Structural and magnetic properties of $R_2Fe_{17-x}Be_x$ compounds with R = Y, Pr, Nd, Sm, Gd, Tb and Dy

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Abstract. The effect of partial Fe substitution by Be on structure and magnetic properties has been studied across the $R_2Fe_{17-x}Be_x$ series, where R = Y, Pr, Nd, Sm, Gd, Tb and Dy. On Be substitution, the Th_2Zn_{17} type rhombohedral structure is stabilized across the series, even for R = Dy and Tb which stabilize in the Th_2Ni_{17} type hexagonal structure without Be substitution. Depending on the R element, one or more Be atoms (up to five) per formula unit can be retained in the Th_2Zn_{17} type structure. The lattice parameters, magnetic ordering temperature and saturation magnetic moment decrease upon Be substitution. The easy magnetization direction of the samples with a higher magnetic ordering temperature is still within the basal c plane. The variation of magnetic properties is discussed in correlation with volume effects, dilution effects and electron hybridization.

1. Introduction

R_2Fe_{17} type compounds (phases) where R = Y or a rare earth element have magnetic ordering temperatures that are extraordinarily lower than those of their R_2Co_{17} counterparts [1, 2]. A Th_2Zn_{17} type rhombohedral structure is stabilized when R is a light rare-earth element and a Th_2Ni_{17} type structure is stabilized for the R = heavy rare earth elements [1, 3]. The two structures coexist for some of the R elements (in the middle of the lanthanide series) [1, 3]. A number of studies have been conducted to partially substitute Fe with other elements and to introduce small atoms at the interstitial sites in this structure [4–17]. It has been shown that up to almost three N atoms per formula unit can be added to R_2Fe_{17} compounds at interstitial sites [4–6]. This addition of N atoms at the interstitial sites leads to an increase in the lattice volume and the exchange coupling between Fe atoms is enhanced. Consequently, the magnetic ordering temperature and magnetic moment increase significantly. These features make this class of materials attractive for permanent magnet applications. These discoveries

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have provided impetus for additional studies, where small atoms are introduced into the lattice either interstitially, such as carbon [7–15], or substitutionally, such as Al [16, 17]. Be is about 8% smaller in size than the Fe atom (0.114 versus 0.124 nm). In this paper, the substitution of Fe with Be in the R_2Fe_{17} series with R = Y, Pr, Nd, Sm, Tb and Dy and the effects of substitution on the structure and magnetic properties are studied.

2. Experimental details

$R_2(Fe,Be)_{17}$ samples with R = Y, Pr, Nd, Sm, Gd, Tb and Dy were prepared by arc-melting the appropriate amounts of constituent elements in an inert Ar atmosphere to obtain the desired compositions. The starting materials were of a 99.9% or better purity. The arc-melted alloy buttons were turned over and re-melted to ensure compositional uniformity and homogeneity. Subsequently, the samples were wrapped in Mo foil and annealed for a week at 950 °C in evacuated quartz tubes. In order to avoid a possible phase transition during cooling, the quartz tubes were water quenched. Fine powder samples were prepared later by grinding and sieving to make their size below 35 μm. The magnetically aligned samples were prepared by mixing the fine powders with epoxy resin and drying up the mix in the presence of a magnetic field of 1 T to allow the powder to be fixed with the easy magnetization direction along the applied-field direction.

For x-ray diffraction studies a Siemens D5000 diffractometer and Cu Kα radiation were used to check the phases present and to determine their lattice parameters on the unaligned powder sample, and to study the easy magnetization direction on the magnetically aligned sample. A Quantum Design SQUID magnetometer was used to measure the Curie temperature and other magnetic properties in the 5–350 K range in fields up to 5.5 T. At higher temperature, a vibrating sample magnetometer was used to measure the Curie temperatures. For magnetic properties measured by SQUID or vibrating sample magnetometer, the Curie temperature is obtained from the fixed small bulk sample while others from free fine powder samples.

3. Results and discussion

The x-ray measurements show that one or more Fe atoms can be replaced by a Be atom in the R_2Fe_{17} series (R = Y, Pr, Nd, Sm, Gd, Tb and Dy). The Th_2Zn_{17} type rhombohedral (2:17R) structure is retained throughout the series upon Be substitution, indicated in table 1. Figures 1 and 2 display the selected x-ray powder diffraction patterns. Those of $R_2Fe_{16}Be$ taken on unaligned powders for R = Y, Pr, and Nd are displayed in figure 1(a). The Th_2Zn_{17} type rhombohedral (2:17R) structure has been indexed in the figure. For R = Pr and Nd, the extent of Be substitution in the $R_2Fe_{17-x}Be_x$ series is limited to one to two atoms per formula unit. Small traces of secondary phase(s) start appearing at $x = 1$ for R = Pr and $x = 2$ for R = Nd, whereas for $x = 2$ for Pr and $x = 3$ for Nd a secondary phase R(Fe, Be)$_{13}$ (R = Pr or Nd) with the cubic $NaZn_{13}$ structure becomes the majority phase.

For R = Y or heavy rare-earth elements Gd, Tb or Dy, four to five Be atoms can be substituted for Fe atoms in the 2:17R structure. It is interesting to note that heavy rare-earth elements such as Tb and Dy which are known to form the Th_2Ni_{17} type hexagonal (2:17H) structure without Be substitution transform into the Th_2Zn_{17} type rhombohedral (2:17R) structure on Be substitution. For the $Dy_2Fe_{17-x}Be_x$ series (figure 2), all x-ray peaks can be indexed to the 2:17H structure when $x = 0$, with the exception of a small broad peak between angles 44 and 45°, that can possibly be associated with α-Fe. When the Be component is increased to $x = 1$ or higher, the 2:17R type structure is stabilized. A trace amount of $FeBe_2$

Table 1. Phases obtained, crystal structure, Curie temperature (T_c), saturation magnetization (M_s) and lattice parameters (a and c) of $R_2Fe_{17-x}Be_x$ compounds.

R	x	Phase (XRD)	a (Å)	c (Å)	M_s (μ_B fu^{-1}) 10 K	T_c (K)
Y	0	$Th_2Ni_{17} + Th_2Zn_{17}$	8.479	8.237	35	313
	1	Th_2Zn_{17}	8.419	12.287	24.6	270
	2	Th_2Zn_{17}	8.393	12.325	18.1	175
	3	Th_2Zn_{17}	8.378	12.101	16.7	115
	4	Th_2Zn_{17}	8.319	12.027	15.1	115
	5	Th_2Zn_{17} + 1:13 + Be_2Fe	8.243	11.907	—	—
	6	Th_2Zn_{17} + 1:13 + Be_2Fe	8.246	11.912	—	—
Pr	0	Th_2Zn_{17}	8.585	12.464	33.4	298.5
	1	Th_2Zn_{17} + 1:13	8.537	12.353	—	266.5
	2	1:13 + Th_2Zn_{17}			—	—
Nd	1	Th_2Zn_{17} + 1:13	8.512	12.321	34.4	294
	2	Th_2Zn_{17} + 1:13	8.471	12.227	—	285
	3	1:13 + Th_2Zn_{17}			—	280
Sm	0	$Th_2Zn_{17} + \alpha$-Fe	8.433	12.200	—	—
	1	$Th_2Zn_{17} + \alpha$-Fe	8.395	12.109	—	—
	2	$Th_2Zn_{17} + \alpha$-Fe	8.419	12.161	—	—
	3	$Be_2Fe + Th_2Zn_{17} + \alpha$-Fe	8.372	12.067	—	—
Gd	1	Th_2Zn_{17}	8.496	12.358	16.9	421
	3	Th_2Zn_{17}	8.399	12.110	10.2	388
	5	Th_2Zn_{17}	8.323	12.056	8.6	379
	7	$Th_2Zn_{17} + Be_2Fe$	8.293	11.968	—	—
Tb	1	Th_2Zn_{17}	8.408	12.272	10.9	358
	2	Th_2Zn_{17}	8.404	12.182	7.7	296
	3	Th_2Zn_{17}	8.358	12.114	5.6	286
	4	Th_2Zn_{17}	8.335	12.036	4.2	281
	5	$Th_2Zn_{17} + Be_2Fe$			—	—
	6	$Th_2Zn_{17} + Be_2Fe + X$			—	—
Dy	0	Th_2Ni_{17}	8.447	8.294	18.9	368
	1	Th_2Zn_{17}	8.418	12.253	10.8	335
	2	Th_2Zn_{17}	8.374	12.132	7.8	255
	3	Th_2Zn_{17}	8.334	12.059	6.4	245
	4	Th_2Zn_{17}	8.298	11.994	4.3	245
	5	$Th_2Zn_{17} + Be_2Fe$	8.264	11.941	—	240
	6	$Th_2Zn_{17} + Be_2Fe + X$	8.252	11.913	—	240

X—unknown phase.

phase with cubic structure is detected in the sample with $x = 5$. For $x = 6$, the 2:17R phase is still in the majority; however, $FeBe_2$ indexed in figure 2 and another secondary phase of unknown composition denoted as X in table 1 also appeared. In a similar manner, four or five Be atoms can substitute Fe in the Y, Gd and Tb series. We infer solubility close to five Be atoms per formula unit in heavy rare-earth compounds.

The light and heavy rare-earth elements have a similar electronic configuration. Hence, it is perhaps the smaller size of Y, Gd, Tb and Dy relative to Pr and Nd that facilitates the retention of additional Be atoms in the 2:17 lattice.

The lattice parameters decrease on Be substitution for all series samples. The lattice parameter data are given in table 1 and figure 3 shows the lattice parameters a and c as a
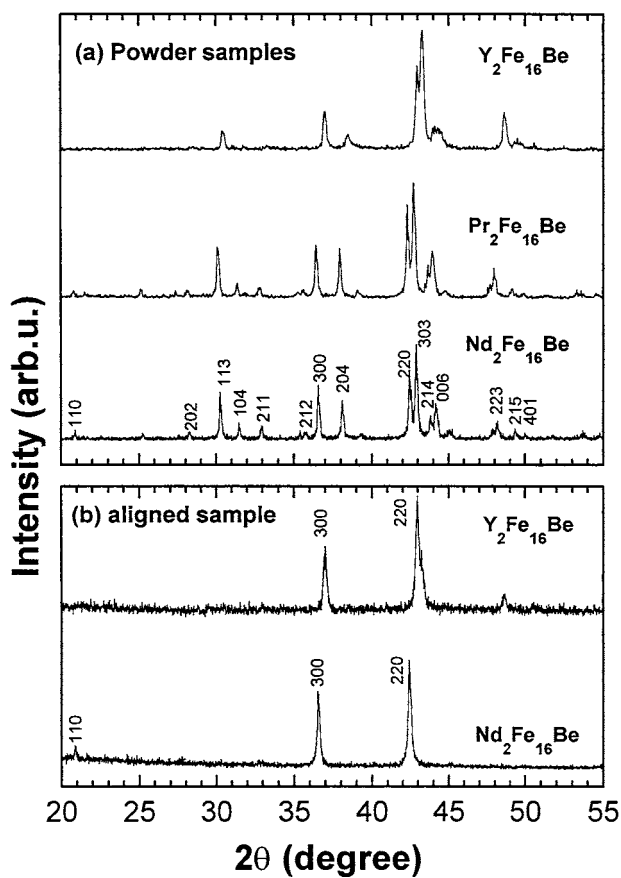
Figure 1. (a) Powder x-ray diffraction patterns at 300 K on unaligned $R_2Fe_{16}Be$ compounds, where R = Y, Pr and Nd. (b) X-ray diffraction patterns at 300 K on an aligned $Nd_2Fe_{16}Be$ sample. The powder sample was aligned at 300 K in 1 T field in an epoxy matrix.

function of Be content in $R_2Fe_{17-x}Be_x$ (R = Y, Tb, Dy) compounds. Lattice parameters a and c decrease almost linearly with x. The average c decrease rate is about 0.09 Å/Be atom, and the average a decrease rate is 0.04 Å/Be atom. The c rate of decrease is almost two times larger than the rate of decrease of a. The a and c rates of decrease in the $Y_2Fe_{17-x}Si_x$ are about 0.03 and 0.015 Å/Si, respectively [18]. The larger decrease rates can be understood because the atomic radius of Be is smaller than that of Si. The continuous decrease in the lattice parameters suggests that Be is being located at the lattice sites, and is not entering the interstitial sites. Otherwise the lattice would expand, as is the case for other interstitial modifications by C and N [4–17]. Ohkubo *et al* have also suggested based upon Mössbauer studies that Be in the R_2Fe_{17} compound may prefer to locate at interstitial 2a sites [19].

The binary phases R_2Fe_{17} have the Th_2Zn_{17}-type structure for the light rare earths, both Th_2Zn_{17} and Th_2Ni_{17} types for the middle rare earths from Gd to Tb and Y and only the Th_2Ni_{17}-type structure for the heavy rare earths, Dy and beyond. There is a tendency to adopt the Th_2Zn_{17} or Th_2Ni_{17} structure for compounds with a relatively large or small volume per formula unit, respectively [1]. In the Be-substituted case, the lattice parameters a and c decrease with x as shown above, and all compounds with one atom Be substitution crystallize with the Th_2Zn_{17} structure. Therefore that unit volume consideration is apparently not observed.
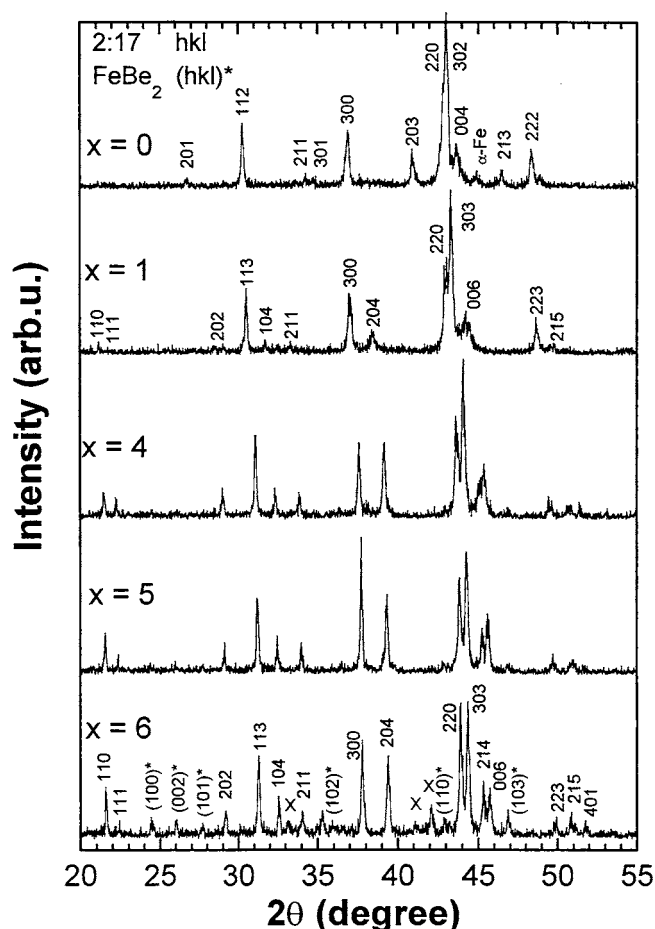
Figure 2. Powder x-ray diffraction patterns across the $Dy_2Fe_{17-x}Be_x$ series.

This behaviour may be associated with the site affinity of the substituent Be atoms, i.e., with the type of electronic interaction between the d electrons of Fe and s electrons of Be.

In the case of the Sm compounds, however, we have had difficulty in preparing good Sm sing phase compounds due to the presence of a second α-Fe phase. This has prevented us from obtaining their magnetic properties similar to those studied below.

The x-ray spectra of the aligned powder indicate that the easy magnetization direction is perpendicular to the c axis for all compounds with a higher magnetic ordering temperature T_C. Figure 1(b) depicts spectra of the aligned powder for R = Y and Nd with $x = 1$; only the lines having $l = 0$ are present in the aligned spectra. Although the magnetic ordering temperature of $YFe_{16}Be$ is lower than room temperature, its powder was aligned in a magnetic field of 1 T when the sample was cooled with a cooled nitrogen gas, and then it was fixed in epoxy. Its EMD is still in the basal plane as shown in figure 2(b). The EMD of the other Y-series compounds with larger Be substitution, however, is not known.

Figure 4 displays the magnetization versus magnetic field at 10 K of the $Y_2Fe_{17-x}Be_x$ and $Dy_2Fe_{17-x}Be_x$ series. The magnetic field is first taken to -5.5 T, then is increased to 5.5 T. The magnetization is almost saturated at 5.5 T for $Y_2Fe_{17-x}Be_x$ with $x = 0$–2
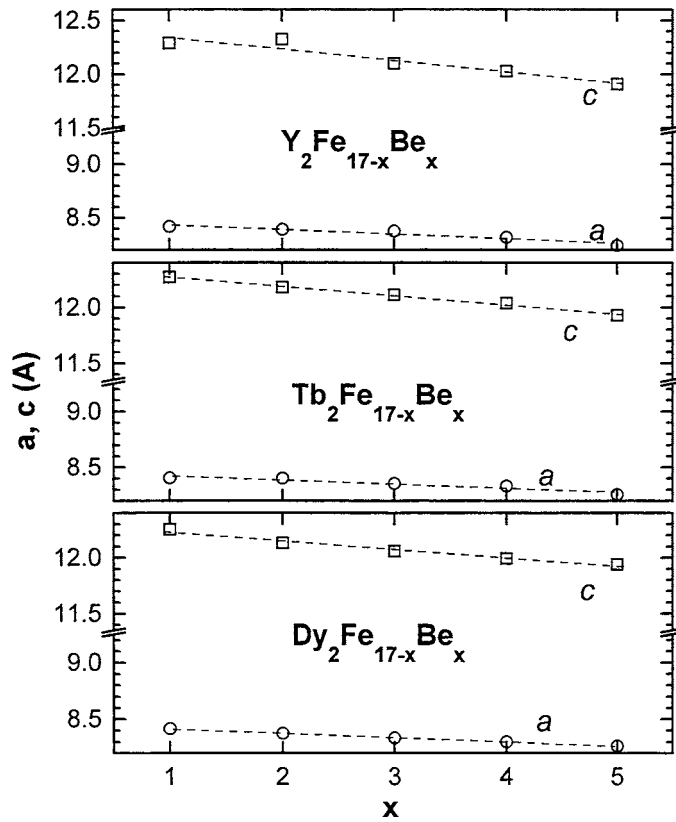
Figure 3. The lattice parameters a and c as functions of Be content in $R_2Fe_{17-x}Be_x$ ($R = Y$, Tb, Dy) compounds.

and for $Dy_2Fe_{17-x}Be_x$ with $x = 0$–4. The saturation magnetization is listed in table 1. The saturation magnetization monotonically decreases with x in both series, but the decrease rate of the saturation magnetization is not a constant in this range. At the initial stage, the rate is largest, and then it reduces gradually. From $x = 0$ to 1, the M_s decreases by 10.4 and 8.1 μ_B fu^{-1}/Be in the Y and Dy series, respectively. From $x = 1$ to 2, it is 6.5 and 3.0 μ_B fu^{-1}/Be, respectively. Beyond $x = 2$, the average rate is small, about 1.6 μ_B fu^{-1}/Be. According to the simple dilution model, the decrease rate should be a constant throughout with a calculated value of 2.05 μ_B fu^{-1}/Be. Obviously, the initial decrease rate is much larger than that due to the simple dilution effect, and it may come from the electronic hybridization. The 2s electrons of the Be atom may have transferred heavily to the 3d electronic band of the Fe atom and affected the magnetization strongly. With increasing Be concentration, the effect decreases noticeably.

In contrast to the normal ferromagnetic behaviour for $Y_2Fe_{17-x}Be_x$ with $x = 0$–2, no saturation is observed in the fields up to 5.5 T for $x = 3$ and 4. This may be a spin-glass characteristic in which magnetic clusters are surrounded by non-magnetic clusters. The same conclusion can also be drawn from the magnetization versus temperature curves of the fixed bulk sample (figure 5). The samples were cooled to low temperature without an applied magnetic field before they were measured. The spin-glass-like behaviour becomes manifest in the form of a sharper cusp, compare curves for $x = 2$ and 3. A similar phenomenon was also observed in the substitution of Al in the Y_2Fe_{17} compound, [20]. For $x = 1$, there is
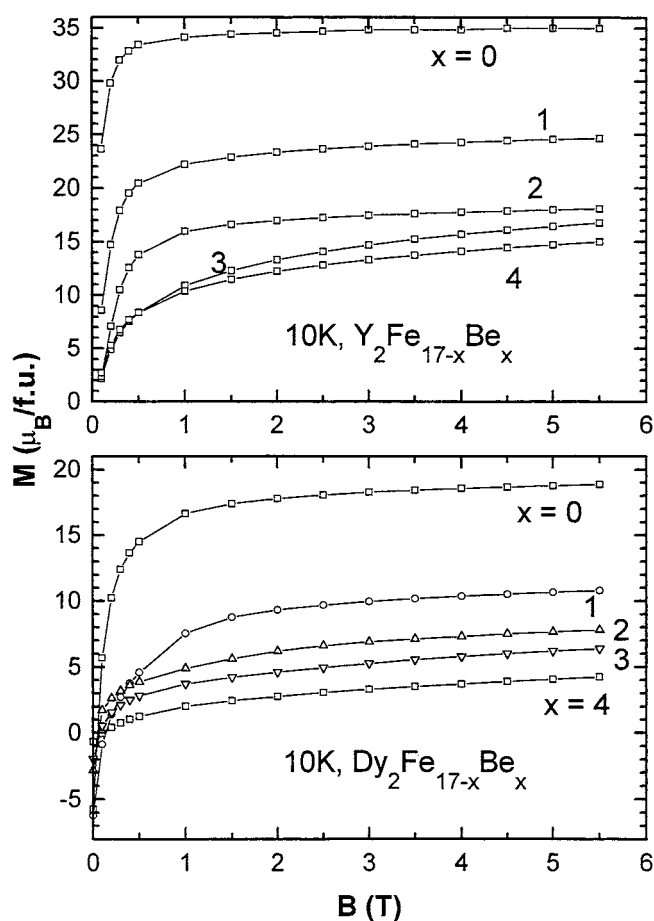
Figure 4. The magnetization versus magnetic field at 10 K in free powder specimens of $R_2Fe_{17-x}Be_x$ series (R = Y and Dy).

an increase in magnetization at low temperature and there are two drops near the magnetic ordering temperature. The former is related to the decrease of anisotropy with increasing temperature. The latter may haver resulted from the two structures, 2:17H and 2:17R, but the amount of 2:17H must be very small because it cannot be detected in the XRD pattern.

The magnetic ordering temperature also decreases as the Be content, x, increases in all $R_2Fe_{17-x}Be_x$ series (see table 1). Figure 6 displays the T_C of $R_2Fe_{17-x}Be_x$ with $x = 0$ and 1 as a function of rare-earth element, and the change in T_C is more or less independent of the R element. $Gd_2Fe_{16}Be$ compound has the largest T_C among all Be-substituted compounds made. The tendency of T_C variation among the various rare-earth compounds may have resulted from the effect of the rare earth on the exchange interaction J_{R-Fe}. From table 1, it can be seen that the magnetic ordering temperature decreases rapidly in the initial stage, and more slowly later on with increase in x of $R_2Fe_{17-x}Be_x$. This has been discussed one of our other papers [21].

Figure 7 displays the magnetization–temperature data on powder samples across the $Dy_2Fe_{17-x}Be_x$ series progressively cooled in a constant magnetic field of 5 T (unless mentioned otherwise) in the temperature range of 5–350 K. It is also inferred that the saturation magnetization decreases rapidly from $x = 0$ to $x = 2$, and more slowly later on through almost
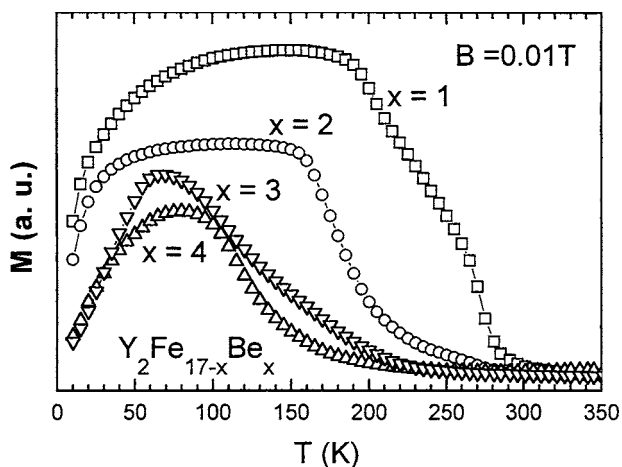
Figure 5. Magnetization as a function of temperature in 0.01 T on fixed bulk $Y_2Fe_{17-x}Be_x$ samples ($x = 1$–4). The compounds were cooled to low temperature without a magnetic field before it was measured.
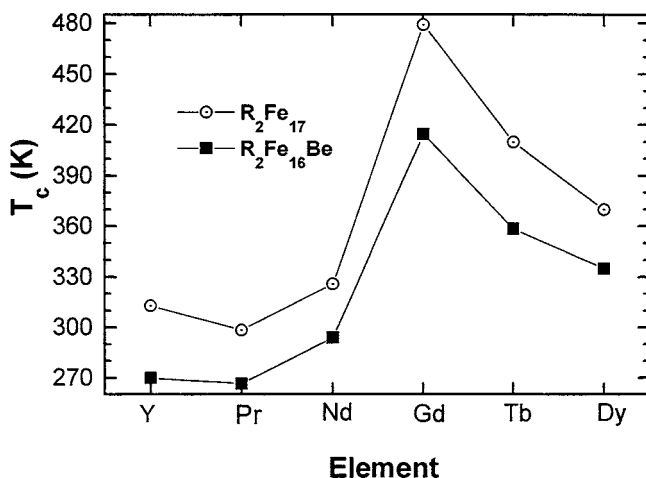

Figure 6. The dependence of the magnetic ordering temperature on Be content in the $R_2Fe_{17-x}Be_x$ ($x = 0, 1$) compound.

the entire temperature range. In addition, the magnetization initially increases monotonically as the temperature is lowered, and exhibits a broad maximum between 150 and 230 K for $x = 1$. Below the maximum, the magnetization decreases with decreasing temperature. This decrease in magnetization with decreasing temperature is attributed to the fact that Dy moments are aligned opposite to the Fe moments. At high temperature the Fe moments are dominant and are aligned in the applied field direction and Dy moments are aligned opposite to the field direction. As the temperature is lowered the magnetization associated with Dy moments increases faster than that associated with Fe moments. Therefore, the increase of net magnetization stops at a certain temperature. The net magnetization attains a maximum value and then begins to decrease as the temperature is lowered; thus a maximum in M–T data appears. An interesting feature is that for $x = 0$ Dy moments are quite weak even at low
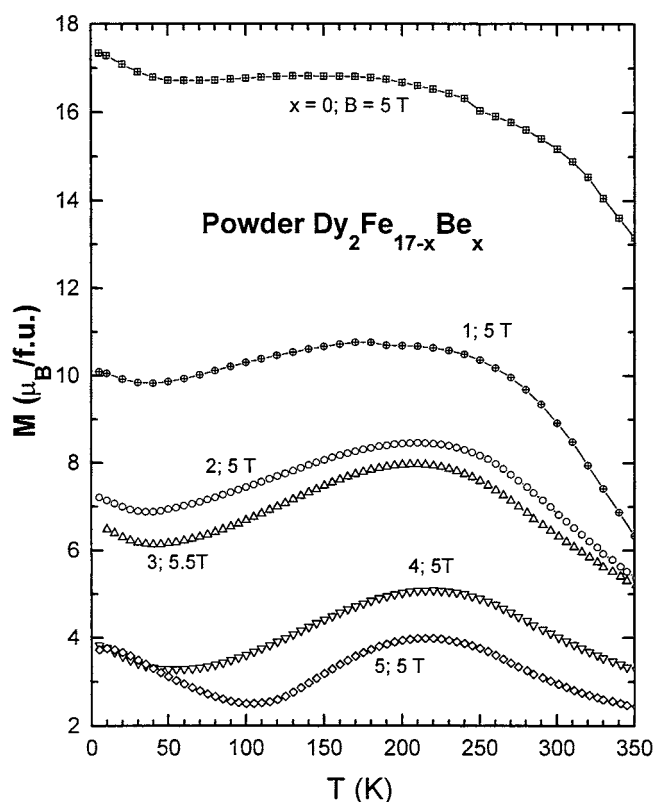
Figure 7. Magnetization–temperature data at 5.0 T across in free powder specimens of the $Dy_2Fe_{17-x}Be_x$ series ($x = 1$–5).

temperature, and magnetization does not show any appreciable decrease below the maximum. Whether it is due to the Th_2Ni_{17}-H structure type prevalent at this composition is not known. However, upon Be substitution, the structure changes to Th_2Zn_{17}-R type, the strength of Dy moments relative to Fe moments increases, and the rate of decrease of magnetization below the maximum increases with increasing x.

Below 50 K, there is a slight upturn in magnetization with decreasing temperature for $R_2Fe_{17-x}Be_x$ ($x = 0$–4) and this may be related to a very small amount of magnetic impurities present in the samples. For $x = 5$, there may be a compensation temperature at around 100 K, at which the opposing Dy and Fe moments are equal to each other. Because second phases exist in this sample, the net magnetization does not approach zero.

The magnetic data for the $Tb_2Fe_{17-x}Be_x$ series is qualitatively similar to those for the $Dy_2Fe_{17-x}Be_x$ series, as expected. Important information related to these data has been included in table 1 and has not been displayed in figures or discussed in detail to avoid repetition.

4. Conclusion

It is clearly established that Be can be substituted for Fe in significant amounts in the R_2Fe_{17} phases. Substitution of Be helps to stabilize the Th_2Zn_{17} type structure (2:17R), even when R = Tb, or Dy; the latter would otherwise stabilize the Th_2Ni_{17} type structure (2:17H). The extent of Be that can be retained in the 2:17R structure is one to two atoms per formula unit for

R = light rare-earth elements Pr and Nd, and four to five atoms per formula unit for R = Y, Tb and Dy in the $R_2Fe_{17-x}Be_x$ series. The lattice parameters and magnetic moment decrease with Be substitution. The strong initial decrease of the magnetic moment may be the result of initial strong electronic hybridization between the Be and Fe states.

Acknowledgment

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