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^{155}Gd Mössbauer effect and magnetic properties of novel RT_2B_2C compounds with T≡Ni, Co

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Abstract

We have prepared the compounds $GdNi_2B_2C$ and $GdCo_2B_2C$ and investigated their magnetic properties by means of ^{155}Gd Mössbauer spectroscopy. From the temperature dependence of the hyperfine field, we derived that these two compounds give rise to magnetic ordering at 5.5 ± 0.5 K and 21 ± 1 K respectively. Large values of the electric field gradient V_{zz} were found, reminiscent of compounds of the related $ThCr_2Si_2$ type. A quantitative explanation of the origin of these field gradients is presented by ab initio band structure calculations. The experimental values of V_{zz} have been used to estimate values for the second-order crystal field parameter in $GdNi_2B_2C$ ($A_2{}^0 = -428Ka_0{}^{-2}$) and $GdCo_2B_2C$ ($A_2{}^0 = -346Ka_0{}^{-2}$).

Keywords: Mössbauer effect; Magnetic properties; Crystal field; Electric field gradient; Band structure calculations

1. Introduction

Recently, a new class of quaternary superconducting materials was discovered by Cava et al. [1] who showed that in $LuNi_2B_2C$ the superconducting transition temperature can reach values as high as 16.6 K. In compounds of the type RNi_2B_2C, the superconducting transition temperature becomes strongly lowered when R carries a magnetic moment owing to the pair-breaking effect of the rare earth spin [2]. The largest effect in this respect is expected for $GdNi_2B_2C$, for which no magnetic data have been reported yet. For this reason we have studied the magnetic properties of $GdNi_2B_2C$ by means of ^{155}Gd Mössbauer spectroscopy. For comparative purposes, we also prepared the isotypical compound with Co and included this material in our investigation. A detailed study of the magnetic properties of these compounds investigated by other techniques will be given elsewhere [3].

The prime reason for our interest in these compounds is their crystal structure, which is related to the tetragonal $ThCr_2Si_2$ type. The Gd compounds of several series of compounds of this type (GdT_2X_2 with T≡3d, 4d, 5d, X≡Si, Ge, Sn, Sb) have been used by us in several investigations [4–7] to show that the electric field gradient at the nuclear Gd site changes its sign when passing through a d transition metal series. A similar behaviour is expected for the second-order crystal field parameter $A_2{}^0$ and the macroscopic anisotropy constant. It is of substantial interest to investigate whether the introduction of carbon atoms into the parent $ThCr_2Si_2$-type structure leads to very different values of the electric field gradient.

2. Experimental details

The samples used in the present investigation were prepared by arc melting and subsequent annealing at 1050 °C for at least 24 h. The quality of the samples was verified by X-ray diffraction. The $GdNi_2B_2C$ sample was found to be almost single phase. The $GdCo_2B_2C$ sample was found to contain an amount of an unidentified second phase, negligibly small, however, to hamper the Mössbauer and magnetic measurements. The crystal structure of the GdT_2B_2C compounds was identified as the tetragonal type (space group *I*4/*mmm*) reported recently by Siegrist et al. [2] for RNi_2B_2C compounds. From a refinement of the corresponding

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X-ray diagram, the lattice parameters of $GdCo_2B_2C$ were found to be $a = 3.548$ Å and $c = 10.271$ Å.

The Mössbauer spectra of $GdNi_2B_2C$ and $GdCo_2B_2C$ were obtained by means of the 86.5 keV resonance of ^{155}Gd. The source consisted of neutron-irradiated $SmPd_3$ prepared with Sm enriched to 98% in ^{154}Sm [8].

3. Results and discussion

3.1. ^{155}Gd Mössbauer spectroscopy

Representative results of the ^{155}Gd Mössbauer experiments on $GdNi_2B_2C$, corresponding to four different temperatures (4.2 K, 15 K, 20 K, 25 K), are presented in Fig. 1. The spectra were analysed by means of a least-squares fitting procedure based on the diagonalization of the full nuclear hamiltonian and using a transmission integral. The source linewidth was constrained to 0.37 mm s^{-1}, whereas the absorber linewidths are listed in Table 1. The independently refined variables consisted of the isomer shift IS, the effective hyperfine field $\mu_0 H_{eff}$, and the quadrupole splitting QS which is proportional to the crystalline electric field gradient (EFG) V_{zz} at the nucleus: $QS = (1/4)\, eQV_{zz}(3\cos^2\theta - 1)$ (the value for the nuclear quadrupole moment Q was taken from Ref. [9]). Values of the various physical quantities obtained from the Mössbauer spectra in Fig. 1 are listed in Table 1.

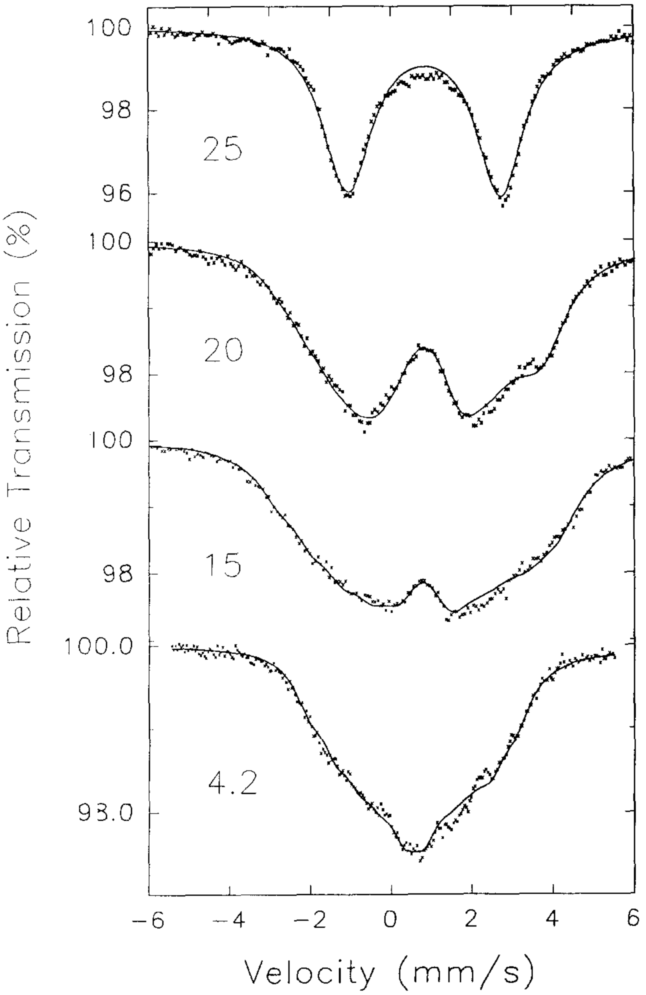

Fig. 1. Mössbauer spectra for $GdNi_2B_2C$ at the temperatures indicated (kelvin).

Table 1
Hyperfine parameters for $GdNi_2B_2C$

T (K)	V_{zz} ($\times 10^{21}$ V m^{-2})	$\mu_0 H_{eff}$ (T)	θ (deg)	IS (mm s^{-1})	Γ (mm s^{-1})
25	11.9	0.0	–	0.54	0.49
23	11.8	−0.8	±90	0.53	0.49
22	11.8	−1.7	±90	0.53	0.49
21	11.8	−5.8	90	0.53	0.49
20	11.9	−17.3	90	0.54	0.49
15	11.9	−22.3	64	0.53	0.49
4.2	12.1	−27.9	56	0.56	0.49

Special attention should be paid to the quite substantial values of the field gradient V_{zz}, which are of the same order of magnitude as the values found for instance in some $ThCr_2Si_2$-type compounds, the crystal structure of which is related to the crystal structure of the RT_2B_2C compounds [1]. However, the values of V_{zz} are large when compared with V_{zz} values of $GdNi_2Si_2$ ($V_{zz} = -1.2 \times 10^{21}$ V m^{-2}) and $GdCo_2Si_2$ ($V_{zz} = -5.2 \times 10^{21}$ V m^{-2}) [4]. The existence of large EFGs can be of great importance in connection with the magnetic anisotropy of the R sublattice. It is interesting to observe that above the magnetic ordering temperature the value of V_{zz} appears to be larger than below. This behaviour of V_{zz} has been observed in several other Gd intermetallic compounds and will be discussed extensively in a forthcoming paper [10].

The temperature dependence of the hyperfine field in $GdNi_2B_2C$ is displayed in Fig. 2. From these data it can be inferred that magnetic ordering in this compound sets in below 21 ± 1 K.

It is important to note the high values for the observed absorber linewidth Γ, listed in Table 1. These values are about two to four times the values of the natural linewidth Γ_{nat}, which suggests the presence of lattice imperfections, i.e. ions of different elements might occupy the same lattice sites. Considering the size of the different ions, only interchange of B and C ions, possibly accompanied by fluctuations in the stoichiometry, seems to be a realistic suggestion in this respect. It is also possible, however, that the C positions are not fully occupied. Unfortunately, because of the low X-ray scattering of B and C, it is impossible to distinguish between these two possibilities by X-ray diffraction.

Finally, it should be noted that IS is almost a constant for all different spectra of $GdNi_2B_2C$ taken at different temperatures.

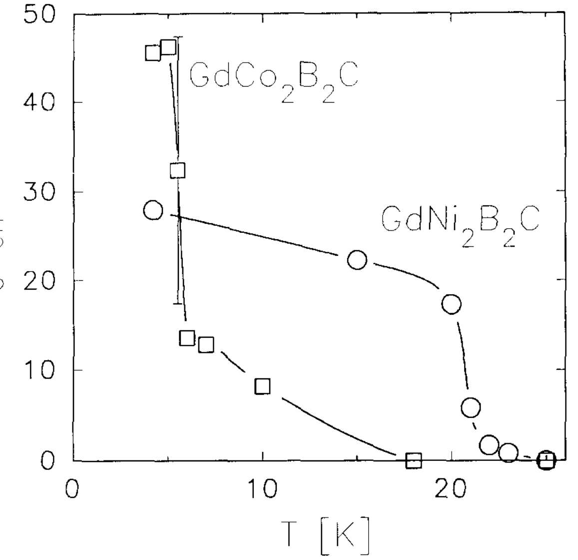

Fig. 2. Strength of the effective hyperfine field of $GdNi_2B_2C$ and $GdCo_2B_2C$ as a function of temperature.

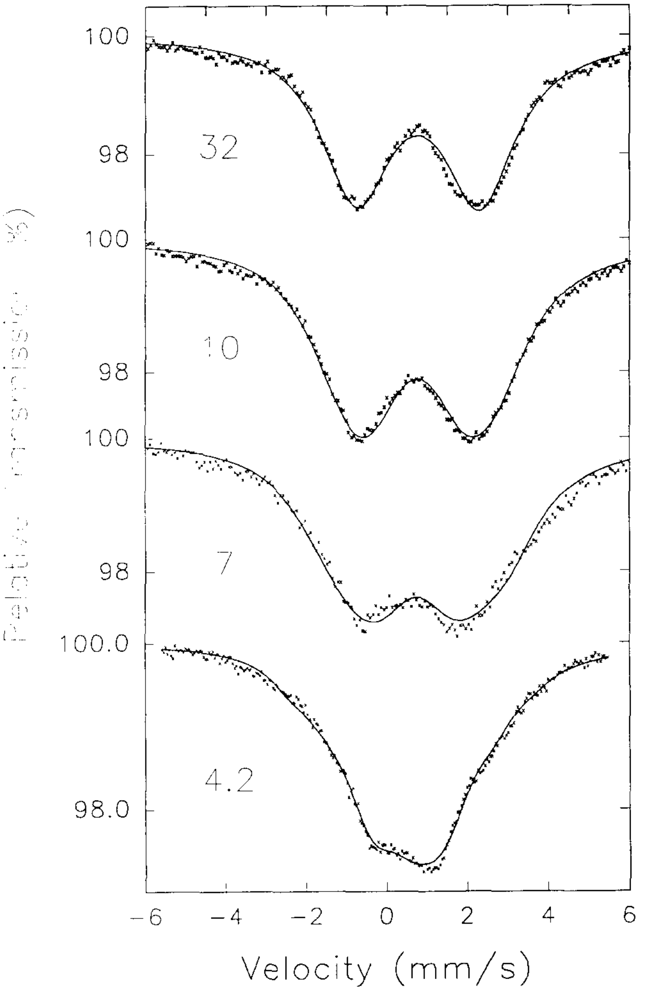

Fig. 3. Mössbauer spectra for $GdCo_2B_2C$ at the temperatures indicated (kelvin).

In Fig. 3, the Mössbauer spectra of $GdCo_2B_2C$ at four different temperatures are presented (T = 4.2 K, 7 K, 10 K, 32 K). The hyperfine parameters, derived from these spectra in a way similar to the case of $GdNi_2B_2C$, are listed in Table 2.

In $GdCo_2B_2C$, the field gradients at particular temperatures are slightly smaller than the field gradients observed in $GdNi_2B_2C$. An interesting observation is that in $GdCo_2B_2C$ the field gradients vary significantly with temperature, more than in $GdNi_2B_2C$. A similar statement applies to the hyperfine field $\mu_0 H_{eff}$.

At 4.2 K, $\mu_0 H_{eff}$ for $GdCo_2B_2C$ has an exceptionally large negative value of −45.6 T. Values reported for a large number of other Gd–3d intermetallics range from −40 T to +45 T (see, for example, Ref. [4]). The strongly negative $\mu_0 H_{eff}$ value in $GdCo_2B_2C$ suggests a large Gd–Gd exchange, which would be the result of a strong hybridization in this particular compound. Above 5 K, there is a sharp decrease in $\mu_0 H_{eff}$ to lower values. At temperatures higher than 6 K, there appear to be some short-range magnetic fluctuations, resulting in a sizeable $\mu_0 H_{eff}$, as can be seen from Fig. 2. From the temperature dependence of the hyperfine field, it can be derived that magnetic ordering in $GdCo_2B_2C$ occurs below about 5.5 ± 0.5 K. The spectrum taken at 5.5 K could be fitted on the basis of two significantly different sets of hyperfine parameters. Such a situation corresponds to relaxation effects and is quite usual for spectra measured at temperatures near the magnetic ordering temperature.

The isomer shifts listed in Table 2 are almost independent of temperature in the temperature range under investigation.

From the Mössbauer measurements it is clear that there has to be a fairly large number of lattice imperfections, although the crystal structure is found to be essentially single phase by X-ray diffraction.

With the Mössbauer linewidth as an indication of the number of imperfections, it may be concluded that there are more imperfections in the Co compound than in the Ni compound (the linewidth is largest for the Co compound). When there is an interchange of B

Table 2
Hyperfine parameters for $GdCo_2B_2C$

T (K)	V_{zz} ($\times 10^{21}$ V m^{-2})	$\mu_0 H_{eff}$ (T)	θ (deg)	IS (mm s^{-1})	Γ (mm s^{-1})
32	9.6	0.0	–	0.50	0.97
25	9.7	0.0	–	0.51	0.97
18	9.5	0	–	0.49	0.97
10	9.5	−8.2	90	0.50	0.97
7	9.4	−12.8	90	0.50	0.97
6	9.3	−13.6	82	0.52	0.97
5.5	7.4, 9.4	−47.4, −27.4	46	0.51	0.97
5	7.4	−46.3	42	0.52	0.97
4.2	7.4	−45.6	44	0.50	0.97

and C, or there is a C atom missing at a certain site, the magnetic interaction between the four nearest-neighbour Gd atoms may be influenced substantially. Probably, the strength or even the sign of the magnetic interactions is influenced. It is well known that when there is a certain randomness in the magnetic interactions between the magnetic ions, or the magnetic system is diluted, the long-range magnetic ordering temperature may be suppressed, and substantial short-range order may be present above this ordering temperature (e.g. Refs. [11–13]).

On the basis of the Mössbauer measurements, the Co compound shows the peculiarity of two different magnetic ordering phenomena: long-range order up to 5.5 ± 0.5 K and a region up to about 18 K where the hyperfine field has still sizeable values which may be explained in terms of short-range magnetic ordering. The Ni compound shows a much smaller short-range order regime, but it shows a long-range magnetic ordering at 21 ± 1 K (comparable with 18 K). The larger number of imperfections in the Co compound than in the Ni compound (as judged by the Mössbauer linewidth) and the larger amount of randomness in the magnetic interaction strength between the Gd moments resulting from that may explain the much lower long-range ordering temperature of the Co compound. In addition, it may provide a likely explanation for the presence of the short-range ordering regime in $GdCo_2B_2C$, while this regime is almost absent in $GdNi_2B_2C$.

The observed values of the absorber linewidth Γ are large and subject to the same considerations as the linewidths for $GdNi_2B_2C$. As in $GdNi_2B_2C$, the extensive broadening of the spectra of $GdCo_2B_2C$ might be attributed to lattice imperfections in the specimen.

3.2. *Ab initio calculation of the electric field gradient*

The EFG V_{zz} at the Gd nuclei reflects the asphericity of the electron charge density of (mainly) Gd 6p valence electrons in a region with a radius of about 2 Å around the atoms [4]. The large positive value of V_{zz} that is observed for $GdNi_2B_2C$, as well as for $GdCo_2B_2C$, indicates that the contribution to this charge density of orbitals pointing in a direction in the plane of the Gd–C layers, i.e. $6p_x$ and $6p_y$ orbitals, is much larger than that of $6p_z$ orbitals, pointing in the direction normal to the layers. This situation is quite different from those in the the structurally related $ThCr_2Si_2$-type compounds $GdNi_2Si_2$ and $GdCo_2Si_2$, where smaller negative V_{zz} values have been observed ($V_{zz} = -1.2 \times 10^{21}$ V m^{-2} and $V_{zz} = -5.2 \times 10^{21}$ V m^{-2} respectively). The large $6p_x$ and $6p_y$ contributions to the charge density around Gd atoms point towards the formation of covalent bonds with the C atoms in the basal plane.

We have analysed the origin of the EFG quantitatively by performing first-principles augmented spherical wave band structure calculations for $GdNi_2B_2C$. Ferromagnetic ordering for the magnetic moments was assumed, since no information is available yet on the true antiferromagnetic spin structure. For the present purposes, this assumption is not expected to yield serious errors, since it can be seen from Table 1 that the EFG of this system is almost independent of temperature. These calculations have been performed within the framework of a more extended study on the electronic structure of RTM_2B_2C and related compounds (R ≡ rare element, TM ≡ transition metal element) [14]. The total calculated moment (in μ_B per atom) on the Gd, Ni, B and C sites is 7.27, 0.03, 0.00, and −0.01 respectively. We have calculated the EFG using the method described in detail in Ref. [4], where the following expressions have been given for the electric field gradient in terms of the occupation numbers n_i of the three 6p and five 5d orbitals and the expectation values of the radial charge densities, within atomic spheres around Gd atoms with (in the present calculations) a radius of 1.91 Å:

$$\begin{aligned} V_{zz}(6\mathrm{p}) &= 7.74[\tfrac{1}{2}(n_x + n_y) - n_z]\langle r^{-3}\rangle_{6\mathrm{p}} \\ V_{zz}(5\mathrm{d}) &= 5.54[n_{x^2-y^2} + n_{\mathrm{xy}} - \tfrac{1}{2}(n_{xz} + n_{\mathrm{yz}}) - n_{3z^2-r^2}]\langle r^{-3}\rangle_{5\mathrm{d}} \end{aligned} \qquad (1)$$

The units of V_{zz} thus obtained are 10^{21} V m^{-2}, if the radial expectation value is expressed in atomic units. It should be noted that, in order to keep the notation as simple as possible, we have omitted the spin label. In Table 3, the calculated occupation numbers and radial expectation values have been given. It can be seen that the $\langle r^{-3}\rangle$ expectation value for 6p orbitals is much larger than for 5d orbitals, as is generally found [4]. As a consequence, V_{zz} is almost entirely determined by the asphericity of the on-site 6p charge density. The total calculated value of the EFG $V_{zz}^{\mathrm{calc}} = +12.8 \times 10^{21}$ V m^{-2} is in very good agreement with the experimental value $V_{zz}^{\mathrm{expt}} = +11.9 \times 10^{21}$ V m^{-2}.

Table 3
Results of augmented spherical wave calculations of the electric field gradient V_{zz} at the Gd nuclei in $GdNi_2B_2C$

	Spin ↑	Spin ↓
n_x $(=n_y)$	0.173	0.165
n_z	0.147	0.132
n_{x2-y2}	0.216	0.148
n_{xy}	0.304	0.278
n_{xz} $(=n_{yz})$	0.235	0.178
n_{3z2-r2}	0.285	0.227
$\langle r^{-3}\rangle_{6p}$ (a_0^{-3})	25.9	29.0
$\langle r^{-3}\rangle_{5d}$ (a_0^{-3})	1.83	1.44
$V_{zz}(6p)$ (10^{21} V m^{-2})	5.21	7.41
$V_{xx}(5d)$ (10^{21} V m^{-2})	0.00	0.16

The existence of such a high EFG can be of great importance in connection with the macroscopic magnetic anisotropy and with the occurrence of crystal field splittings in rare earth compounds of the RNi_2B_2C and RCo_2B_2C series. If we use the relation $-\omega V_{zz}$ (with $\omega=36$ when V_{zz} and $A_2{}^0$ are expressed in 10^{21} V m^{-2} and $Ka_0{}^{-2}$ [15]) we find $A_2{}^0=-346Ka_0{}^{-2}$ for compounds of the RCo_2B_2C series and $A_2{}^0=-428Ka_0{}^{-2}$ for the RNi_2B_2C series (at about 15 K). In this respect, it is also interesting to note that both the measured and the calculated V_{zz} values in $GdNi_2B_2C$ and $GdCo_2B_2C$ are comparable in magnitude with the field gradients observed in R–3d permanent magnetic materials such as $R_2Fe_{14}B$ [16], $Sm_2Fe_{17}N_3$ [17], and RCo_5 [18].

Another interesting aspect of the compounds under investigation is the large differences between the observed V_{zz} values in the $GdCo_2B_2C$ and $GdNi_2B_2C$ compounds and those reported for $GdCo_2Si_2$ and $GdNi_2Si_2$ compounds. The origin of this difference is to some extent analogous to that of a similar observation with respect to Sm_2Fe_{17} and $Sm_2Fe_{17}N_3$. In the latter case, the uptake of nitrogen by Sm_2Fe_{17} causes an increase in the V_{zz} value of about 100%. This effect is directly related to the nitrogen surrounding of the R ions in $Sm_2Fe_{17}N_x$ compounds. As mentioned earlier, the crystal structure of the RT_2B_2C compounds can be looked on as a "carbon-filled" variant of the $ThCr_2Si_2$ structure, and is characterized by the presence of C ions near the R sites in particular. In Sm_2Fe_{17}-based compounds, the effect of interstitial carbon on V_{zz} is analogous to the effect of interstitial nitrogen [19], and therefore the differences between the V_{zz} values in $GdCo_2B_2$ and $GdNi_2B_2$ and those in $GdCo_2B_2C$ and $GdNi_2B_2C$ may also be related to the presence of carbon surrounding the R ions in the latter compounds.

4. Conclusions

We have shown the existence of RCo_2B_2C compounds, with the same structure as the $GdNi_2B_2C$ compounds reported earlier [1,2].

^{155}Gd Mössbauer spectroscopy reveals the existence of high crystalline EFGs in both $GdCo_2B_2C$ and $GdNi_2B_2C$ and gives evidence for magnetic ordering at temperatures below 5.5 K and 23 K in $GdCo_2B_2C$ and $GdNi_2B_2C$ respectively. Furthermore, the observed linewidths suggest that both the $GdNi_2B_2C$ and the $GdCo_2B_2C$ specimens used in the present investigation are not completely homogeneous on an atomic scale.

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