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INTRINSIC AND EXTRINSIC MAGNETIC PROPERTIES OF RARE EARTH-TRANSITION METAL-METALLOID ALLOYS

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ABSTRACT

Several groups of rare earth-iron-boron or transition metal alloys have been examined by various experimental techniques with the aim to understand the magnetic properties at the atomic level and relate them to the macroscopic magnetic properties. Investigations of substituted $R_2Fe_{14-x}Co_xB$ alloys (R=Y,Dy; x=0,1,2) have shown that Co enters preferentially in the c or k_2 site of the $R_2Fe_{14}B$ structure. The change of the easy direction of magnetization from the plane to the c axis has been studied in a series of pseudoternary alloys of the type $Er_{2-x}Dy_xFe_{14}B$ with $0 < x < 1.5$. Within the R-Fe-B system the compounds of the type $R_{1+e}Fe_4B_4$ and RFe_4B were also investigated. The first group forms across the whole lanthanide series. Magnetic ordering occurs at temperatures between 4.2 and 25 K for R=Pr, Nd, Sm, Gd, Tb, Dy, Ho. The RFe_4B compounds (R=Er,Tm) have axial anisotropy. The distribution of Fe and B in the i and (c,d) sites of the hexagonal P6/mmm structure was investigated by Moessbauer and X-ray measurements. A series of new alloys of the pseudobinary type $RFe_{12-x}T_x$ (R=Gd, Nd; T=Ti, V, Cr, Mo) crystallizing in the $ThMn_{12}$ structure has been prepared. They show axial anisotropy and anisotropy fields $H_A \gtrsim 3$ kA/m. A two phase system prepared by annealing melt spun samples with composition $R_2Fe_7B_3$ was found to possess high coercivities at room temperature.

INTRODUCTION

The full understanding of the outstanding magnetic properties of R-Fe-B alloys and more particularly $Nd_2Fe_{14}B$ requires the knowledge of magnetic parameters at the atomic level. This knowledge is also essential in the search of new alloys with similar or improved properties. With this aim in mind, the work accomplished by our group within the CEAM project was focused in the following areas:

(a) Investigations of modified $R_2Fe_{14}B$ compounds by substitution of Fe or the R element in order to establish the site preferences, if any, and the effect on magnetic anisotropy.

(b) Studies of other compounds in the R-Fe-B system as $R_{1+e}Fe_4B_4$ and RFe_4B.

(c) Search for new magnetic phases with the $ThMn_{12}$ type structure.

(d) Studies of the high coercivities developed in two phase systems prepared by proper thermal treatment of alloys with composition $Nd_2Fe_7B_3$.

A variety of preparative and analytical techniques were used for these investigations including arc melting and melt spinning, X-ray

diffraction (XRD), Moessbauer and magnetization measurements and differential thermal analysis (DTA). A summary of the results obtained is given in the following sections. Part of this investigation has been given in greater detail in journal articles. (Kostikas et al., 1985, Niarchos et al., 1986a, Niarchos and Simopoulos, 1986b, Simopoulos and Niarchos, 1988).

EXPERIMENTAL PROCEDURES

Ingots of the studied alloys were prepared by arc melting stoichiometric amounts of the elements (purity 3N for the rare earths, 4N for Fe and B) in Ar atmosphere. Bulk samples were studied as prepared or after annealing at appropriate temperatures for several days. Melt spun samples were prepared in a locally constructed melt spinning system with the following features: Cu wheel diameter 17 cm, width 1.5 cm, speed variable up to a maximum of 80 m/s.

Moessbauer spectra were obtained with polycrystalline or oriented absorbers using a conventional constant acceleration spectrometer with a ^{57}Co in Rh source. Magnetization measurements were carried out with a PAR 55 vibrating sample magnetometer in fields up to 2.0 T. The phase constitution and crystal structure was checked by X-ray powder patterns using Co-Kα radiation. DTA data were obtained with a Perkin Elmer Thermal Analyzer.

Oriented samples were prepared by mixing fine powder with epoxy and letting the mixture to harden in an applied field of 1.8 T.

RESULTS

Studies of substituted $R_2Fe_{14-x}Co_xB$ alloys (x=1,2,4; R=Y,Dy).

Substitution of Fe by Co in the $Nd_2Fe_{14}B$ alloy leads to an increase of the Curie temperature while the spontaneous magnetization decreases. (F. Bolzoni et al. 1987). In connection with this effect it is of interest to determine the site preference, if any of the Co atoms. We have studied a series of Co substituted alloys of the type $R_2Fe_{14-x}Co_xB$ near the low Co concentration side (x=1,2,4). As it has been shown by several studies (e.g. Kostikas et al.,1985), the Moessbauer spectra of the unsubstituted compounds have sufficient resolution to distinguish different Fe sites in the $Nd_2Fe_{14}B$ structure by their hyperfine parameters. The sites where Co enters can therefore be inferred from the changes in the ^{57}Fe spectrum. Since the reliability of this assignment depends on the

knowledge of the hyperfine parameters for the unsubstituted compounds, we have reexamined the fitting of Moessbauer spectra especially with regard to the parameters of the c and e sites for which there is no general agreement. We have shown that in $Dy_2Fe_{14}B$ and $Nd_2Fe_{14}B$ a better fit can be obtained by assigning a value of 31.0 T for the c-site which is higher than that used in other simulations (Fruchart et al., 1987). This value, however, gives better agreement with neutron diffraction data (Givord et al., 1985).

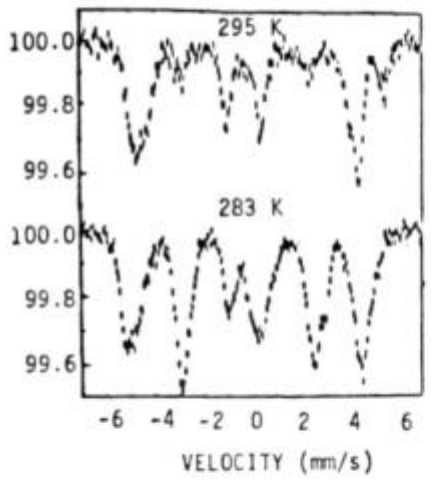
Another point that must be taken into account in simulating spectra of the substituted compounds is the line broadening resulting from a possible distribution of Co. We have accounted for this by allowing for a spread ΔH in hyperfine fields. A comparison of the spectra of the Dy compound for x=0 (unsubstituted) and x=2 shows clearly that there is a reduction in intensity in the line near -5 mm/s. Satisfactory fits can be obtained by assuming that the Fe atoms are substituted either at the k_2 or c site. It is interesting to note that these are the sites with the shortest average Fe-Fe distances (0.2535 and 0.2532 nm respectively). Similar conclusions were reached with the analysis of the Y alloy.

Complementary information on site substitution was obtained by Moessbauer measurements on an ^{57}Fe doped sample of $Nd_2Co_{14}B$ with stoichiometry $Nd_2{}^{57}Fe_{0.75}Co_{13.25}B$ (Simopoulos and Niarchos,1988). We conclude that Fe enters preferentially into the j_2 site, in agreement with a similar previous investigation (Van Noort, 1985a). As noted by Bolzoni et al. (1987), this is the site with the highest Fe-Fe distance (0.2698 nm) and fewest Nd neighbors.

Spin Reorientation in $Er_xDy_{2-x}Fe_{14}B$ alloys

Crystalline electric field (CEF) interactions induce uniaxial anisotropy in $R_2Fe_{14}B$ compounds for the rare earths with negative Stevens factor ($a_j<0$) while the elements with $a_j>0$ display basal anisotropy. In the latter case basal anisotropy prevails at low temperatures, but as the temperature increases the uniaxial anisotropy of the Fe sublattice dominates. The change of direction of the magnetization from the plane to the c axis, known as spin reorientation, occurs for $Er_2Fe_{14}B$ ($a_j<0$) near 325 K and is absent in $Dy_2Fe_{14}B$ ($a_j>0$). The effect on the spin reorientation of the coexistence of two rare earth elements with competing anisotropy was studied in the pseudoternary system $Er_{2-x}Dy_xFe_{14}B$ with Moessbauer spectroscopy of oriented samples (Niarchos and Simopoulos,

1986b). The spin reorientation temperature was determined by the change in the intensity of the Δm=0 Moessbauer absorption lines. Since the absorbers are polarized at 320 K, well above the spin reorientation temperature (Tr), in a direction parallel to the gamma rays, this direction coincides with the c axis of the crystallites. Above T_r therefore, the magnetization is parallel to the gamma rays and the Δm=0 lines must vanish. This effect is shown in Fig.1 for the compound $Er_{1.95}Dy_{0.05}Fe_{14}B$. The disappearance of the Δm=0 lines proceeds gradually within an interval of 12 K. The width of the transition may be attributed to inhomogeneities depending on sample preparation and the distribution of Dy. In fact water quenched samples display a narrower width of the transition than slowly cooled samples. Alternatively this effect may be due to a gradual spin reorientation which increases with Dy concentration.



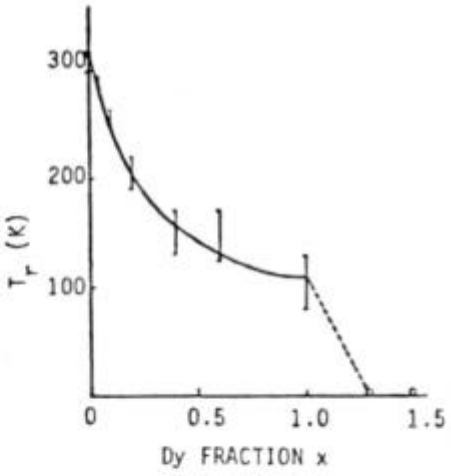


Fig. 1 (left) Moessbauer spectra above (T=295 K) and below (T=283 K) the spin reorientation temperature for an oriented sample of $Er_{1.95}Dy_{0.05}Fe_{14}B$.

Fig. 2 (right) The variation of the spin reorientation temperature in the series of $Er_{2-x}Dy_xFe_{14}B$ as a function of x.

The dependence of T_r on the concentration of Dy is shown in Fig. 2. The error bars indicate the temperature range where intermediate intensities were observed for the Δm=0 Moessbauer lines. The two samples with values of x equal to 1.3 and 1.5 did not show any spin reorientation down to temperatures of 6 K. This behavior is different than that observed for the $Er_{2-x}Gd_xFe_{14}B$ system (Vasquez and Sanchez, 1987) where T_r decreases

Magnetization measurements have shown that with the exception of La, Ce, Er and Tm all other compounds exhibit magnetic ordering transitions in the range between 4.2 and 25 K. Transition temperatures, determined by Arrot plots are given in Table 1. In the same table are also listed the magnetic moments per formula unit as calculated from the value of the magnetization at 4.2 K in a field of 1.8 T.

TABLE 1. Magnetic data and hyperfine parameters of $R_{1+e}Fe_4B_4$

R	T_c(K) Exp	Cal.	M(BM)	I.S.[a] (mm/s) at 300 K	ΔE_Q (mm/s)
La	-	-	-	0.034(5)	0.632(5)
Ce	(b)	0.3	-	0.010(5)	0.530(5)
Pr	7.5(5)	1.2	1.50	0.032(5)	0.584(5)
Nd	16.0(5)	2.9	2.40	0.026(5)	0.582(5)
Sm		7.1		0.023(5)	0.566(5)
Gd	24.0(5)	24.0	6.02	0.022(5)	0.556(5)
Tb	16.0(5)	16.0	3.50	0.018(5)	0.528(5)
Dy	11.5(5)	11.2	5.70	0.014(5)	0.532(5)
Ho	6.5(5)	7.11	5.50	0.037(5)	0.544(5)
Er	(b)	4.03	-	0.024(5)	0.548(5)
Tm	(b)	1.84	-	0.024(5)	0.546(5)

a. With respect to iron at room temperature.
b. No transition observed down to 4.2 K.

In a simple molecular field modeling of the magnetic interactions, the transition temperatures are expected to follow the de Gennes values, i.e. $T_c \propto (g-1)^2 J(J+1)$. Values calculated from this relation and normalized to the experimental result for Gd are compared with experimental values in Fig. 3. It is seen that the de Gennes rule is followed very well by the heavy rare earth compounds but significant discrepancy is observed for the light rare earths. Deviations of this type may be attributed to CEF effects (Noakes et al., 1983). The presence of CEF effects is also indicated by the reduced values of the high field magnetic moments listed in Table 1.

The magnetization results imply that the Fe atoms do not carry a magnetic moment in agreement with reported measurements of Givord et al., (1986). A clear demonstration of the absence of magnetic moment for Fe has been given by Moessbauer measurements. The Moessbauer spectra of all compounds consist of a simple quadrupole doublet down to 4.2 K, with

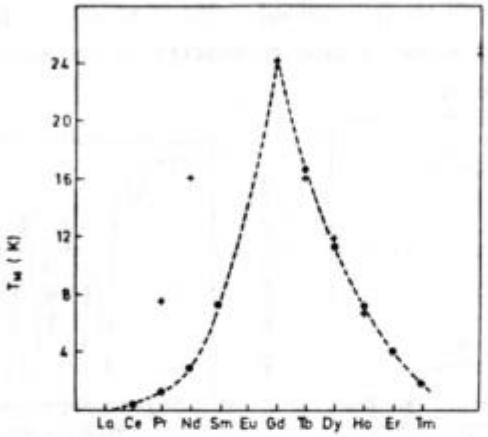


Fig. 3 Magnetic ordering temperatures of the $R_{1+e}Fe_4B_4$ compounds; (+) experimental results; (o) values calculated from $T\ (g-1)^2J(J+1)$ and normalized to the value for Gd.

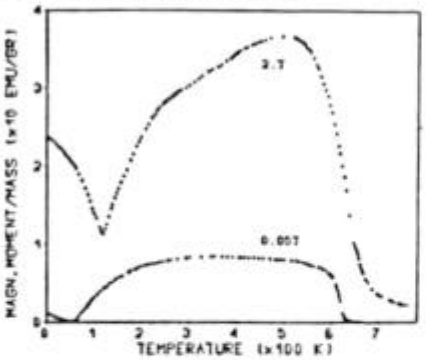
parameters listed in Table 1. The possibility of a small magnetic moment at the Fe atom was further probed by the application of an external field of 0.65 T perpendicular to the gamma rays. For the Gd compound at 4.2 only a broadening of the quadrupole doublet was observed. A simulation of this spectrum assuming an effective field at various directions to the EFG and taking a powder average yields an estimate of the effective field of 0.7±0.2 T which, within the experimental accuracy, is equal to the applied field.

Structure and magnetic properties of RFe_4B alloys (R=Er,Tm)

Previous work on RFe_4B compounds (R=Lu,Er,Tm) has established the uniaxial ferrimagnetic structure of these alloys and their basic magnetic parameters (Van Noort et al. 1985b, Vaishnava et al. 1985). Hyperfine magnetic fields have been obtained from Moessbauer spectra but there are discrepancies in site assignments, mainly due to the possibility of Fe and B disorder in the i and (c,d) sites of the $CeCo_4B$ structure assumed for these compounds.

We have obtained magnetization data vs T in the temperature range of

4.2 to 700 K and in applied fields of 40 and 1600 kA/m. The $ErFe_4B$ data (Fig. 4) show a clearly defined compensation point arising from antiferromagnetic coupling of the Er and Fe sublattices. The compensation point in the Tm alloy is apparent only in the high field data. There is no anomaly, indicative of a spin reorientation, as suggested in previous investigations (Van Noort et al., 1985b). The absence of spin reorientation was verified by Moessbauer spectra of an oriented sample at 77 K and room temperature.



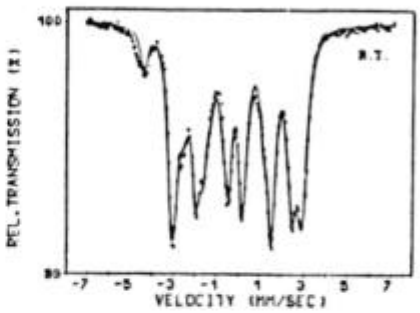


Fig. 4 (left) Temperature dependence of the magnetization of a $ErFe_4B$ alloy in fields of 0.05 and 2.0 T.

Fig. 5 (right) Moessbauer spectrum of a $TmFe_4B$ alloy at room temperature. The solid line is a computer fit with the distribution model described in the text.

Powder X-ray diffraction diagrams were indexed with the reflections of the space group P6/mmm corresponding to the $CeCo_4B$-type structure. A notable feature of the data is the absence of (h,k,2l+1) lines. This indicates that instead of a fully ordered $CeCo_4B$ structure, a disordered configuration of Fe and B in the (c,d) and i sites may occur. To test this assumption we have calculated intensities with occupation probabilities as determined by the Moessbauer data (see below). This resulted in an improvement of the reliability factor from 15% for a fully ordered structure to 7% for the disordered structure.

Moessbauer spectra were obtained with polycrystalline absorbers at room temperature and 4.2 K. The spectra for the two alloys at both temperatures are similar. We have analyzed these spectra with a model which assumes different probabilities p_i and p_c for occupation by B of the sites i and (c,d). The 2c and 2d sites were taken equivalent since they correspond to the same site of the parent $CaCu_5$ structure. Assuming

binomial distribution of the B atoms in the i and (c,d) sites we can readily calculate the probabilities of nearest neighbor configuration for an Fe atom in the i and (c,d) sites. A more detailed account of this calculation will be given in a forthcoming publication.

The Moessbauer lineshape calculated with this model is compared with the experimental data in Fig. 5. The main result of this analysis is that the values of p_i and p_c are significantly different (p_i=0.033, p_c=0.339), i.e. there is a preference of B to occupy the (c,d) site. For a statistical distribution p_i=p_c=0.2. The observed values of p_i and p_c imply an average site occupation in the unit cell as follows: i-site (0.2B, 5.8Fe), (c,d)-site (1.4B, 2.6Fe). These values do not agree exactly with stoichiometry but the discrepancies are probably within the uncertainty of the determination of p_i and p_c.

Magnetic properties of $RFe_{12-x}T_x$ alloys

Within the scope of the search for new permanent magnet materials we have started an extensive study of pseudobinary alloys with general formula $RFe_{12-x}T_x$ which may crystallize in the tetragonal $ThMn_{12}$ type structure.

The value of x was chosen near the composition predicted by the phenomenological method of Pettifor (1986), applied to pseudobinary alloys with the $ThMn_{12}$ structure. Samples were prepared for the following combinations of R and T: (R=Gd; T=Ti, Cr, Mo), (R=Nd; T=V), (R=Y; T=Mo,Ti), (R=Sm, T=Mo,Ti). In the case of the Gd-Mo alloys a series of samples with x=1.8, 2.0, 2.2 was prepared in order to test the homogeneity, patterns can be indexed with the reflections of the $ThMn_{12}$ type structure as the dominant phase.

TABLE 2. Lattice constants and magnetic data for $RFe_{12-x}T_x$ alloys

Alloy	a (nm)	b (nm)	T_c (K)	M_s (μ_B)
$Nd_{1.2}Fe_{9.8}V_{2.2}$	0.855	0.477	525	15.05
$Gd_{1.1}Fe_{9.5}Cr_{2.5}$	0.845	0.475	608	10.62
$Gd_{1.1}Fe_{10.2}Mo_{1.6}$	0.854	0.479	446	7.00
$Gd_{1.1}Fe_{10}Mo_2$	0.856	0.480	410	5.69
$Gd_{1.1}Fe_{9.8}Mo_{2.2}$	0.858	0.480	345	4.52

We report here results for the Nd and Gd alloys. The lattice constants, Curie temperatures and magnetization in Bohr magnetons per formula unit at room temperature are listed in Table 2. Magnetization measurements with oriented samples in applied fields up to 2T give an extrapolated estimate of H_c=250 kA/m. The temperature dependence of the magnetization for the Mo alloys is shown in Fig. 6.

Moessbauer spectra show considerable broadening of the magnetic transition metal T in the sites i,j and f of the $ThMn_{12}$ structure. Fig. 8 shows the simulation of the spectrum of $GdFe_{11}Ti$ with the assumption that Ti is statistically distributed over the lattice sites. A spread of

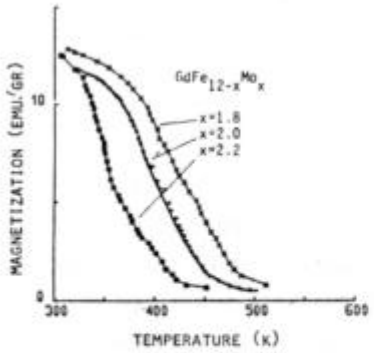


Fig. 6 (left) Temperature dependence of the magnetization of $GdFe_{12-x}Mo_x$ alloys in a field of 50 mT.

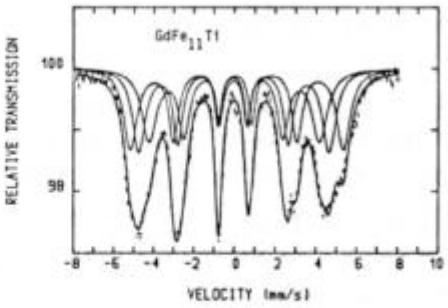


Fig. 7 (right) Moessbauer spectrum of a $GdFe_{11}Ti$ alloy at room temperture. The solid line is a simulation assuming that Ti is statistically distributed in the i,j and f sites.

hyperfine fields has been taken into account for each site in this simulation.

Similar results on this type of alloys have been reported by de Boer et al. (1987). It appears that these alloys have sufficiently high anisotropy but their saturation magnetization is low compared to the $R_2Fe_{14}B$ phases.

We have made also preliminary measurements on a series of Sm alloys with T=V, Si, Ti and x=2 provided within the CEAM project by RARE EARTH PRODUCTS. XRD and Moessbauer measurements show significant iron content in the V and Si alloys.

High Coercivity R-Fe-B two phase alloys (R=Pr,Nd,Sm).

The possibility of preparation of high coercivity alloys with more than one crystalline phases and the appropriate microstructure was explored in R-Fe-B alloys with nominal stoichiometry $Nd_2Fe_7B_3$. Samples were prepared from ingots of this composition by melt spinning and subsequent annealing at various temperatures.

Differential thermal analysis (DTA) measurements on the melt spun samples show a sharp peak near 870 K indicating the precipitation of a new phase. The nature of this transformation was examined by magnetization and Moessbauer measurements. The magnetization of the melt spun samples of the three alloys studied drops to a value close to zero in the range of 310 to 330 K. Upon further heating to the temperature of the transformation and cooling back, the presence of a new phase with a Curie temperature near 580 K is ascertained. Moessbauer spectra were obtained at room temperature for a $Nd_2Fe_7B_3$ sample before and after the thermal cycling. The spectrum of the melt spun sample is typical of an amorphous phase. The spectrum of the annealed sample on the other hand shows clearly a magnetic and a paramagnetic phase. The magnetic pattern is typical of $Nd_2Fe_{14}B$ while the parameters of the paramagnetic doublet fit those of $Nd_{1+e}Fe_4B_4$ (Kostikas et al., 1985, Niarchos et al., 1986a). A computer fit of the spectrum with two components verifies this assignment and yields an approximate phase

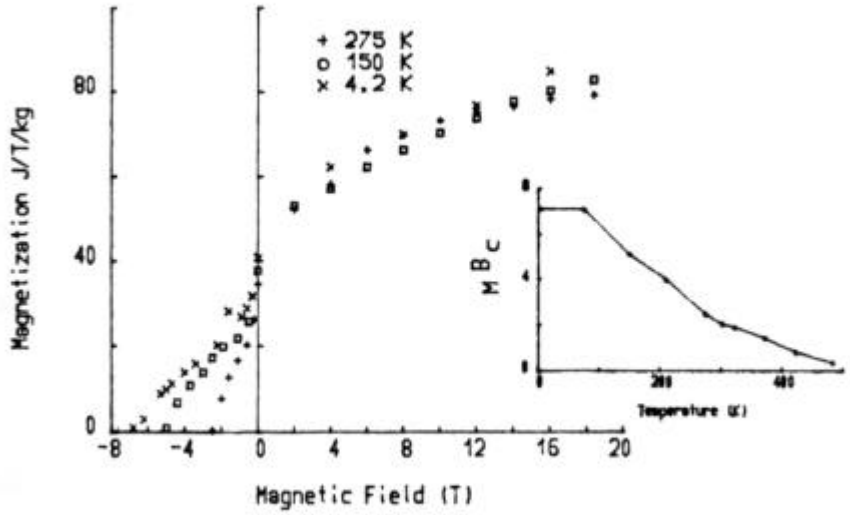


Fig. 8 Coercivity of two phase $Pr_2Fe_7B_3$ alloys. The insert shows the variation of $_MB_C$ with temperature.

composition for the iron containing phases of 30% $Nd_2Fe_{14}B$ and 70% $Nd_{1+e}Fe_4B_4$.

The coercivity of the melt spun and annealed samples was studied in the temperature range of 4.2 to 500 K. Results obtained at three different temperatures at the high field facility of SNCI are shown in Fig. 8 for a sample of $Pr_2Fe_7B_3$. The coercive field $_MB_C$ rises from about 2T at room temperature to 7T at 4.2K. The insert shows the temperature variation of $_MB_C$ up to 500 K. Preliminary measurements on samples annealed at different temperatures show that the coercive field is strongly dependent on the annealing temperature. The remanent magnetization, however, is low, 30 J/T/kg presumably due to the presence of the paramagnetic phase. Further study is required to optimize the properties of these alloys with respect to composition and thermal treatment. The data of Fig. 8 also show that the sample must contain up to 30% of an additional magnetic phase if we assume similar M_S. The same result could also be explained with about 15% Fe content. The magnetization and Moessbauer data, however, do not show evidence for an additional magnetic iron containing phase. The reason for this discrepancy is not clear at present.

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