2Fe_{17}$  compound. Introduction of carbon atoms as interstitials proved to be more successful and in most respects the results are similar to those of  $R_2Fe_{17}N_x$ . In fact, it is possible to introduce carbon atoms into  $R_2Fe_{17}$  directly by alloying and some improvements in the magnetic properties were observed.<sup>6</sup> However, only one carbon atom per formula unit could be added by alloying technique. Similar to the case of  $R_2Fe_{17}N_x$ , only  $Sm_2Fe_{17}C$ proved to be promising, with a uniaxial anisotropy field of 5.3 T at room temperature<sup>7</sup> and a 200 K enhancement in  $T_c$ . Gas-phase carbiding, i.e., annealing R<sub>2</sub>Fe<sub>17</sub> in gaseous hydrocarbons, proved to be successful and a  $T_c$  of 680 K for Sm<sub>2</sub>Fe<sub>17</sub>C<sub>2</sub> was obtained<sup>8</sup> with a room temperature uniaxial anisotropy field  $\mu_0 H_a$  of 13.9 T (Ref. 9).

Following the success of nitriding and carbiding R<sub>2</sub>Fe<sub>17</sub> compounds, other R-Fe systems were investigated. The most notable success was achieved in rare-earth iron compounds based on the tetragonal ThMn<sub>12</sub> structure, which is also a derivative of the CaCu<sub>5</sub> structure. The general formula can be written as  $RFe_{12-x}T_x$  (T=Ti, V, Cr, Mo, W, or Si, x=1 to 2). Unlike the R<sub>2</sub>Fe<sub>17</sub> system all R  $Fe_{12-x}T_x$  alloys (except for R=Tb) have uniaxial anisotropy above room temperature. Nitriding these alloys through a gas-solid reaction gives a 3% volume expansion with about one nitrogen atom per formula unit.<sup>10,11</sup> Moderate increases in  $T_c$  of 150 K to 230 K were observed.<sup>10-12</sup> In contrast to  $R_2Fe_{17}N_x$  compounds, R=Sm leads to basal-plane anisotropy upon nitriding of R Fe<sub>12-x</sub> $T_x$  as the close proximity of N atoms to the R atoms significantly alters the R sublattice anisotropy. Thus useful magnetic materials are expected for R=Nd or Pr. Room temperature anisotropy fields of 7.8 T and 7.6 T were obtained for  $NdFe_{10}Mo_2N_{0.5}$  and  $NdFe_{10}V_2N$ , respectively.<sup>12</sup>

In this article, we will concentrate on nitrides and carbides of  $R_2Fe_{17}$  alloys obtained through gas-solid reactions. The structure and magnetic properties of R-Fe-N and R-Fe-C will be presented and discussed. We will also introduce a novel technique in which  $R_2Fe_{17}N_xC_y$  alloys are obtained through a single or two stage gas-solid reactions. It will be shown that the carbonitrides offer improved thermal stability over the ternary compounds.

### **II. EXPERIMENTAL TECHNIQUES**

All alloys were prepared by induction/arc-melting appropriate amounts of Fe (99.99%), R (99.9%), and T (99.9%) on a water cooled-copper boat under Ti-gettered prepurified Ar. To ensure the homogeneity of the ingots, all alloys were melted at least three times. To improve the homogeneity of Sm containing alloys, we used elemental powders which were pressed into a pellet prior to induction melting. An excess of 4% Sm was added to the samples to partially compensate the mass loss due to evaporation of Sm during melting. All alloy ingots were wrapped in Ta foil and annealed in vacuum at 1170 K for 1 week.

Structural data on R-Fe before and after gas-solid reactions were obtained by an automated Nicolet-Stöe powder diffractometer with graphite monochromated Cu K $\alpha$ radiation. Magnetic transition temperatures  $T_c$ , were measured by thermomagnetometry using a Perkin-Elmer thermogravimetric analyzer (TGA-7) in a small magnetic field gradient. The thermomagnetic measurements were done under a flow of prepurified Ar gas. The anisotropy field and its temperature dependence were determined using the singular point detection (SPD) method<sup>13</sup> in a pulsed field of up to 20 T. Samples for SPD measurements were prepared by mixing the alloy powders with epoxy resin and aligned in a field of 1.5 T. Sample temperature was maintained to within  $\pm 1$  K during the measurements.

For the gas-solid reactions, the annealed samples are ground into powders (  $< 20 \ \mu m$ ) and a small quantity, 20 to 30 mg, is used for the reaction with various gasses. The reactions were carried out in a thermopiezic analyzer (TPA)<sup>14</sup> in which the sample is sealed in a small volume  $(\approx 3 \text{ cm}^3)$  and heated by means of a computer controlled furnace at uniform heating rates. Isothermal annealing, typically in the range 723-823 K, were also performed in the TPA. Pressure changes are measured by a sensitive solid state sensor which allows quantitative analyses to be made throughout the gas-solid reaction. The simplest gas for nitriding R-Fe compounds is nitrogen. Dissolution of the gas in the alloy is possible if the binding energy of the interstitial gas atoms in the lattice exceed the molecular binding energy in the gas phase. This happens when the reaction enthalpy of the process

$$2R_2Fe_{17} + xN_2 \Leftrightarrow 2R_2Fe_{17}N_x \tag{1}$$

is sufficiently negative to make the equilibrium nitrogen pressure less than one atmosphere even at high temperatures. At low temperatures, the nitriding process takes a long time to reach the equilibrium state because the diffusion kinetics are slow. This is due in part to the relatively large atomic size of N. The reaction enthalpy of the process

$$R_2Fe_{17} + N_2 \Longrightarrow 2RN + 17Fe \tag{2}$$

is more negative than process (1) and at high temperatures the alloy may disproportionate into rare-earth nitride and  $\alpha$ -Fe. The range of temperature where it is possible to form the nitride is, therefore, quite restricted. It follows from the above discussion that nitriding is irreversible and the ternary nitrides are metastable. The nitrogen content in the compound is obtained directly from the pressure change during the reaction given in Eq. (1).

The carbiding process is similar to that of nitriding. Various hydrocarbon gasses such as acetylene,  $C_2H_2$ , ethylene,  $C_2H_4$ , butane  $C_4H_{10}$  or methane,  $CH_4$  can be used. The carbiding reaction, in the case of acetylene, can be described as

$$yC_{2}H_{2}+2R_{2}Fe_{17} \Longrightarrow 2R_{2}Fe_{17}C_{y}+yH_{2}.$$
(3)

The residual gases are pumped out, immediately after the reaction is completed, to remove the hydrogen atoms from the alloys and obtain the right hand side of Eq. (3). This is not strictly true as small amounts of H may still be present in the samples. However, since the isothermal annealing is carried out in the temperature range 723-823 K, well above 573 K, where significant H outgassing occurs, we can consider the H content in the samples to be negligible. The carbon content (y) of the  $R_2Fe_{17}C_y$  compounds is determined from the increase in pressure due to the release of  $H_2$ , except for  $C_2H_2$  which shows no change in pressure as the pressure increase due to  $H_2$  is compensated by the pressure drop due to dissociation of C<sub>2</sub>H<sub>2</sub>. In this case, the carbon content may be estimated from the mass increase after the gas-solid reaction. The carbonitriding process can be done either using  $N_2$  gas mixed with hydrocarbons at different ratios or sequentially. A gas mixture of nitrogen and methane proved to be successful for obtaining carbo-



●6h @121

(III) 2d

● 5c ●9d @18f @18h

FIG. 1. Crystal structure of rhombohedral  $R_2Fe_{17}$ . The R atoms occupy the 6c site while the Fe atoms occupy the 6c, 9d, 18f, and 18h sites. Interstitial atoms occupy the 9e site.

nitrides of R–Fe alloys with different nitrogen to carbon ratios. The reaction for a simultaneous carbonitriding in a mixture of  $N_2$  and  $CH_4$  can be written as

$$xN_2 + yCH_4 + R_2Fe_{17} \Longrightarrow R_2Fe_{17}C_yN_x + 2H_2, \qquad (4)$$

where, again, the sample chamber is pumped out to remove the hydrogen gas. For the same reason given for the carbides, the H content of R<sub>2</sub>Fe<sub>17</sub> carbonitrides is negligible. Carbon and nitrogen contents in the compound cannot be determined in a direct way. We can obtain, however, the carbon to nitrogen ratio (y/x), from the amount of gases present in the TPA prior to the gas-solid reaction. For the sequential process, we find that carbiding, followed by nitriding produced only the ternary carbides, R<sub>2</sub>Fe<sub>17</sub>C<sub>v</sub>. Apparently, a carbon layer formed on the surface of the particles effectively prevented nitrogen atoms from entering the particles. The R<sub>2</sub>Fe<sub>17</sub> alloys were nitrided first, followed by a carbiding reaction in acetylene. The nitrogen content in the compound was determined from the pressure change during the first reaction and the carbon content was estimated from the overall mass increase. Details of the carbonitriding process will be presented elsewhere.<sup>15</sup>

## **III. RESULTS AND DISCUSSION**

X-ray diffraction scans of all as-made samples showed the single phase nature of the  $R_2Fe_{17}$  alloys. The crystal structure of the rhombohedral and hexagonal  $R_2Fe_{17}$  compounds is shown in Figs. 1 and 2, respectively. The gassolid reactions occur over a narrow temperature range. Figure 3 shows some typical TPA scans for nitriding in  $N_2$ carbiding in CH<sub>4</sub> and carbonitriding in a mixture of  $N_2$  and CH<sub>4</sub>. The increase in pressure for CH<sub>4</sub> is due to the release of H<sub>2</sub> gas during the reaction

$$yCH_4 + R_2Fe_{17} \Longrightarrow R_2Fe_{17}C_{\nu} + 2yH_2.$$
<sup>(5)</sup>

Unlike the case of nitriding, the amount of C-atoms in the compound, y, is determined from the sample mass change.

FIG. 2. Crystal structure of hexagonal  $R_2Fe_{17}$ . The R atoms occupy the 2b and 2d sites while the Fe atoms occupy the 4f, 6g, 12i, and 12k sites. Interstitial atoms occupy the 6h site.

@12k

We find y to be  $2.0 \pm 0.1$  for all R. X-ray diffraction results on the nitrided, carbided, and carbonitrided samples  $R_2Fe_{17}C_{\mu}N_{x}$  show an almost constant (within experimental errors) unit cell volume expansion of between 6% and 7%. Table I lists the lattice parameters for the R<sub>2</sub>Fe<sub>17</sub> compounds before and after the various gas-solid reactions. The data for the carbonitrides corresponds to the sequentially prepared compounds. Data for the  $R_2Fe_{17}$  nitrides were taken from Sun *et al.*<sup>16</sup>  $T_c$  of our nitrides have slightly higher values than those of Ref. 16, which may be attributed to the different measurement techniques. The volume expansion is accompanied by a large increase in  $T_c$  as can be seen in Table I. Carbiding increases  $T_{c}$ , on the average, by about 300 K. The average increase in  $T_c$  upon nitriding/carbonitriding is about 380 K. We should emphasize that no differences in the unit cell expansion is observed for the different gas-solid reactions. Typical thermomagnetic scans for R = Sm are shown in Fig. 4. The large increases in  $T_c$  are indicative of the volume dependence of the exchange interactions.



FIG. 3. Isothermal TPA scans for  $Dy_2Fe_{17}$  annealed at 773 K in  $N_2$ ,  $CH_4$ , and 1:10 mixture of  $N_2$  and  $CH_4$ .

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TABLE I. Lattice parameters and Curie temperature for  $R_2Fe_{17}C_yN_x$  compounds. Data for  $R_2Fe_{17}N_x$  are from Ref. 16.

Compound	a (nm)	c (nm)	$T_c$ (K)
Ce <sub>2</sub> Fe <sub>17</sub>	0.849	1.240	238
$Ce_2Fe_{17}C_2$	0.872	1.264	589
Ce <sub>2</sub> Fe <sub>17</sub> N <sub>2.8</sub>	0.873	1.265	713
$Ce_{7}Fe_{17}C_{\mu}N_{\mu}$	0.873	1.268	721
Pr <sub>2</sub> Fe <sub>17</sub>	0.857	1.244	283
Pr <sub>2</sub> Fe <sub>17</sub> C <sub>2</sub>	0.878	1.265	654
Pr <sub>2</sub> Fe <sub>17</sub> N <sub>25</sub>	0.877	1.264	728
$Pr_{2}Fe_{17}C_{\mu}N_{\mu}$	0.879	1.266	737
Nd <sub>3</sub> Fe <sub>17</sub>	0.857	1.245	325
Nd <sub>2</sub> Fe <sub>17</sub> C <sub>2</sub>	0,876	1.264	658
Nd <sub>2</sub> Fe <sub>17</sub> N <sub>23</sub>	0.876	1.263	732
Nd <sub>2</sub> Fe <sub>17</sub> C <sub>2</sub> N <sub>2</sub>	0.876	1.265	740
Sm <sub>2</sub> Fe <sub>17</sub>	0.854	1.243	390
Sm <sub>2</sub> Fe <sub>17</sub> C <sub>2</sub>	0.873	1.265	680
Sm <sub>2</sub> Fe <sub>17</sub> N <sub>2</sub>	0.873	1.264	749
$Sm_2Fe_{17}C_vN_x$	0.875	1.265	758
Gd <sub>2</sub> Fe <sub>17</sub>	0.850	1.243	475
Gd <sub>2</sub> Fe <sub>17</sub> C <sub>2</sub>	0.868	1.266	712
Gd <sub>2</sub> Fe <sub>17</sub> N <sub>24</sub>	0.868	1.266	712
$Gd_2Fe_{17}C_{\nu}N_{\nu}$	0.870	1.267	764
Tb <sub>2</sub> Fe <sub>17</sub>	0.847	1.244	408
Tb <sub>2</sub> Fe <sub>17</sub> C <sub>2</sub>	0.865	1.266	680
Tb <sub>2</sub> Fe <sub>17</sub> N <sub>2</sub>	0.866	1.266	733
Tb <sub>2</sub> Fe <sub>17</sub> C <sub>v</sub> N <sub>x</sub>	0.865	1.271	748
Dy <sub>3</sub> Fe <sub>17</sub>	0.845	0.829	377
$Dy_2Fe_{17}C_2$	0.863	0.842	683
$Dy_2Fe_{17}N_{2.8}$	0.864	0.845	725
$Dy_2Fe_{17}C_vN_x$	0.866	0.845	724
Er <sub>2</sub> Fe <sub>17</sub>	0.842	0.828	305
$Er_2Fe_{17}C_2$	0.863	0.844	675
Er2Fe17N2.7	0.861	0.846	697
$Er_2Fe_{17}C_vN_x$	0.863	0.849	700
$Y_2Fe_{17}$	0.846	0.828	322
$Y_2Fe_{17}C_2$	0.867	0.840	668
$Y_2Fe_{17}N_{2.6}$	0.865	0.844	694
$Y_2 Fe_{17} C_y N_x$	0.866	0.848	717

The easy magnetization direction switches from the basal plane to the *c* axis after the gas-solid reaction for R=Sm only. This change can be clearly seen from the x-ray diffraction patterns shown in Fig. 5 for a specimen of  $Sm_2Fe_{17}C_2$  aligned in a magnetic field. The enhancement of the (001) diffraction peaks reflects the uniaxial anisotropy



FIG. 4. Thermomagnetic scans for  $Sm_2Fe_{17}$ ,  $Sm_2Fe_{17}C_2$ , and  $Sm_2Fe_{17}N_{2.3}$ .

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FIG. 5. X-ray diffractometer scans for  $Sm_2Fe_{17}C_2$  (a) isotropic powders and (b) aligned in a magnetic field.

developed in the material. The anisotropy field was measured using the SPD technique. In this technique, the second derivative of the magnetization  $d^2M/dt^2$  is measured during a field sweep. The singularity in  $d^2M/dt^2$  occurs at a field value which corresponds to the anisotropy field. Figure 6 shows some examples of the SPD signals for Sm<sub>2</sub>Fe<sub>17</sub>C<sub>2</sub>.

The temperature dependence of the anisotropy field shown in Fig. 7 also compares the temperature dependence of  $H_A$  of a sintered  $Nd_2Fe_{14}B$  permanent magnet.<sup>17</sup> The extrapolation of the data for  $Sm_2Fe_{17}C_2$  gives an anisotropy field of 13.9 T at 300 K which is close to the value reported for the nitride.<sup>5</sup> Here,  $\mu_0H_a$  values for  $Sm_2Fe_{17}C_yN_x$ , as shown in Fig. 7, are about 10% higher than that of the carbides/nitrides over the whole temperature range. The extrapolation of  $\mu_0H_a$  to room temperature, for  $Sm_2Fe_{17}C_yN_x$ , gives a value of 15 T. Similar to the case of  $RFe_{12-x}T_x$  alloys, the close proximity of N and C atoms to the rare-earth atoms is responsible for the dra-



FIG. 6. Examples of SPD signals:  $d^2M/dt^2$  versus external magnetic field at various temperatures for Sm<sub>2</sub>Fe<sub>17</sub>C<sub>2</sub>. The kinks are related to the anisotropy field.



FIG. 7. Temperature dependence of the anisotropy field of  $Sm_2Fe_{17}C_2$ and  $Sm_2Fe_{17}C_yN_x$ . Data for  $Nd_2Fe_{14}B$ , from Ref. 21, are shown for comparison.

matic changes in the magnetocrystalline anisotropy. Neutron diffraction experiments<sup>18</sup> have shown that N atoms occupy the 9e(6h) site in the unit cell of the rhombohedral(hexagonal) structure (see Figs. 1 and 2). Each R-atom has three N-atoms as nearest neighbors in the a-b plane. If all the sites are occupied there would be three N atoms per formula unit. Contrary to some published results,<sup>19</sup> we believe the 9e site is the only available site for N or C in the  $Th_2Zn_{17}$  structure, in agreement with the conclusions reached by Capehart et al.<sup>20</sup> The relatively large size of C atoms and slower diffusion result an average occupancy of 70% of the 9e sites. The three in-plane N atoms around the R atom produce a large negative crystal field parameter,  $A_2^0$  and as Sm has a positive second-order Stevens coefficient, the uniaxial anisotropy constant  $K_1$  $= -\alpha_J A_2^0$  becomes positive, increasing H<sub>4</sub>.

The saturation magnetization increases upon nitriding/carbiding for all rare-earth compounds. The relatively large increase for the light rare-earths  $(Th_2Zn_{17}$ structure) indicates ferromagnetic spin structure. The in-



FIG. 8. The <sup>57</sup>Fe hyperfine field,  $B_{hf}$ , averaged over all Fe sites as a function of interstitial content for R = Y, Sm.



FIG. 9. Thermomagnetic scans for  $Y_2Fe_{17}C_{p}N_{x}$ 

crease in magnetization is almost 50% for Sm<sub>2</sub>Fe<sub>17</sub> nitride.<sup>3</sup> The increase in magnetization could be related to the average increase in the iron moments. <sup>57</sup>Fe hyperfine fields, measured from Mössbauer spectroscopy, show an overall increase upon nitriding and carbiding. Figure 8 shows the hyperfine field  $B_{hf}$  averaged over all the sites against interstitial content. It is clear the  $B_{hf}$  is larger for the nitride than for the carbide and depends on the C/N ratio for the carbonitrides. There are also subtle differences between the Mössbauer spectra for the nitrides and carbides. The spectra for  $Sm_2Fe_{17}C_pN_x$  can be fitted by using a linear combination of the spectra for the nitrided and the carbided R<sub>2</sub>Fe<sub>17</sub> compounds. This suggests that N- and C-rich regions exist in the carbonitrides. Details of the Mössbauer study on  $R_2Fe_{17}C_{\nu}N_x$  are given elsewhere in this conference.<sup>21</sup> As our experiments in sequential carbonitriding show that nitriding of  $R_2Fe_{17}C_p$  is not possible, we can conclude, therefore, that once a particle's surface is carbided, it becomes very difficult for nitrogen atoms to penetrate the carbided layer and diffuse into the core of the particle. We expect that, during the simultaneous carbonitriding process or carbiding R<sub>2</sub>Fe<sub>17</sub>N<sub>x</sub>, N- and C-rich regions are created. The  $T_c$  transitions for the carbonitrides remain sharp and do not show two transitions as shown in Fig. 9 for  $Y_2Fe_{17}C_vN_x$ . The unit cell volume expansions are also very similar for all carbonitrides irrespective of x/yratio. The existence of a single  $T_c$  transition can be understood from the stress strain analysis of Coey and Hurley<sup>22</sup> for  $Sm_2Fe_{17}N_x$ . They show that the uniaxial strain near the surface of the particle (N-rich) leads to the expansion of the core (N-poor) resulting in a homogenization of the magnetic properties of the particle.

Incorporating C atoms into  $\text{Sm}_2\text{Fe}_{17}$  or  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$  results in significant improvements in material properties. For all  $R_2\text{Fe}_{17}$  nitrides,  $\alpha$ —Fe is inevitably precipitated during nitriding. The strain near the particle surface, caused by strong uniaxial deformation, causes disproportionation of  $R_2\text{Fe}_{17}\text{N}_x$  into  $\alpha$ —Fe and RN. For  $R_2\text{Fe}_{17}$  carbides, the short reaction time causes very little disproportionation. In addition, a small amount of Fe<sub>3</sub>C, detected only by a TGA scan, is formed rather than  $\alpha$ —Fe in



FIG. 10. X-ray diffractometer scans for  $Dy_2Fe_{17}$  (a) starting compound, (b) nitirde, and (c) carbonitride. Notice the absence of  $\alpha$ -Fe in (c).

the final product. Figure 10 compares diffraction scans of  $Dy_2Fe_{17}$ ,  $Dy_2Fe_{17}N_x$  and  $Dy_2Fe_{17}C_yN_x$ . The absence of  $\alpha$ -Fe for the carbonitride is clearly seen in scan (c) of Fig. 9. Another significant advantage of the carbonitrides is their stability. For  $Sm_2Fe_{17}N_x$ , at atmospheric pressures and at a temperature of about 570 K, nitrogen atoms start to diffuse out of the sample.<sup>23</sup> For the carbides, carbon atoms do not form gas molecules and, in addition, the carbon-rich layers on the surface reduce the diffusion rate of N atoms in the carbonitrides. To demonstrate the more stable nature of carbonitrides, we show in Fig. 11 TPA scans, under vacuum, for  $Sm_2Fe_{17}N_x$  and  $Sm_2Fe_{17}C_yN_x$ . The onset of the nitrogen outgassing temperature is increased by about 180 K for the carbonitride, demonstrating its improved thermal stability.



FIG. 11. TPA scans, under vacuum, for  $Sm_2Fe_{17}$  annealed in (a)  $N_2$  gas at 773 K for 100 min (b) followed by an additional anneal in  $C_2H_2$  at 773 K for 20 min.

#### **IV. CONCLUSIONS**

Introduction of small atoms such as C and/or N into the structure of  $R_2Fe_{17}$  compounds causes a dramatic increase in  $T_c$ . The volume dependence of the Fe-Fe exchange interaction is the principal reason for the enhancement of  $T_c$ . A strong uniaxial anisotropy is developed for R=Sm after the gas-solid reactions in  $R_2Fe_{17}$ . The high values for  $T_c$  and  $H_A$  in these compounds make them very promising as permanent magnet materials. The nature of the interstitial atoms plays a definite role in the magnetic properties as demonstrated by the changes in the average hyperfine field in  $Sm_2Fe_{17}C_vN_x$ . The carbon atoms in the carbides and carbonitrides play an important role in improving the hard magnetic property of the compound as demonstrated by the absence of  $\alpha$ -Fe formation. The thermal stability is also improved as the N<sub>2</sub> outgassing temperature is increased by about 180 K for the carbonitride.

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