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Magnetic properties of $Ce_{3-x}Gd_xCo_{11}B_4$ borides

N. Kervan [a,*], S. Kervan [a], H. Sözeri [b], A. Gencer [c]

[a] Nevşehir University, Faculty of Arts and Sciences, Physics Department, 50300, Nevşehir, Turkey
[b] TUBİTAK-UME, National Metrology Institute, P.O. Box 54, 41470 Gebze-Kocaeli, Turkey
[c] Ankara University, Faculty of Sciences, Physics Department, 06100, Beşevler, Ankara, Turkey

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ABSTRACT

The structure and magnetic properties of $Ce_{3-x}Gd_xCo_{11}B_4$ borides have been studied by X-ray powder diffraction (XRPD), magnetization and differential scanning calorimetry (DSC) measurements. X-ray analysis reveals that the compounds crystallize in the hexagonal $Ce_3Co_{11}B_4$-type structure with $P6/mmm$ space group. The substitution of Gd for Ce leads to an increase of the unit-cell parameter a and the unit-cell volume V, while the unit-cell parameter c decreases linearly. Magnetic measurements indicate that all samples are ordered magnetically below the Curie temperature. The Curie temperatures increase as Ce is substituted by Gd. The saturation magnetization at 4 K decreases upon the Gd substitution up to $x = 1$, and then increases.

1. Introduction

The ternary rare earth (R)–transition metal (T) borides attract considerable attention since they often exhibit very interesting magnetic properties [1–3]. For example, $R_2Fe_{14}B$ compounds (R = rare earth) are excellent materials for the production of high-energy permanent magnets [4]. The $R_3Co_{11}B_4$ compounds, where R is a rare earth, crystallize in hexagonal structure of $Ce_3Co_{11}B_4$-type having the space group $P6/mmm$ [5]. These compounds belong to the $R_{n+1}Co_{3n+5}B_{2n}$ (n = 0, 1, 2, 3, ∞) family. The unit cells of the $R_{n+1}Co_{3n+5}B_{2n}$ compounds are formed by alternative stacking of one layer of RCo_5 and n layers of RCo_3B_2 unit cells along the c-axis. As can be seen in Fig. 1, in $Ce_3Co_{11}B_4$-type structure (n = 2), the rare earth atoms occupy two types of sites (1a, 2e), the cobalt atoms are distributed over three different positions (2c, 3g, 6i) and boron atoms are located on one type of site (4h).

Previous investigations on $R_3Co_{11}B_4$ compounds have shown that $Ce_3Co_{11}B_4$ is ferromagnetically ordered while in the case of $Gd_3Co_{11}B_4$, a ferrimagnetic-type ordering was shown [6–9]. The Curie temperatures are 265 K for $Ce_3Co_{11}B_4$ and 460 K for $Gd_3Co_{11}B_4$, respectively. The compound $Gd_3Co_{11}B_4$ has also the compensation point T_{comp} at 433 K. This paper presents the effect of Gd substitution for Ce on the crystal structure and magnetic properties of $Ce_{3-x}Gd_xCo_{11}B_4$ compounds.

2. Experimental

The $Ce_{3-x}Gd_xCo_{11}B_4$ compounds with x = 0, 1, 2, and 3 were prepared by arc-melting of mixtures of Ce (99.9%), Gd (99.9%), Co (99.5%), and B (99.7%) in an argon atmosphere using a non-consumable tungsten electrode and a water-cooled copper hearth. The compound was re-melted several times to achieve a homogeneous composition. X-ray diffraction studies were carried out by using a Bruker D8 Advance diffractometer with Cu Kα radiation. The characterization of the samples by differential scanning calorimetry (DSC) was performed using DSC 2010 (TA Instruments) in an alumina box under protective nitrogen gas above room temperature. The heating ramp was run at 20 K/min. The magnetic properties of the $Ce_{3-x}Gd_xCo_{11}B_4$ compounds were studied by means of a SQUID magnetometer (Quantum Design) in the temperature range 4–400 K in magnetic fields up to 5 T. Magnetic measurements were conducted with powder samples fixed in the sample holder. The value of the Curie temperature (T_C) has been estimated from the minimum in the temperature derivative of the magnetization (dM/dT) versus temperature curve. The compensation temperature (T_{comp}) was defined by the minimum appearing in the M–T curve.

3. Results and discussion

The X-ray patterns confirm the existence of a hexagonal main phase having the $Ce_3Co_{11}B_4$-type structure with the space group $P6/mmm$ and small amounts of foreign phases. The lattice parameters a and c determined using the standard pattern matching method of the FULLPROF [10] program, c/a, and the unit-cell volume V for the $Ce_{3-x}Gd_xCo_{11}B_4$ samples at room temperature are shown in Fig. 2, while the refined unit-cell parameters a and c, c/a and unit-cell volume V are given in Table 1. It can be seen that substitution of Gd for Ce causes a linear increase in the lattice constant a and unit-cell volume V together with a linear decrease in the lattice constant c and c/a. The lattice parameters obtained for x = 0 and

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[*] Corresponding author. Tel.: +90 384 215 3900; fax: +90 384 215 3948.
E-mail address: nazmiye.kervan@nevsehir.edu.tr (N. Kervan).

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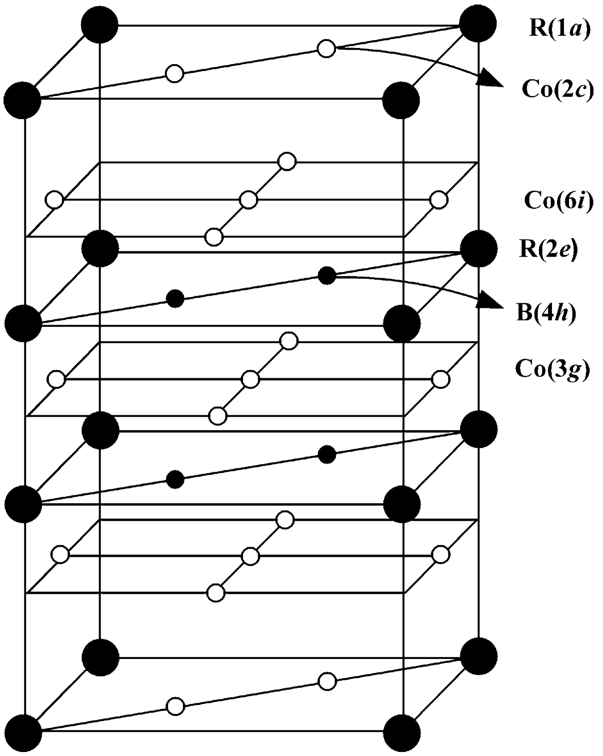

Fig. 1. The unit-cell of the $Ce_3Co_{11}B_4$-type structure.

Table 1
The lattice constants *a* and *c*, the unit-cell volume *V*, *c*/*a*, the Curie temperature (T_C), the compensation temperature (T_{comp}) and the saturation magnetization M_S for the $Ce_{3-x}Gd_xCo_{11}B_4$ compounds.

x	*a* (Å)	*c* (Å)	*V* (Å^3)	*c*/*a*	T_C (K)	T_{comp} (K)	M_S (μ_B/f.u.)
0	5.0433 (4)	9.9224 (6)	218.57	1.9674	256		2.10
1	5.0498 (4)	9.8988 (8)	218.61	1.9603	301	40	1.54
2	5.0671 (4)	9.8756 (6)	219.59	1.9490	376	286	6.39
3	5.0805 (4)	9.8327 (8)	219.80	1.9354	464	435	13.45

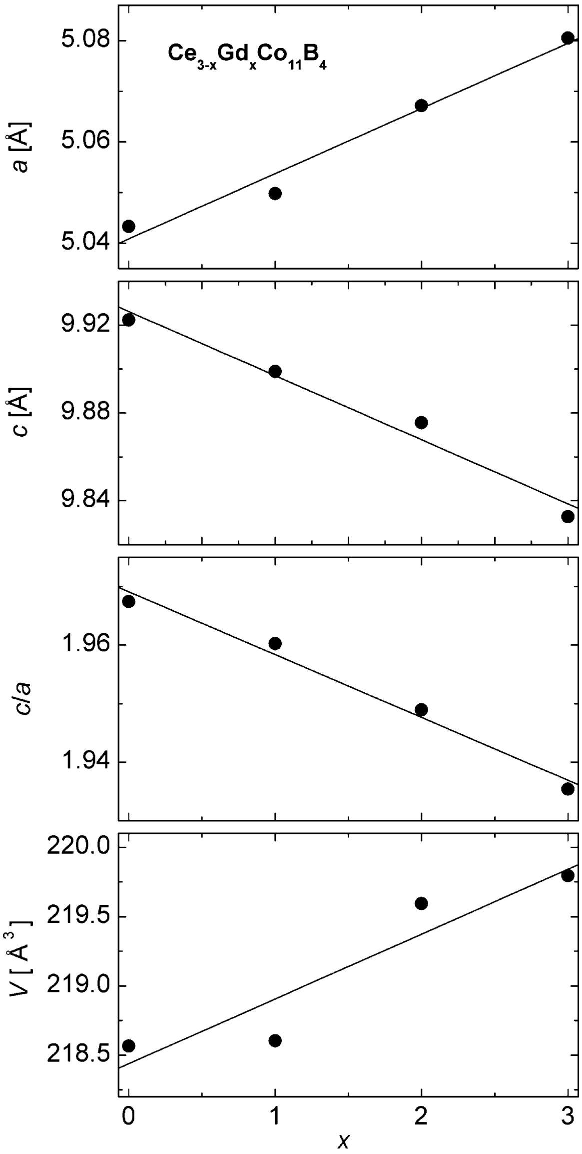

Fig. 2. Variation of the lattice constants *a* and *c*, *c*/*a*, and the unit-cell volume *V* with Gd concentration *x* at room temperature for the $Ce_{3-x}Gd_xCo_{11}B_4$ borides.

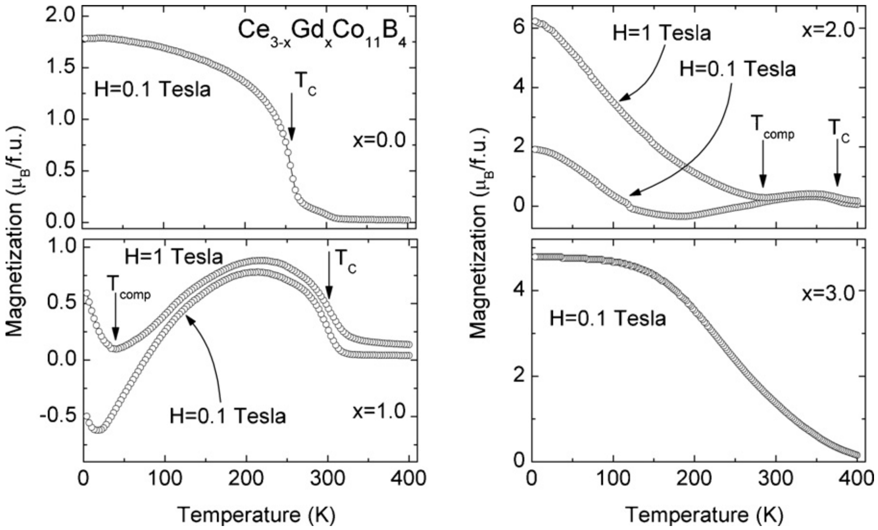

Fig. 3. Temperature dependence of magnetization for the $Ce_{3-x}Gd_xCo_{11}B_4$ compounds.

$x = 3$ are in good agreement with previously reported values in the literature [5,6,8,11,12].

The temperature dependence of the magnetization of the $Ce_{3-x}Gd_xCo_{11}B_4$ compounds in the temperature range 4–400 K in an applied field of 0.1 Tesla is shown in Fig. 3. It can be seen that all samples order magnetically. The magnetization as a function of temperature behaves differently for the different compositions. $Ce_3Co_{11}B_4$ is a ferromagnet below $T_C = 256$ K. The samples for $x \geq 1$ have a compensation point (T_{comp}). Bearing in mind that the magnetic moment of the *R* sublattice decreases more rapidly with increasing temperature than the magnetic moment of the Co sublattice and taking into account that the total magnetic moment of *R* sublattice increases with increasing Gd content *x*, the Co sublattice moment can cancel the *R* sublattice moment at higher temperatures. Therefore, the compensation temperature increases monotonously. The Curie temperatures increase with increasing Gd content *x*. As Ce is replaced by Gd, the exchange interactions in the system increase due to the larger Gd 4f localized moments. This behavior may be responsible for the increase in the Curie temperature. Similar behavior has been observed in the $(Gd_xY_{1-x})_3Co_{11}B_4$ [13].

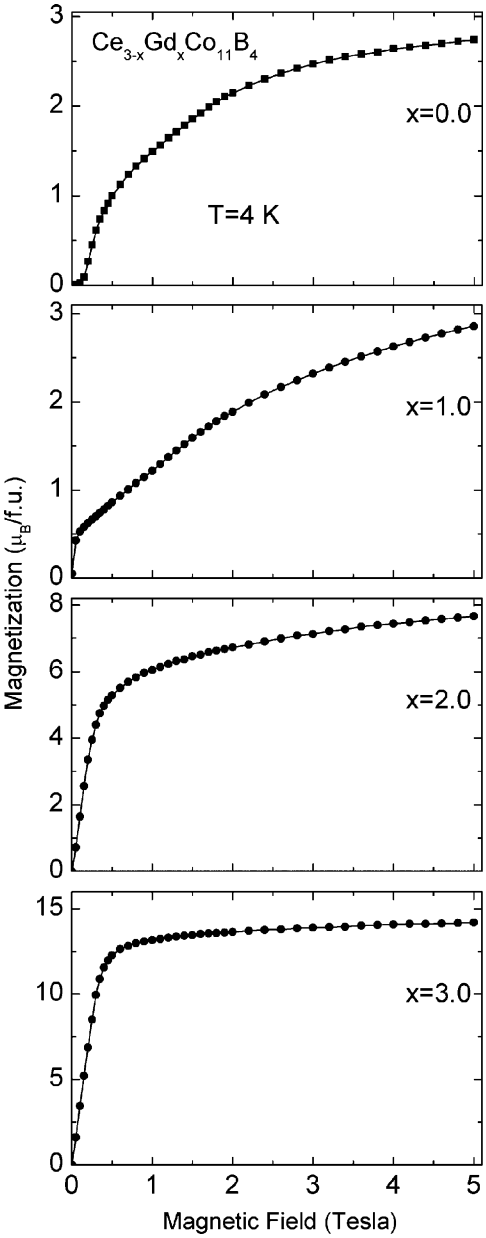

Fig. 4. The magnetization of $Ce_{3-x}Gd_xCo_{11}B_4$ borides as a function of applied field at 4 K.

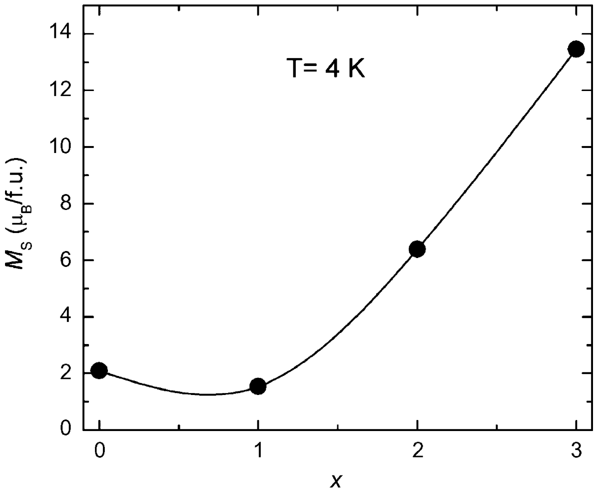

Fig. 5. The saturation magnetization M_S at 4 K.

Fig. 4 shows the magnetization of the $Ce_{3-x}Gd_xCo_{11}B_4$ compounds at 4 K as a function of applied magnetic field up to 5 Tesla. The values of saturation magnetization as a function of Gd concentration, extracted by extrapolating the high field part of magnetization down to the zero field, are presented in Fig. 5 and also listed in Table 1. In *R*–*T* intermetallic compounds, it is well established that the exchange interaction between the 3d spins of the *T* elements and the 4f spins of the *R* elements, exhibits ferromagnetic coupling for light *R* elements (less than half-full 4f shell), and antiferromagnetic or ferrimagnetic coupling for heavy *R* elements (more than half-full 4f shell) [14–16]. Therefore, the competition between the total magnetic moment of the rare earth sublattice and the magnetic moment of the Co sublattice occur. So, the saturation magnetization with increasing *x* at 5 K decreases up to the $x = 1$, and then increases. At about $x = 0.7$, the cobalt and rare earth magnetization in $Ce_{3-x}Gd_xCo_{11}B_4$ compounds compensate at 4 K. Similarly, at low temperatures, the compensation has been observed in the $(Gd_xY_{1-x})_3Co_{11}B_4$ compounds at $x = 0.31$ [13]. Assuming the free-ion magnetic moment value for Gd^{+3} (7 μ_B), the mean cobalt moment of 0.69 μ_B/Co was determined from the saturation magnetization at 4 K in $Gd_3Co_{11}B_4$ compound. This value is in good agreement with previously reported values [6,7].

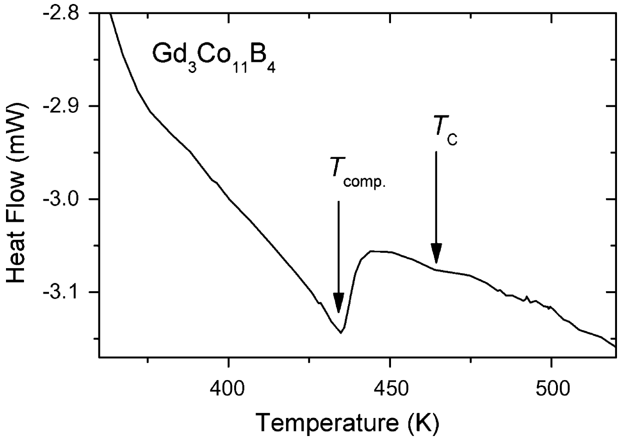

Fig. 6. DSC measurements taken above room temperature for the $Gd_3Co_{11}B_4$ compounds.

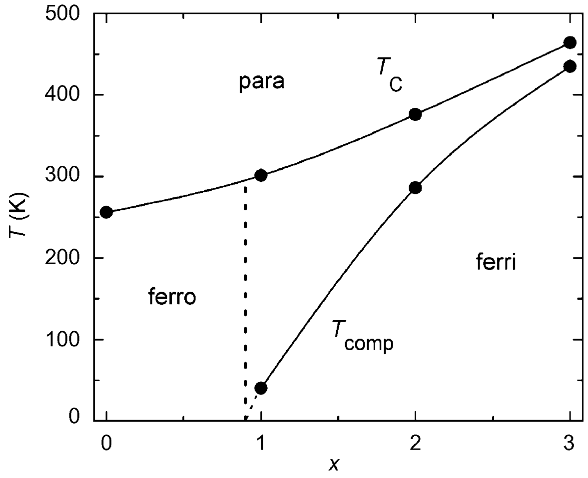

Fig. 7. The magnetic phase diagram for the $Ce_{3-x}Gd_xCo_{11}B_4$ compounds.

Fig. 6 shows the heat flow of the $Gd_3Co_{11}B_4$ sample during the heating at a constant ramp of 20 K/min. Endothermic reactions take place at 435 K and 464 K. These temperatures correspond to the compensation and Curie temperature, respectively. These transition temperatures obtained by our DSC results are in good agreement with previously reported findings [6–8].

The magnetic phase diagram, showing the transition temperatures as a function of the Gd concentration x, is represented in Fig. 7. The transition temperatures are also listed in Table 1. The Curie temperature increases with increasing x from 256 K for $x = 0$ to 473 K for $x = 3$, while the compensation temperature increases with increasing x from 40 K for $x = 1$ to 433 K for $x = 3$.

4. Conclusion

The $Ce_{3-x}Gd_xCo_{11}B_4$ compounds with $x = 0, 1, 2$, and 3 have been synthesized. They crystallize in the $Ce_3Co_{11}B_4$-type structure. The substitution of Gd for Ce leads to an increase of the unit-cell parameter a and the unit-cell volume V, while the unit-cell parameter c decreases. All compounds are ordered magnetically and the Curie and compensation temperatures increase with increasing Gd concentration x. The saturation magnetization at 4 K decreases upon the Gd substitution up to $x = 1$, and then increases again.

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