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Nuclear magnetic resonance study of the RE(Co, B)$_5$-type compounds (RE ≡ Y, Gd)

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Abstract

The nuclear magnetic resonance spin echo spectra of RECo$_5$, RECo$_4$B, RE$_3$Co$_{11}$B$_4$, RE$_2$Co$_7$B$_3$ and RECo$_3$B$_2$ (RE ≡ Y, Gd) at 4.2 K are presented. An assignment of the resonance lines to the various cobalt sites in these compounds is proposed. The variations in the cobalt hyperfine field observed between different cobalt sites and different compounds are analysed in terms of spin and orbital contributions to the cobalt moments. The cobalt hyperfine fields at sites of the same symmetry and nearest-neighbour configuration are similar in the different compounds. The gadolinium hyperfine field in GdCo$_3$B$_2$ is close to the free ion value. The temperature-independent Knight shift of cobalt and boron observed in YCo$_3$B$_2$ indicates that this compound is a Pauli paramagnet.

1. Introduction

The ternary RE(Co, B)$_5$ compounds studied in the course of the present investigation are structurally related to SmCo$_5$ which has a very large uniaxial magnetocrystalline anisotropy originating from both rare earth and cobalt sublattices. A large increase in the magnetocrystalline anisotropy due to an ordered substitution of boron for cobalt has been reported for Sm$_3$Co$_{11}$B$_4$ [1] and SmCo$_4$B [2]. Recent Mössbauer studies [3, 4] on the gadolinium-based RE(Co, B)$_5$ series have shown that boron increases significantly the rare earth sublattice anisotropy via an enhancement of the second-order crystal electric field parameter at the RE sites. A significant contribution of cobalt to the magnetocrystalline anisotropy of these compounds is exemplified by YCo$_5$. The strength of the individual contributions to the magnetocrystalline anisotropy and magnetic moments of the non-equivalent cobalt sites in these compounds was thoroughly studied by several researchers [5–12] using nuclear magnetic resonance (NMR) and neutron diffraction. However, the

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large spread in values observed for hyperfine fields, the orbital moments and the individual anisotropy contributions shows that this problem is still not satisfactorily solved.

The $\mathrm{RECo_5}$ compounds crystallize in the hexagonal system (space group, *P6/mmm*). The RE atoms occupy a single crystallographic site (1a). The cobalt atoms are located at two inequivalent sites (2c and 3g).

The strong intrasublattice coupling between the cobalt atoms leads to a parallel spin alignment. Owing to the antiferromagnetic interaction between the cobalt and RE spins $\mathrm{GdCo_5}$ is ferrimagnetic. The introduction of boron leads to an ordered replacement of the Co(2c) sites in the layers perpendicular to the crystallographic c axis [13]. The occupation of all 2c sites by boron leads to the compound $\mathrm{RECo_3B_2}$. Because the atomic radius of boron is much smaller than that of cobalt, the lattice constant c is also smaller than that of $\mathrm{RECo_5}$.

The average cobalt moment decreases with boron substitution and the values reported are $1.7\mu_B$ (Co atom)$^{-1}$, $1.0\mu_B$ (Co atom)$^{-1}$, $0.8\mu_B$ (Co atom)$^{-1}$, $0.6\mu_B$ (Co atom)$^{-1}$ and $0.0\mu_B$ (Co atom)$^{-1}$ for $\mathrm{RECo_5}$, $\mathrm{RECo_4B}$, $\mathrm{RE_3Co_{11}B_4}$, $\mathrm{RE_2Co_7B_3}$ and $\mathrm{RECo_3B_2}$ respectively [4, 14–16].

The unit cells of the compounds of the RE(Co, B)$_5$ series are built up from the unit cells of $\mathrm{RECo_5}$ and $\mathrm{RECo_3B_2}$ as schematically shown in Fig. 1. The general formula of these compounds can be written as $\mathrm{RE}_{k+1}\mathrm{Co}_{3k+5}\mathrm{B}_{2k}$. This corresponds to $\mathrm{RECo_5}$ for $k=0$, $\mathrm{RECo_4B}$ for $k=1$, $\mathrm{RE_3Co_{11}B_4}$ for $k=2$, $\mathrm{RE_2Co_7B_3}$ for $k=3$ and $\mathrm{RECo_3B_2}$ for $k=\infty$. The number of inequivalent RE sites is 2 in $\mathrm{RECo_4B}$, 2 in $\mathrm{RE_3Co_{11}B_4}$, 3 in $\mathrm{RE_2Co_7B_3}$, and 1 in $\mathrm{RECo_3B_2}$. The number of inequivalent cobalt sites is 2, 3, 3 and 1 respectively.

In order to study the magnetic state of the cobalt atoms in the $\mathrm{RE}_{k+1}\mathrm{Co}_{3k+5}\mathrm{B}_{2k}$ series and its dependence on the type of crystallographic site and boron substitution we have studied the yttrium- and gadolinium-based series with zero field spin echo NMR. For the compound $\mathrm{YCo_3B_2}$ exhibiting no magnetic order down to 4.2 K the NMR spectra under an applied magnetic field were taken. Information about the magnetic state of cobalt is gained via the hyperfine fields at the cobalt nuclei.

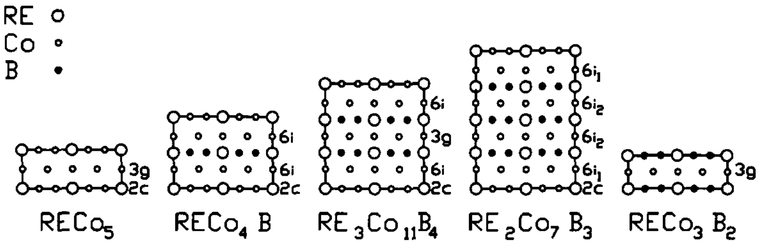


Fig. 1. Schematic representation of the crystallographic structure of the RE(Co, B)$_5$ compounds. The layers of inequivalent cobalt sites are marked.

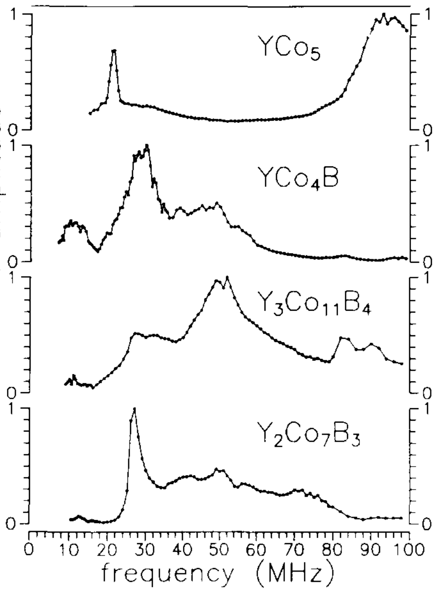
2. Experimental details

The samples were prepared by arc melting from starting materials of at least 99.9% purity. After arc casting the alloy buttons were wrapped in tantalum foil and vacuum annealed inside evacuated silica tubes for several

TABLE 1

The lattice constants of the Y(Co, B)$_5$ and Gd(Co, B)$_5$ series

Compound	RE ≡ Y		RE ≡ Gd	
	a (pm)	*c* (pm)	*a* (pm)	*c* (pm)
RECo$_5$	493.7	396.3	497.3	396.9
RECo$_4$B	500.7	686.2	505.9	690.4
RE$_3$Co$_{11}$B$_4$	508.3	981.2	507.2	983.9
RE$_2$Co$_7$B$_3$	504.4	1288	506.7	1294
RECo$_3$B$_2$	502.1	302.5	506.5	301.8



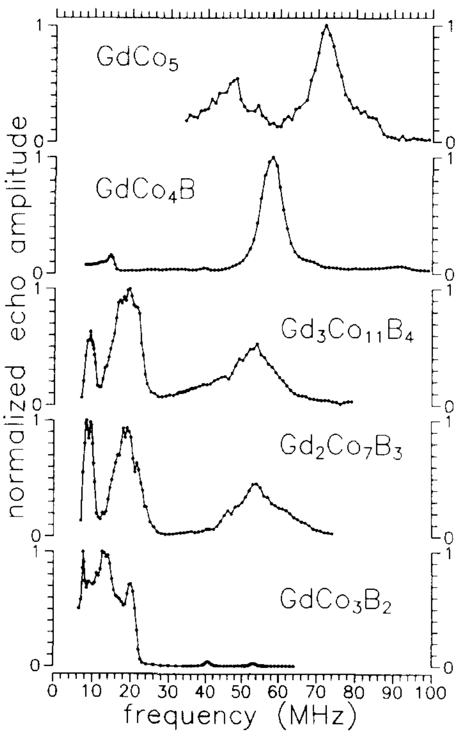


Fig. 2. The NMR spin echo spectra of the yttrium-based RE(Co, B)$_5$ series at 4.2 K, under zero applied magnetic field.

Fig. 3. The NMR spin echo spectra of the gadolinium-based RE(Co, B)$_5$ series at 4.2 K, under zero applied magnetic field.

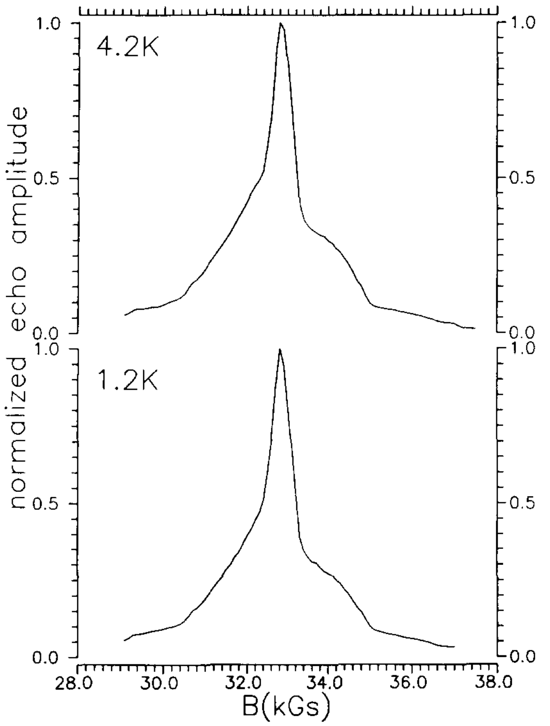


Fig. 4. The ^{59}Co NMR spin echo spectra of YCo_3B_2 at the frequency 33 MHz under an applied magnetic field.

weeks in the temperature range 1000–1050 °C. After vacuum annealing the samples were investigated by X-ray diffraction and found to be approximately single phase. The lattice constants derived from the X-ray diagrams are listed in Table 1.

The zero applied field NMR measurements have been carried out at 4.2 K using a spin echo NMR spectrometer [17]. Coarsely powdered samples were used. The pulse sequence 0.5 μs–30 μs–0.7 μs was applied. For the peak frequencies the transverse relaxation times T_{tr} were measured. The obtained spectra are presented in Figs. 2 and 3. The resonance line positions and the values of transverse relaxation times are collected in Table 2.

The measurements under applied field have been performed at the Institute of Solid State Physics, KFA Jülich, at 4.2 K and 1.2 K. A pulse sequence of 4 μs–100 μs–8 μs at a fixed frequency of 33 MHz was used. The applied magnetic field was varied in the range 0–6.5 T. The spectra are shown in Figs. 4 and 5.

Discussion

In the zero applied field NMR experiments, the magnetic field measured at a cobalt nucleus can be expressed as

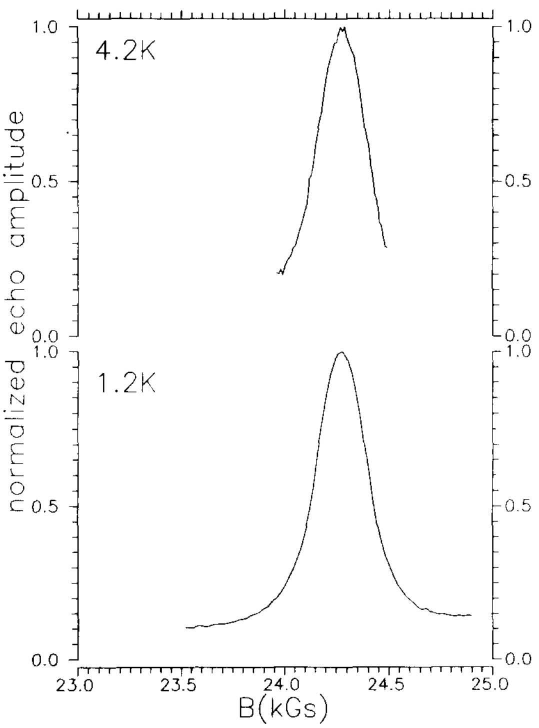


Fig. 5. The ^{11}B NMR spin echo spectra of YCo_3B_2 at the frequency 33 MHz under an applied magnetic field.

$$B_e = B_{hf} + B_{loc} \tag{1}$$

where B_{hf} is the hyperfine field expressed as a sum:

$$B_{hf} = B_s + B_{orb} + B_N \tag{2}$$

B_s is the term originating from core and conduction electron polarization by the cobalt spin moment itself, B_{orb} is the orbital field of 3d electrons and B_N is the polarization contribution from neighbouring magnetic atoms often called the "transferred hyperfine field". The orbital contribution can be expressed as

$$B_{orb} = 3\langle \mu_L \rangle \langle r^{-3} \rangle \mu_0 \tag{3}$$

where $\langle \mu_L \rangle$ is the expectation value of the orbital moment of the cobalt atoms. The contribution B_{orb} can vary with the direction of cobalt moment and follows the changes in μ_L. Its sign is positive, *i.e.* parallel to μ_L, and opposite to the contribution produced by the spin moment.

B_{loc} represents the local field. The only contribution to B_{loc} which can significantly vary across our series is the dipolar field B_{dip}. This is an anisotropic term represented by a vector sum of the magnetic fields produced at the nucleus by the magnetic moments of the neighbouring atoms. B_{dip} can be different between atoms belonging to the same crystallographic site.

TABLE 2

The numbers and the types of nearest-neighbour atoms to the crystallographic sites, the calculated values of dipolar fields B_{dip}, the resonant frequencies ν, the absolute values $|B_e|$ of the effective fields and the transverse relaxation times T_{tr}

Site	Nearest neighbours	B^c_{dip} (T)	B^a_{dip} (T)	ν (MHz)		$\|B_e\|$ [T]		T_{tr} (μs)	
				Y	Gd	Y	Gd	Y	Gd
$ReCo_5$									
RE(1a)	$2RE_a$ $6Co_c$	0.20	−0.10	21.3	–	10.2	–	597	–
	$12Co_g$	0.29	−0.14						
Co(2c)	$3RE_a$ $3Co_c$	0.70	−0.35	20	48	2.0	4.8	–	88
	$6Co_g$	0.45	−0.22						
Co(3g)	$4RE_a$ $4Co_c$	−0.07	−0.50, 0.30	93	72	9.2	7.1	162	168
	$4Co_g$	0.03	−0.51, 0.23						
$RECo_4B$									
RE(1a)	$2RE_b$ $6Co_c$	0.39	−0.20	10	–	4.8	–	758	–
	$12Co_i$	0.19	−0.09						
RE(1b)	$2RE_a$ $12Co_i$	0.39	−0.20	–	–	–	–	–	–
	$6B_d$	0.08	−0.04						
Co(2c)	$3RE_a$ $3Co_c$	0.53	−0.27	48	54	4.8	5.3	137	88
	$6Co_g$	0.20	−0.10						
Co(6i)	$2RE_a$ $2RE_b$ $2Co_c$	0.14	−0.79, 0.29	30	58	3.0	5.7	177	83
	$5Co_i$ $2B_d$	−0.02	−0.22, 0.12						
B(2d)	$3RE_b$ $2Co'_c$	−0.53	0.27	10	14	0.73	1.02	–	65
	$6Co_i$ $2B_d$	−0.36	0.18						
$RE_3Co_{11}B_4$									
RE(1a)	$2RE_e$ $6Co_c$	0.49	−0.24	10	–	4.8	–	740	–
	$12Co_i$	0.19	−0.09						
RE(2e)	$1RE_a$ $1RE_e$ $6Co_g$	0.49	−0.24	–	–	–	–	–	–
	$6Co_i$ $6B_h$	0.07	−0.04						
Co(2c)	$3RE_a$ $3Co_c$	0.53	−0.26	51	54	5.0	5.3	–	133
	$6Co_g$	0.13	−0.07						
Co(3g)	$4RE_e$ $4Co_g$	0.18	−0.85, 0.29	27	9	2.7	0.9	230	134
	$2Co_i$ $4B_h$	−0.02	−0.12, 0.07						
Co(6i)	$2RE_a$ $2RE_e$ $2Co_c$	0.22	−0.91, 0.29	54	18	5.3	1.8	244	173
	$4Co_i$ $1Co_g$ $2B_h$	−0.02	−0.17, 0.10						
B(4h)	$3RE_e$ $6Co_g$	−0.52	0.26	–	9.3	–	0.68	–	–
	$4B_h$	−0.26	0.13						
$RE_2Co_7B_3$									
RE(1a)	$2RE_e$ $6Co_c$	0.52	−0.26	10	–	4.8	–	385	–
	$12Co_{i1}$	0.14	−0.07						
RE(1b)	$2RE_e$ $12Co_{i2}$	0.52	−0.26	–	–	–	–	–	–
	$6B_d$	0.02	−0.01						

(continued)

TABLE 2 *(continued)*

Site	Nearest neighbours	B^{c}_{dip} (T)	B^{a}_{dip} (T)	ν (MHz)		$\lvert B_e \rvert$ [T]		T_{tr} (μs)	
				Y	Gd	Y	Gd	Y	Gd
RE(2e)	$1RE_a$ $1RE_b$ $6Co_{i1}$	0.52	−0.26	–	–	–	–	–	–
	$6Co_{i2}$ $6B_h$	0.08	−0.04						
Co(2c)	$3RE_a$ $3Co_c$	0.53	−0.26	51	54	5.0	5.3	111	178
	$6Co_g$	0.10	−0.05						
Co($6i_1$)	$2RE_a$ $2RE_e$ $2Co_c$	0.24	−0.93, 0.29	57	18	5.6	1.8	–	201
	$4Co_{i1}$ $1Co_{i2}$ $2B_h$	−0.02	−0.13, 0.08						
Co($6i_2$)	$2RE_b$ $2RE_e$ $1Co_{i1}$	0.19	−0.88, 0.29	27	9	2.7	0.9	95	–
	$4Co_{i2}$ $2B_d$ $2B_h$	−0.03	−0.08, 0.06						
B(2d)	$3RE_b$ $6Co_{i2}$	−0.53	0.27	–	9.7	–	0.71	–	101
	$3B_h$ $3B_d$	−0.21	0.10						
B(4h)	$3RE_e$ $3Co_{i1}$ $3Co_{i2}$	−0.52	0.26	–	8.5	–	0.62	–	137
	$3B_h$ $1B_d$	−0.19	0.09						
$GdCo_3B_2$									
RE(1a)	$2RE_a$ $6B_c$	−0.80	−0.40	–	40.5^1	–	31.1	–	1850
	$12Co_g$			–	53.0^2	–		–	1380
Co(3g)	$4RE_a$ $4B_c$	0.20	−0.98, 0.34	–	14	–	1.4	–	530
	$6Co_g$								
B(2c)	$4RE_a$ $5B_c$	0.54	0.27	–	7.6	–	0.56	–	412
	$6Co_g$								

The values of B_{dip} are calculated for the magnetic moments along c and a axes and projected on the directions of atomic moments (resulting magnetization in the case of boron sites): upper row, gadolinium contributions; lower row, cobalt contributions. The atoms corresponding to the second values of B^{a}_{dip} have a two times larger population than those with the first value. The superscripts 1 and 2 at the resonant frequencies denote the ^{155}Gd and the ^{157}Gd resonances respectively.

The hyperfine field of the S state gadolinium ion does not include an orbital contribution. The hyperfine fields at the nuclei of the nonmagnetic atoms of yttrium and boron are almost entirely of transferred origin.

The calculations of the dipolar fields have been carried out for various directions taking the values of the magnetic moment $\mu_{\mathrm{Gd}} = 7\mu_B$, $\mu_y = 0$ and the average values $\mu_{\mathrm{Co}} = 1.7\mu_B$, $1\mu_B$, $0.8\mu_B$, $0.6\mu_B$ and 0 for $RECo_5$, $RECo_4B$, $RE_3Co_{11}B_4$, $RE_2Co_7B_3$ and $RECo_3B_2$ respectively. The contributions of all atoms within a sphere of radius 8 Å were taken into account.

The maximum absolute value that can be reached for the dipolar fields at a given site amounts to 1.2 T. Dependent on the directions of the magnetic moments within the plane perpendicular to the c axis, three different values of the dipolar field become possible for all sites except the 2c sites. The variation in B_{dip} at a given site can be as large as 1.8 T. The difference in dipolar fields between the alignment of the magnetic moments along the c axis and perpendicular to it amounts to 1.7 T, which corresponds to about 17 MHz on the frequency scale.

The values of B_{dip} collected in Table 2 represent the components of the dipolar field in the easy magnetization direction oriented either along the c or along the a axis.

3.1. Gadolinium-based compounds

The zero applied field NMR signal observed in magnetically ordered materials usually originates from domain walls. However, signals originating from domains were also observed in recent experiments made on $RECo_5$ compounds under applied magnetic fields [11, 12].

The positions of the ^{59}Co resonance lines of $GdCo_5$ observed by us at 48 MHz and 72 MHz are in good agreement with the values +6 T and −7 T (60 MHz and 70 MHz respectively) obtained by extrapolation of the values reported in ref. 11 to zero field. The 48 MHz and 72 MHz lines can therefore be assigned to the 2c and 3g sites respectively. These zero field resonance lines can be interpreted as being domain wall edge (DWE) signals. The directions of the magnetic moments in the DWE of $GdCo_5$, being a compound with an easy c axis, are close to the directions in the domains themselves, *i.e.* parallel to the c axis.

The resonance lines of the gadolinium-based compounds are narrower than those of yttrium-based compounds. As the dipolar fields alone can give rise to an 18 MHz splitting of the resonance lines of the 6i and 3g sites when the magnetic moments are perpendicular to the c axis this result can be taken to be in favour of the DWE character of the NMR signals of $GdCo_4B$, $Gd_3Co_{11}B_4$ and $Gd_2Co_7B_3$ as well.

The 54 MHz line observed in $Gd_2Co_7B_3$ and $Gd_3Co_{11}B_4$ is not observed in the spectrum of $GdCo_3B_2$. Instead, two weak narrow lines at 40.5 MHz and 53 MHz, as well as a broad intense line with maxima at 7.6 MHz, 14 MHz and 20 MHz, are detected. The weak, narrow lines at 40.5 MHz and 53 MHz with much longer relaxation times T_{tr} are assigned to the ^{155}Gd and ^{157}Gd resonances respectively. The corresponding effective field amounts to 31.1 T. This value is only slightly smaller than the core polarization term (33.2 T) which shows that B_{loc}, B_s and B_N are probably of minor importance.

The 54 MHz line of $Gd_2Co_7B_3$ and $Gd_3Co_{11}B_4$ can be assigned to the 2c sites in a similar way as the 48 MHz line in $GdCo_5$. This line is probably overlapped with a strong 58 MHz line in $GdCo_4B$. Its shift to higher frequencies between $GdCo_5$ and $GdCo_4B$ can be explained by the replacement of the six nearest-neighbour Co(3g) atoms with six Co(6i) atoms. The 6i atoms have two nearest-neighbour boron atoms and are assumed to carry much smaller magnetic moments than the 3g atoms in $GdCo_5$, so that the magnetic moment of the 2c site is supposed to change between $GdCo_5$ and $GdCo_4B$ but to remain the same in $Gd_3Co_{11}B_4$ and $Gd_2Co_7B_3$ where the environments of the 2c site are similar.

The 3g site of $RECo_5$ corresponds to the 6i site in $RECo_4B$ having two of the neighbouring cobalt atoms replaced by boron. The strong 58 MHz line of $GdCo_4B$ can therefore be assigned to the 6i site. The replacement of one neighbouring 6i cobalt atom by a Co(3g) atom in $Gd_3Co_{11}B_4$ and $Gd_2Co_7B_3$ is thought to lead to a further decrease in the magnetic moment on this site, because the Co(3g) atoms in the compounds have four boron neighbours at a very close distance (2.1 Å) and are supposed to carry a vanishing magnetic moment. Consequently, a much lower hyperfine field of a predominantly spin origin is expected and the strongest 18 MHz resonance lines of $Gd_3Co_{11}B_4$ and $Gd_2Co_7B_3$ can be assigned to the 6i and $6i_1$ sites respectively.

A weaker 9 MHz line of $Gd_3Co_{11}B_4$ we assigned to the 3g site and a stronger 9 MHz line of $Gd_2Co_7B_3$ to the $6i_2$ site with an environment similar to that of 3g in $Gd_3Co_{11}B_4$.

The very narrow peaks on the low frequency lines at 7.6 MHz in $GdCo_3B_2$, 8.5 MHz and 9.7 MHz in $Gd_2Co_7B_3$ as well as at 9.3 MHz in $Gd_3Co_{11}B_4$ and 14 MHz in $GdCo_4B$ can be assigned to ^{11}B resonances. The corresponding effective fields amounting to 0.56 T, 0.62 T, 0.71 T, 0.68 T and 1.0 T are close to the values of the dipolar fields at the boron sites: 0.54 T at the 2c site in $GdCo_4B$, 0.74 T at the 2d site in $Gd_3Co_{11}B_4$, 0.71 T and 0.78 T at 4h sites in $Gd_2Co_7B_3$ and 0.89 T at the 2c site in $GdCo_3B_2$.

The peak at 20 MHz as well as the low frequency shoulder of the main 14 MHz line in $GdCo_3B_2$ have similar positions to the 6i lines in $Gd_3Co_{11}B_4$ and $Gd_2Co_7B_3$ and can be interpreted as caused by site interchange of boron atoms into cobalt layers [18]. The effect can lead to the appearance of local cobalt environments of the 6i type in this compound.

3.2. Yttrium-based compounds

Much more structured spectra than those of the gadolinium-based compounds have been obtained for most of the yttrium-based compounds studied. The reason is that in this case the NMR signal originates from planes perpendicular to the c axis. For a magnetization direction perpendicular to the c axis one expects a splitting of the low symmetry cobalt sites such as 6i, $6i_1$, $6i_2$ and 3g into two or three magnetically inequivalent sites, which leads to a differentiation of the effective fields. The differences between the dipolar fields can already give rise to an 18 MHz splitting of the resonance line of a given site.

The NMR spectrum of YCo_5 consists of an intense broad line at 93 MHz and a narrow line at 21.3 MHz located on top of a broad background. The narrow line, according to previous reports, can with confidence be assigned to the ^{89}Y resonance. The previously reported ^{59}Co spectra [6–8, 11, 12] are characterized by a large scattering of the resonance line positions in the range from below 100 MHz to 180 MHz. The high frequency lines, often misinterpreted as belonging to the $RECo_5$ compounds, are actually impurity effects caused by the presence of small amounts of RE_2Co_{17}.

Two resonance lines have been observed in the NMR measurements under applied field [11]. After extrapolation to zero field the hyperfine field values are approximately -9.2 T and $+1.5$ T (93 MHz and 15 MHz respectively). The strong line observed by us at 93 MHz and the broadened line at about 20 MHz are in good agreement with the above values.

According to ref. 11 the 93 MHz line has to be assigned to the 3g position and the broad background at about 20 MHz can be assigned to the Co(2c) site.

The spectrum of YCo_4B consists of an intense line at about 30 MHz, a weaker and broader line at about 48 MHz and a weak line at about 10 MHz. In a previously reported spectrum [19] we did not observe the 10 MHz line and the 48 MHz line had a stronger overlap with the 30 MHz line. According to the previous interpretation the 30 MHz and the 48 MHz lines have to be assigned to the 6i and 2c sites respectively. The 10 MHz line on the basis of its low intensity and approximately three times longer relaxation time T_2 can be assigned to the superposition of the ^{89}Y and ^{11}B signals. The corresponding ^{11}B effective field $B_e = 0.73$ T is much larger than the dipolar field produced by cobalt atoms at the boron site which amounts to 0.36 T. This is an indication of the presence of a significant contribution to B_N arising from the magnetic cobalt neighbours. This contribution is supposed to be partially cancelled in the gadolinium-based compound by the gadolinium contribution to B_N, leaving effective field values for ^{11}B close to those of the dipolar field.

The ^{89}Y resonance contributing to the 11 MHz line corresponds to an effective field of 5.3 T. This means a 47% reduction in comparison with YCo_5. The 11 MHz line, exhibiting decreasing intensity in the samples $Y_3Co_{11}B_4$ and $Y_2Co_7B_3$, can be assigned to the Y(1a) sites since their abundance decreases with increasing boron content. The nearest-neighbour shell of the 1a site consists of 2Y, $6Co_c$ and $12Co_i$ atoms.

The effective field at yttrium nuclei is almost entirely of transferred (B_N) origin. Assuming it to be proportional to the surrounding cobalt moments, one derives that there is 47% reduction in the average cobalt moment between YCo_5 and YCo_4B. This compares favourably with bulk magnetization data revealing a 41% reduction. The hyperfine fields at the yttrium sites b and e in the more boron-rich compounds are significantly reduced by the presence of six boron nearest neighbours to these sites. The effect of a drastic reduction of the yttrium hyperfine field by boron, carbon or nitrogen neighbour atoms has been reported by us recently [20, 21].

Since the compound YCo_4B possesses a planar anisotropy [15], the NMR signal arises from the cobalt moments in the in-plane type domain walls.

The spectrum of the $Y_3Co_{11}B_4$ compound consists of a broad intense line centered at 54 MHz, two overlapping weaker lines at 27 and 32 MHz, weak lines at 84 and 91 MHz and a very weak line at 11 MHz. The 91 MHz line can be assigned to the $RECo_5$-type 3g environments appearing in the compound as a result of boron intermixing. The 84 MHz peak can be interpreted as originating from the Co_2B present as a spurious phase.

In a way similar to that for the gadolinium-based compound series we assign the strongest line of $Y_3Co_{11}B_4$ centred at 54 MHz, and having a broad slope to the high frequency side of the spectrum, to the 6i site which has a changed environment with respect to YCo_4B. The Co(6i) line is supposed to overlap a three times weaker Co(2c) signal which, in analogy to the gadolinium-based compounds, is thought to be at a similar position in YCo_4B, $Y_3Co_{11}B_4$ and $Y_2Co_7B_3$ compounds. The 51 MHz peak of $Y_2Co_7B_3$ can consequently be assigned to the 2c site and the broad high frequency part with peaks at 57 MHz and 70 MHz to the $6i_1$ site. A weaker double line at 27–32 MHz of $Y_3Co_{11}B_4$ can be assigned to the 3g site and a relatively strong 27–40 MHz signal of $Y_2Co_3B_7$ to the $6i_2$ site.

Recent magnetic measurements have shown that no magnetic order is present in YCo_3B_2 down to 4.2 K [22]. In order to verify this result we have performed NMR measurements at a fixed frequency of 33 MHz under applied magnetic fields up to 6.5 T and at the temperatures 4.2 K and 1.2 K. The spectra obtained consist of two lines. As may be seen from Fig. 4 the maximum of the stronger line lies at $B = 3.283$ T at both temperatures. The weaker line is about three times narrower and its maximum in both cases corresponds to $B = 2.427$ T. On the basis of the positions and the relative intensities of the lines one can assign the stronger line at 3.28 T to the ^{59}Co resonance and the weaker line to the ^{11}B resonance.

The much larger width and asymmetry of the cobalt line can be attributed to the effect of the quadrupole interaction of ^{59}Co, which has a nuclear quadrupole moment much larger than that of ^{11}B. Furthermore, the local symmetry at the cobalt site is lower than that of the boron site. The positions of the centres of gravity of the resonance lines correspond to 3.274 T and 2.427 T for cobalt and boron respectively.

Taking the gyromagnetic ratio for ^{59}Co equal to 10.103 MHz T^{-1}, one obtains for the frequency 33 MHz a resonance field $B_0 = 3.266$ T. The relative change in the resonance frequency is due to the Knight shift, usually denoted by K, caused by the polarization of the conduction electrons in the applied magnetic field:

$$K = \frac{\nu - \nu_0}{\nu} \tag{4}$$

The obtained value of K for cobalt amounts to $-0.5\% \pm 0.3\%$ at both temperatures.

In a similar way, using the value 13.660 MHz T^{-1} for the gyromagnetic ratio of ^{11}B, one finds $B_0 = 2.416$ T. This corresponds to the value $K = -0.5\% \pm 0.2\%$, which is also temperature independent.

On the basis of the sign and magnitude of K one can deduce that the dominant contribution to the Knight shift is the core polarization term. The temperature independence of K can be interpreted on the basis that YCo_3B_2 as well as YCo_2 are Pauli paramagnets.

The differences between the line positions of the gadolinium- and yttrium-based $RECo_5$ compounds are 28 MHz and 21 MHz for the 2c and 3g sites respectively. These differences cannot be explained exclusively by the dipolar contribution of gadolinium moments, which can give rise to shifts of 7 MHz only. The differences have therefore to be attributed to the contribution of the polarization of conduction electrons by the gadolinium moments B_N(Gd). Correcting the values of the dipolar field produced by gadolinium moments only, one obtains 2.1 T for B_N(Gd) at both the 2c and the 3g cobalt sites. The positive sign of this contribution corresponds to its direction parallel to the overall magnetization, *i.e.* parallel to the cobalt moments.

3.3. Relation to the magnetocrystalline anisotropy

From a comparison of the cobalt effective fields in those yttrium- and gadolinium-based compounds that have different easy magnetization directions one may evaluate the anisotropy of cobalt hyperfine fields. For this purpose, however, one needs to know the value of the gadolinium contribution to B_N. Assuming a negative sign of B_e in $RECo_4B$ and taking for B_N(Gd) the same value as in $GdCo_5$, *i.e.* +2.1 T, by subtracting the values of the dipolar contributions one obtains the difference in B_{orb} between the *c* plane and the *c* axis moment alignment. The values of ΔB_{orb} amount to +3.6 T and −5.2 T for 2c and 6i sites respectively in $RECo_4B$. The values of ΔB_{orb} evaluated in a similar way for $RE_3Co_{11}B_4$ amount to +3.1 T, −1.1 T and +0.5 T for the 2c, 6i and 3g sites respectively. However, because of the assumptions made in estimating these values we will not attempt to evaluate on this basis the anisotropies of orbital moments and the corresponding differences in spin–orbit interaction energies contributing to the anisotropy energies of the cobalt sites.

The opposite anisotropy behaviours of YCo_4B and $GdCo_4B$ mean that gadolinium contributes also to the magnetocrystalline anisotropy. The S state of the gadolinium ion excludes crystal field induced anisotropy contributions. However, the anisotropy of the magnetic dipolar interaction because of its large magnetic moment of $7\mu_B$ can be significant.

One may use the difference in the dipolar fields between the two moment directions (perpendicular and parallel to the *c* axis) for estimating the magnitude of the corresponding dipolar energy difference. Taking the average over both gadolinium sites in the structure one has $\Delta B_{dip} = 0.79$ T, which means a value of 77 J kg^{-1} for the anisotropy energy of the dipolar interaction of gadolinium. The positive value denotes that the easy direction would be along the *c* axis.

Applying the same procedure for the dipolar fields produced by gadolinium at both cobalt sites and taking an average cobalt moment of $1.0\mu_B$ one calculates this contribution to be equal to 51 J kg^{-1}.

The recently reported value of the anisotropy constant K_1 for YCo_4B is −46 J Kg^{-1} [23]. Using this value as an approximation for the anisotropy energy of the cobalt sublattice anisotropy in $GdCo_4B$ and adding the two dipolar contributions one finds the value 82 J kg^{-1} for the total magnetocrystalline anisotropy in $GdCo_4B$. The experimental value of K_1 obtained from magnetic measurements is 50.6 J kg^{-1} [24].

A preferred magnetization direction along the *c* axis due to dipolar interaction involving the gadolinium moments is expected also for the other gadolinium compounds of the series investigated. However, a lack of bulk anisotropy data for the compounds with higher boron concentration does not allow a meaningful comparison of the experimental and theoretical differences of the anisotropy energies between gadolinium- and yttrium-based compounds.

4. Conclusions

The NMR spectra obtained for the compounds YCo_5, $GdCo_5$, $GdCo_4B$, $Gd_3Co_{11}B_4$, $Gd_2Co_7B_3$ and $GdCo_3B_2$ having their easy magnetization direction along the *c* axis are found to be of DWE origin. The NMR signal of the corresponding yttrium compounds having planar anisotropy is found to originate from in-plane-type domain walls.

The hyperfine fields on the various cobalt sites in all these compounds are determined almost entirely by the local environments of the sites. For similar types of sites that keep the same symmetry and environment they are almost independent of the compound within the series, *i.e.* independent of the boron concentration.

The difference in cobalt effective fields between gadolinium and yttrium compounds that have the same type of anisotropy can be explained by the gadolinium contributions to the dipolar field B_{dip} and transferred field B_N. The value of B_N is 2.1 T at both cobalt sites in $GdCo_5$.

The variations in the cobalt hyperfine fields observed with increasing number of boron neighbours and with changing easy magnetization direction are attributed to the simultaneous changes in the spin and orbital contribution to the cobalt moment.

The observed effective fields on the boron sites are below 1 T. These values and their differences between gadolinium- and yttrium-based compounds can be explained by B_{dip} and B_N contributions, being of comparable magnitude.

No magnetic order has been detected in YCo_3B_2 down to 1.2 K. A temperature-independent Knight shift indicates that this compound is a Pauli paramagnet.

The difference in the anisotropy energy between isostructural gadolinium and yttrium compounds has tentatively been explained in terms of differences in dipolar energies, which were estimated to be as large as 128 J kg^{-1} in $GdCo_4B$.

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