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Journal of Alloys and Compounds 262-263 (1997) 356-362

Journal of ALLOYS AND COMPOUNDS

Effect of aluminium on phase stability in the $Gd_3Co_{11}(B,Al)_4$ system

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Abstract

In the $Gd_3Co_{11}B_{4-x}Al_x$ alloys the ternary 3:11:4 phase with $Ce_3Co_{11}B_4$ structure is formed with an Al content $x \approx 0.5$ substituting for boron. The fraction of this phase decreases as the boron content decreases in the samples. The Al, Co and Gd in excess form $Gd(Co,Al)_5$ with $CaCu_5$-type structure, and the fraction of this phase increases with increasing x. X-ray diffraction results show that these phases are not at equilibrium. A strong preference of aluminium for the 3*g* site in the $CaCu_5$-type structure is determined by Rietveld refinement of the X-ray diffraction pattern of the end-series compound ($x = 4$). © 1997 Elsevier Science S.A.

Keywords: X-Ray diffraction; Rietveld refinement; Structural analysis; Preferential occupation; Intermetallic compounds

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1. Introduction

Much research has been devoted to the study of the effects of Al substitution for Co on the crystallographic and magnetic properties of $RE\text{-}Co_5$ and structurally related compounds. Thus, several investigations of the binary RE-Co phases have been concerned with the stability of a structure type at intermediate compositions [1,2], with the extent of homogeneous regions or structural transformations [3] and the study of relationships between the magnetic effects and the degree of order on crystallographic sites [4].

In the $RECo_4M$ systems, ternary compounds with the $CeCo_4B$ structure are formed for M = B [5], whereas in the case M = Al, pseudobinaries with $CaCu_5$ structure crystallize (space group P6/mmm) [6-10]. Aluminium substitution for Co strongly decreases the Curie temperatures and Co magnetic moments, as well as the rare earth and cobalt sublattice magnetocrystalline anisotropies.

The preferential Co site occupation by Al in compounds with $CaCu_5$-type structures has received a particular interest. In a previous X-ray diffraction (XRD) study of $RECo_4Al$, with RE = Y and Nd, the preferential distribution of Al on the 3*g* site was determined [11]. Recently, the investigation of several compounds of cerium by time-of-flight neutron diffraction has shown that Al occupies almost exclusively the 3*g* site, in contrast to the boron preference for the 2*c* site [12]. Based on the structural relationship between the $RECo_5$ and $RE_3Co_{11}B_4$ [5] and in the framework of the individual site contribution to anisotropy (ISA) model [13] we have suggested that Al preferentially occupies the cobalt 2*c* site in $RE_3Co_{11-x}Al_xB_4$ compounds, with RE = Y and Er [14].

Ternary $RE_3Co_{11}B_4$ compounds crystallize in the $Ce_3Co_{11}B_4$ structure (space group P6/mmm). In the unit cell, cobalt is located on three crystallographically inequivalent lattice sites (2*c*, 6*i* and 3*g*, the rare

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PII S0925-8388(97)00408-8

earth ions occupy two inequivalent sites (1*a* and 2*e*) and boron one type of site (4*h*). Taking into account the previous comparative analyses of $RECo_4B$ and $RECo_4Al$, it is of interest to investigate the structural stability of the $RE_3Co_{11}B_4$ phase when aluminium substitutes gradually for boron. Therefore in this paper we present results obtained on the $Gd_3Co_{11}(B,Al)_4$ system.

2. Experimental

Samples of $Gd_3Co_{11}B_{4-x}Al_x$ alloys, with $x = 0$, 0.5, 1, 2, 3 and 4, were prepared by arc-melting high purity constituents in argon atmosphere. The buttons were annealed at 900°C in high vacuum for 1 week and then rapidly quenched.

The phase compositions were investigated by X-ray diffraction on powders with average grain size < 50 μm, using Co-K_α radiation, at room temperature. A thorough scan, with high rate of accumulation was also performed at room temperature on a rotating-anode RIGAKU diffractometer with Cu-K_α radiation. The powder was ground under toluene, vacuum dried and subsequently sieved to give a particle size < 20 μm. The pattern for the sample with $x = 4$ was refined by the Rietveld method, by means of the FULLPROF v. 2.2 software package [15] implemented in a DIGITAL VAX computer. The background was estimated by interpolation from 17 intensity values corresponding to reflection-free angular ranges. The zero shift of the diffractometer, the h parameter of the Voigt function used to model the experimental peak shape and the three parameters of the Cagliotti's function used to describe the 2θ-variation of the FWHM of the reflections were determined by a pattern matching of the whole diffraction pattern.

The thermal variations of magnetizations (TMA) of the samples with $x = 0$ and $x = 4$ were measured in low magnetic field, in the temperature range 300-800 K. Resistivity measurements were carried out using the four-point method (DC) in the temperature range of 4.2-500 K (300-800 K for the sample with $x = 4$).

3. Results and discussion

The XRD patterns of the $Gd_3Co_{11}B_{1-x}Al_x$ series are shown in Fig. 1. An inspection of the experimental and calculated profiles of $Gd_3Co_{11}B_4$ evidence the formation of a single-phase well-crystallized sample with the $Ce_3Co_{11}B_4$ structure. For $x = 0.5$ one may observe that the diffraction pattern does not change significantly, but a small shift of the reflection lines towards smaller angles. Increasing the Al content leads to the appearance of the reflection lines of a secondary phase, with increasing intensities, whereas the peaks of the 3:11:4 phase decrease in intensity. In the end-series sample, $x = 4$, just the diffraction pattern of a Gd-(Co,Al) phase may be observed which has been easily identified and indexed as $Gd(Co,Al)_5$ with the $CaCu_5$ structure. The diffraction profiles have been fit taking into account the coexistence of the 3:11:4 and 1:5 phases, for the samples with $x = 1$, 2 and 3. The lattice constants of the two phases are listed in Table 1 and their relative variations vs. composition, x, in the 3:11:4 phase, are presented in Fig. 2. It is observed that these parameters are not constant, but increase by increasing the aluminium nominal content. Since under equilibrium conditions their values should be constant, the fact that they vary could be an indication that the phases are not in equilibrium.

Comparing the composition dependencies of the lattice constants' relative variations of the 3:11:4 phase, in $Gd_3Co_{11}B_{4-x}Al_x$, with those determined in the $RE_3Co_{11-x}Al_xB_4$ compounds [14], one may observe the same trend for the a constant and different behaviours of the c constant. These results suggest that for small amounts of Al substituting for B, $x \approx 0.5$, the $Gd_3Co_{11}B_{4-x}Al_x$ compound with $Ce_3Co_{11}B_4$ structure may form. Increasing the Al content determines the formation of the $Gd(Co,Al)_5$ phase. The decrease of the c constant of the 3:11:4 phase for $x \geq 1$ may be taken as an indication that a fraction of Al also substitutes for Co in this phase. The formation of a small quantity of 1:5 phase for $x = 0.5$ and $x = 1$ is also likely, although it is not possible to determine its structural parameters from the XRD spectra. Since the 3:11:4 phase forms with a decreasing fraction due to the less B available, the excess Al, Gd and Co form the $Gd(Co,Al)_5$ phase which should have the nominal composition $GdCo_{3.67}Al_{1.33}$ (also determined from the stoichiometry of the $x = 4$ sample). Following the considerations for the 3:11:4 phase, the composition of the 1:5 phase is more likely to be $GdCo_{3.67+\delta}Al_{1.33-\delta}$. Consequently, we consider reasonable to estimate for the two phases in the samples with $x = 1$, 2 and 3 the formulae $Gd_3(Co_{11-\epsilon}Al_\epsilon)(B_{4-\gamma}Al_\gamma)$ and $Gd(Co_{3.67+\delta}Al_{1.33-\delta})$.

Assuming that the relative distances in the 3:11:4 phase will not change significantly (less than 1%) we have estimated the Co-B interatomic distances (with B on 4*h* site and the lattice constants from Table 1). They increase from 2.082 Å for $x = 0$ to 2.141 Å for $x = 0.5$. At Al contents $x \geq 1.0$, the Co-B distances are in the range 2.135-2.140 Å. These values are close to 2.06 Å determined in $GdCo_4B$ [5] and it may represent an upper limit for which the ternary structures are stable in RE-Co-B systems.

The TMA curves of the pure 3:11:4 ($x = 0$) and 1:5 ($x = 4$) compounds are given in Fig. 3 (left). For the

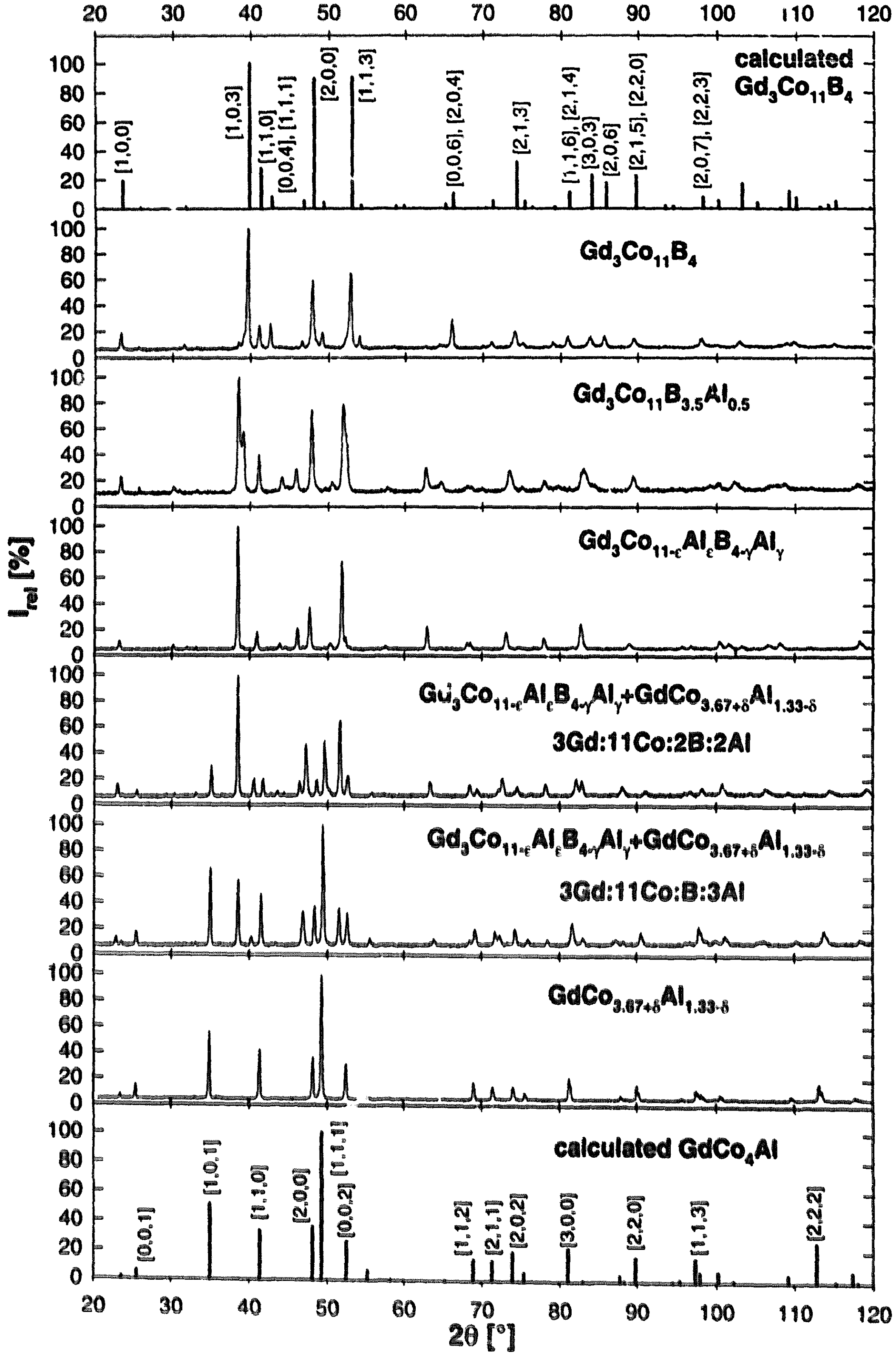

Fig. 1. XRD profiles of $Gd_3Co_{11}B_{4-x}Al_x$ series. Only the main reflexes are indexed.

$Gd_3Co_{11}B_4$ the compensation temperature, T_{comp}, is 433 K and the Curie point is at 473 K, in excellent agreement with the data of Burzo et al. [16]. For the 1:5 sample we have determined a Curie temperature of 440 K, much lower than the value of 613 K reported for $GdCo_4Al$ by Ido et al. [6]. This is an indication of a larger Al content in the $Gd(Co_{3.67+\delta}Al_{1.33-\delta})$ compound, which is also sup-

Table 1
Lattice constants of $Gd_3(Co_{11-\epsilon}Al_\epsilon)(B_{4-\gamma}Al_\gamma)$ and $Gd(Co_{3.67+\delta}Al_{1.33-\delta})$

x	3:11:4		1:5	
	a (Å)	c (Å)	a (Å)	c (Å)
0.0	5.0769(2)	9.8382(6)	—	—
0.5	5.0944(6)	10.288(2)	—	—
1.0	5.117(9)	10.287(1)	—	—
2.0	5.1788(5)	10.236(1)	5.0250(9)	4.044(1)
3.0	5.1995(4)	10.176(1)	5.0513(2)	4.0476(3)
4.0	—	—	5.05095(5)	4.03958(7)

ported by the larger values of the lattice constants obtained in the present study than those given for $GdCo_4Al$ in [6].

The temperature dependencies of resistivities, $\rho(T)$, are plotted in Fig. 3 (right). Distinct dependencies can be observed for end series 3:11:4 and 1:5 samples, whereas the shapes for the other samples are almost identical. The similar resistive behaviour for the samples with $x=0.5$, 1, 2 and 3 suggest the possible existence of small amount of 1:5 phase in the samples with $x=0.5$ and 1, too. From the derivative of the curve for $x=4$, a Curie temperature of 438 K is obtained, in very good agreement with the value obtained from TMA. In the case of the $Gd_3Co_{11}B_4$ sample ($x=0$) we obtained a value of 433 K from $\rho(T)$ curve, which corresponds to the compensation point determined by TMA. The change-of-slope point corresponding to the Curie temperature of this compound is not visible in the resistivity curve because the level of signal between T_{comp} and T_C is lower than the limit of sensitivity of the resistivity measurement setup. The composition dependence of zero-point resistivities, $\rho_0(x)$, is plotted in the inset of Fig. 3 (right). One may observe that $\rho_0(x)$ increase as the Al content increases. Since we replace a metalloid by a metal having a higher electrical conductivity, the observed increase of resistivity may be ascribed to the change in the microstructure of the samples, as the 1:5 phase replaces the 3:11:4 phase. This is supported by the observed change in the brittleness of the samples. The $Gd_3Co_{11}B_4$ sample is of very high hardness, while $Gd(Co,Al)_5$ is extremely brittle.

3.1. Rietveld refinement of the $CaCu_5$-type $Gd(Co,Al)_5$ phase

The structure refinement was carried out in the space group P6/mmm (No. 191) [17] and the scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography [18]. Initial values of the positional parameters were taken from [17,18]. Gadolinium was located on the 1*a* Wyckoff position, whereas Co and Al were assumed to be disordered over the two 2*c* and 3*g* sites, and their occupancies in each individual site were constrained to have equal atomic coordinates and to a full occupation of the two sites. A global isotropic thermal factor was refined. After refinement of the scale and occupancy factors and the global temperature factor, it became evident that the calculated intensities for the reflections (h, k, 0) were much lower than the calculated values. This observation was taken as an indication of the existence of some degree of preferred orientation of the particles in the powder.

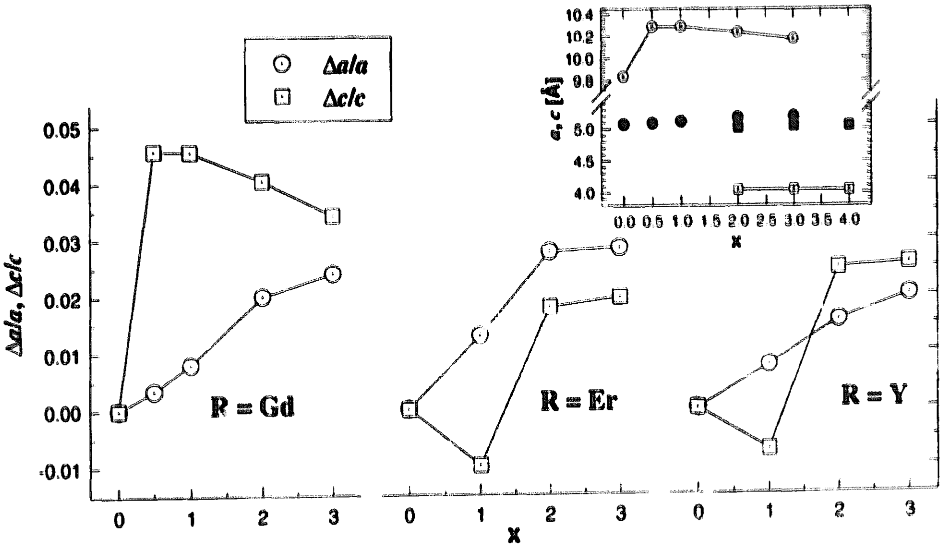

Fig. 2. Relative variations of the lattice constants vs. aluminium content in $Gd_3(Co_{11-\epsilon}Al_\epsilon)(B_{4-\gamma}Al_\gamma)$ (left), $Er_3(Co_{11-x}Al_x)B_4$ (middle) and $Y_3(Co_{11-x}Al_x)B_4$ (left). Inset: Composition dependences of the lattice constants in $Gd_3Co_{11}B_{4-x}Al_x$.

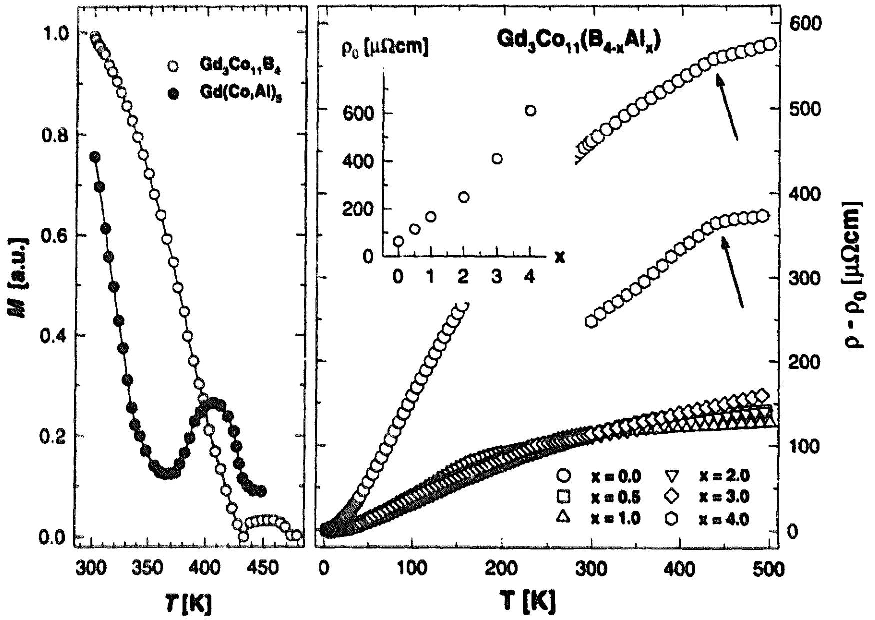

Fig. 3. TMA curves of the $Gd_3Co_{11}B_4$ and $Gd(Co,Al)_5$ (left) and temperature dependences of resistivity in $Gd_3Co_{11}B_{4-x}Al_x$ system (right).

A correction for this effect was introduced in the refinement, following the March function implemented in FULLPROF, leading to an important improvement of the reliability factors and convergence of the refinement (without corrections: $R_{wp} = 0.113$, $R_B = 0.149$, $\chi^2 = 10.3$). The calculated, experimental and difference diffraction profiles after the Rietveld refinement of $Gd(Co,Al)_5$ are shown in Fig. 4. The final values of all the parameters and the reliability factors are given in Table 2 (for the interatomic distances the last digit is significant).

Some small additional lines can be observed in Fig. 4 for this sample. They could not be explained on the bases of the structural data for binaries or ternaries containing Gd, Co and Al as reported in the CRYSMET Structural Database [19]. In spite of the presence of these lines, the refinement confirms that $GdCo_4Al$ is isotypic with $CaCu_5$. In this structure, Gd

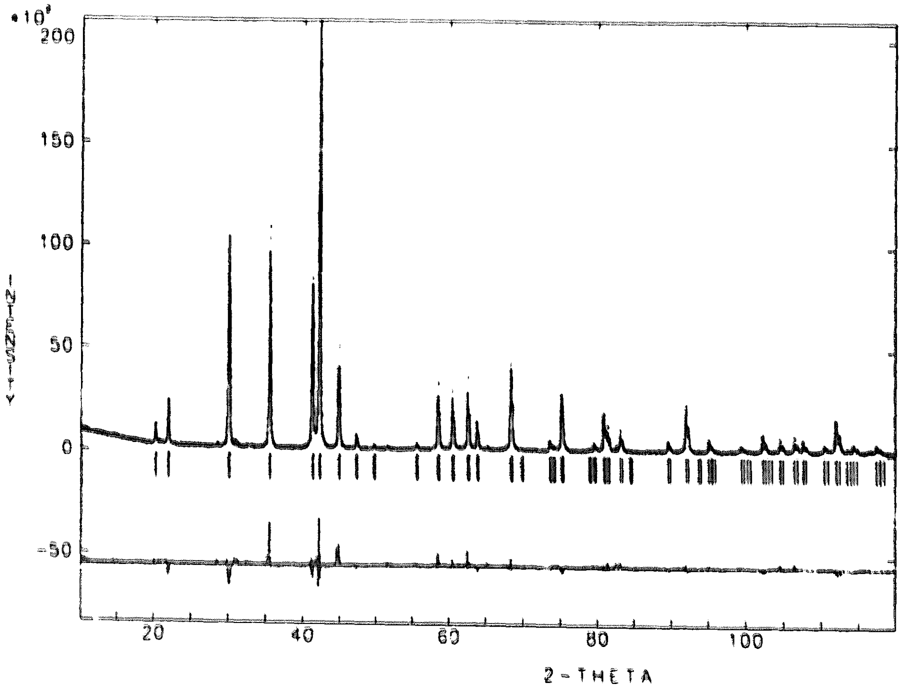

Fig. 4. Calculated (solid line), experimental (points) and difference diffraction profiles after the Rietveld refinement (Cu-K_α radiation) of $Gd(Co,Al)_5$. The tick marks below the data correspond to K_α-K_β doublets and indicate the positions of the allowed reflections.

Table 2
Structure data and profile parameters for $GdCo_4Al$

Atom	Position			B_{ISO} (Å^2)	Occ.	N.N. at $d \leq 3.6$Å		
	x	*y*	*z*			No.	N.N.	*d* [Å]
Gd(1*a*)	0	0	0	0.12(2)	1.000	6	Co/Al(2*c*)	2.916
						12	Co/Al(3*g*)	3.234
Co(2*c*)	1/3	2/3	0	—	1.857(16)	3	Gd(1*a*)	2.916
Al(2*c*)	1/3	2/3	0	—	0.143(16)	3	Co/Al(2*c*)	2.916
						6	Co/Al(3*g*)	2.491
Co(3*g*)	1/2	0	1/2	—	2.115(21)	4	Gd(1*a*)	3.234
Al(3*g*)	1/2	0	1/2	—	0.885(21)	4	Co/Al(2*c*)	2.491
						4	Co/Al(3*g*)	2.526

Refined composition: $GdCo_{3.97(2)}Al_{1.03(2)}$; V/Z [Å^3]: 89.25.
Unit cell parameters (Å): $a = 5.05095(5)$, $c = 4.03958(7)$.
Angular range 2θ (°): 10–120; angular step (°2θ): 0.02.
Total number of reflections: 86; total number of parameters: 12.
Zero shift (°2θ): −0.0077(2); March parameter: 0.151(3).
Profile: pseudo-Voigt, $h = 0.66(3)$, $U = 0.035(3)$, $V = -0.029(4)$, $W = 0.026(1)$.
Reliability factors: $R_{wp} = 0.124$, $R_B = 0.075$, $\chi^2 = 7.1$.

atoms occupy the 1*a* Wyckoff position, whereas Co and Al are distributed over the 2*c* and 3*g* sites. It follows from the refined data that this distribution is far from random, with Al showing a strong preference to substitute for Co on the 3*g* site. This strong preference can be explained on the basis of size and enthalpy effects. The atomic radius (for coordination number 12) of aluminium (1.432 Å) is larger than that of cobalt (1.252 Å) [20]. In $GdCo_4Al$, the metal atoms on 2*c* sites have three Gd and nine Co/Al neighbours, whereas those located on 3*g* are coordinated to four Gd and eight Co/Al atoms. The average distances between the cobalt atoms and their near neighbours are larger for the cobalt atoms in the 3*g* position, and this site should be consequently preferred by aluminium on the basis of size considerations. However, chemical affinity effects must be also considered as controlling factors for site preferences. According to these effects, substituting atoms might occupy those positions which allow the highest amount of bonding interactions, and consequently, the largest reduction in free energy. An estimate for the affinity of one element to another can be obtained from the semi-empirical calculation of the enthalpy of mixing as proposed by Miedema [21]. The enthalpies of mixing between transition metals and the rare earths vary with increasing atomic number along a series, from positive values at the beginning to slightly negative values at the end of the series, whereas the values between rare earths and p elements of the III-b and IV-b Groups are large and negative. On the basis of these considerations, aluminium would prefer to substitute for cobalt on the 3*g* site because it has the highest possible number of rare-earth atoms near neighbours. It follows from these considerations that the strong preference observed for aluminium to occupy the 3*g* sites is the result of the additive effects due to both size and enthalpy factors.

4. Conclusion

In $Gd_3Co_{11}B_{4-x}Al_x$ alloys, Al substitutes for the B 4*h* sites, for $x \approx 0.5$. Further increase of the Al content leads to the formation of two-phase alloys, $Gd_3(Co_{11-\epsilon}Al_\epsilon)(B_{4-\gamma}Al_\gamma)$ with $Ce_3Co_{11}B_4$ structure and $Gd(Co_{3.67+\delta}Al_{1.33-\delta})$ with $CaCu_5$ structure, which are not in equilibrium at intermediary compositions. For $x = 4$, a single phase sample with the Rietveld refined composition $GdCo_{3.97}Al_{1.03}$ is formed. In the $CaCu_5$ structure Al shows a strong preference for the Co(3*g*) site. The 4*h* site in the $Ce_3Co_{11}B_4$ is structurally related to 2*c* site in $CaCu_5$ which is avoided by Al due to both size and mixing enthalpy considerations. Nevertheless, since in the $Gd_3Co_{11}(B_{4-x}Al_x)$ all Co sites are occupied, Al is forced to distribute over the partially vacant 4*h* sites. This leads to an increase of d_{Co-B} to an upper limit of approximately 2.141 Å, above which the ternary structure is not stable. Then the formation of the 1:5 phase is favoured. Following these considerations it would be interesting to study the system in which B is substituted by the smaller radius C atoms.

Acknowledgements

The Spanish Project CICYT MAT Q6-0446 is gratefully acknowledged for financial support. The support of Dr E. Bauer and Prof. J. Bartolome in the accomplishment of this work is also gratefully acknowledged.

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