

Formation and structure of rare-earth intermetallic compounds $R_3Co_{29}M_4B_{10}$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 L159

(<http://iopscience.iop.org/0953-8984/12/8/101>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.218

The article was downloaded on 15/05/2010 at 20:13

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Formation and structure of rare-earth intermetallic compounds $R_3Co_{29}M_4B_{10}$ Heng Zhang[†], S J Campbell and A V J Edge

School of Physics, University College, The University of New South Wales, Australian Defence Force Academy, Canberra, ACT 2600, Australia

Received 16 November 1999

Abstract. The formation and crystal structure of a novel rare-earth compound series, $R_3Co_{29}M_4B_{10}$, have been investigated by electron microscopy, x-ray diffraction and Rietveld refinement. $R_3Co_{29}M_4B_{10}$ can form for $R = La, Ce, Pr, Nd, Sm, Gd, Ho, Tb, Er, Tm, Dy, Lu$ and $M = Si, Al, Ge$, and are isostructural with $Nd_3Ni_{29}Si_4B_{10}$.

1. Introduction

Rare-earth intermetallic compounds have attracted intense interest due to their promise as high performance magnetic materials (Buschow 1991, Li and Coey 1991). After the discovery of ternary $Nd_2Fe_{14}B$ in the 1980s (Sagawa *et al* 1984) and $Sm_2Fe_{17}N_x$ in 1990s (Coey and Sun 1990), the search for novel rare-earth intermetallic compounds with potential for magnetic materials has continued. Our recent studies (Zhang *et al* 1998, Zhang *et al* 1999, Bulcock *et al* 1998) have resulted in the establishment of a new series of quaternary rare-earth intermetallic compounds $Nd_3T_{29}Si_4B_{10}$ following the discovery of a Nd–Co–Si–B compound (Wu *et al* 1993).

It is expected that the lanthanide (Ln) group elements can form isostructural compounds due to the similarity of the chemical properties of the Lanthanide group elements. This has been proved in many binaries, e.g. RT_5 , R_2T_{17} (see, e.g., Franse and Radwanski 1993) and ternaries, e.g. $R_2T_{14}B$, RT_9Si_2 , $RT_{12}B_6$ (see, e.g., Buschow 1988, Li and Coey 1991). The investigation of Ln series compounds is of particular interest, as the magnetic behaviour can be systematically investigated in the isostructural group. The 4f-shell effect on the physical properties can be explored via the Ln compounds.

Our recent investigation indicates that a novel $Nd_3T_{29}Si_4B_{10}$ compound can form for $T = Co$ and Ni (Zhang *et al* 1999). It also demonstrates that the Si composition can vary in a certain range and that Si plays an important role in the formation of the quaternary phase (Zhang *et al* 1999). The consequent question is whether any other element can replace Si to form the quaternary phase. In this work, we first explore the formation of the phase by using different rare-earth elements from La to Lu (other than Yb, Pm and Eu). Then, the effect of replacing Si with some IIIA and IVA elements such as Al, Ge, Sn and Ga for the quaternary phase is investigated. Usually Co-matrix compounds exhibit enhanced magnetic properties relative to the corresponding Ni-matrix compounds, and hence the Co-matrix series was chosen as the objective in this work.

[†] Present address: Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136, USA. E-mail: hgz@mail.ims.uconn.edu.

2. Experimental

The specimens of nominal composition $R_3Co_{29}Si_4B_{10}$ ($R = La, Ce, Pr, Nd, Sm, Gd, Ho, Tb, Er, Tm, Dy, Lu$) and $Nd_3Co_{29}M_4B_{10}$ ($M = Si, Sn, Al, Ge, Ga$) were prepared by arc-melting high purity R (99.9 wt.%), Co (99.99 wt.%), Si (99.999 wt.%), B (99.999 wt.%), M ($M = Sn, Al, Ge, Ga > 99.9$ wt.%) elements in an argon atmosphere. The specimens were then annealed in a sealed evacuated quartz tube (with the samples wrapped in Ta foil) at 900°C for one week.

The microstructure characterisation was performed using a JEOL 6400 scanning electron microscope. X-ray diffraction data were collected using a Philips PW 1050/26 diffractometer with $Cu K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The scanning range is from 10° to 100° in 2θ with a step size of 0.04° . The diffraction patterns were checked and indexed using the Powdmult program (Wu 1989). All of the x-ray diffraction data were analysed with the Rietveld refinement program Lhpm1 (Howard and Hunter 1995).

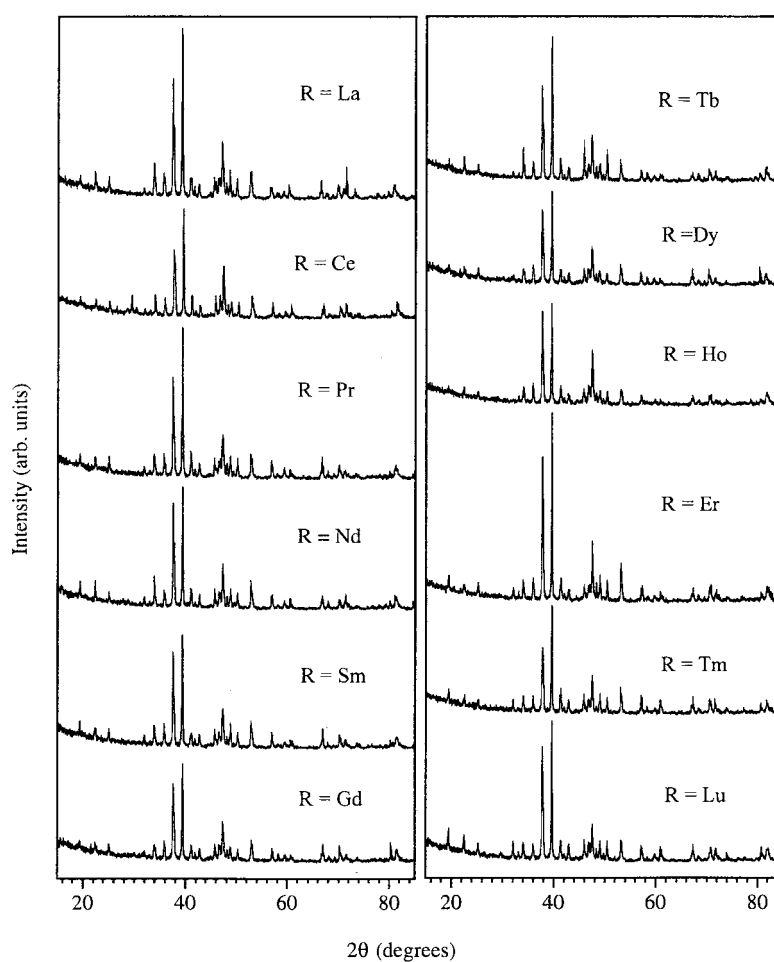


Figure 1. X-ray diffraction patterns of the $R_3Co_{29}Si_4B_{10}$ samples.

3. Results

The x-ray diffraction patterns for the samples with nominal composition $R_3Co_{29}Si_4B_{10}$ ($R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm$ and Lu) are presented in figure 1. Comparing the x-ray diffraction patterns for the whole system, it appears that the $R_3T_{29}Si_4B_{10}$ phase forms for the all investigated Ln elements. After checking the x-ray diffraction patterns, it is found that the possible impurities are at very low level and can be ignored and the 3:29:4:10 phase is the dominant phase in all these samples. The SEM observations as shown in figure 2 from two typical $R_3Co_{29}Si_4B_{10}$ samples ($R = La$ and Tb) further confirm the single phase character for these samples.

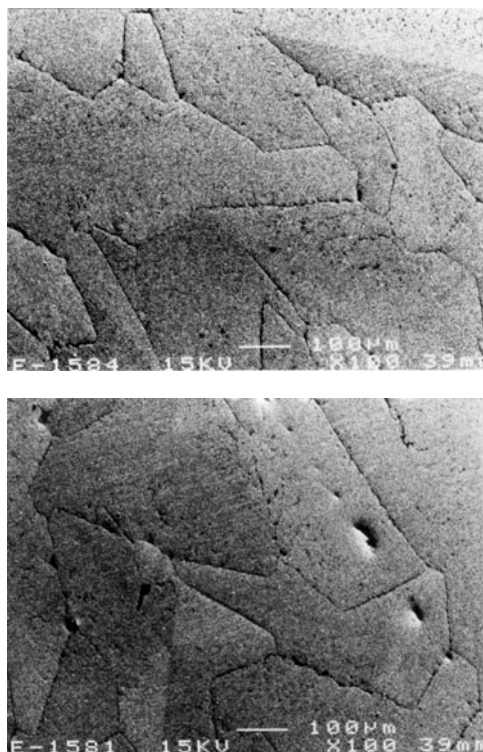


Figure 2. SEM images for (a) $La_3Co_{29}Si_4B_{10}$ and (b) $Tb_3Co_{29}Si_4B_{10}$.

Based on a tetragonal structure, the lattice parameters for the system were determined by using the Powdmult program, and the results are shown in figure 3. With the continuous shrinking of the radius due to the filling up of the 4f shell with increasing atomic number for the Ln group elements, the lattice parameters, both a and c , for the compounds exhibit a monotonic decrease with the atomic number except for Ce. An anomaly for the lattice parameters against atomic number is observed for the $Ce_3Co_{29}Si_4B_{10}$ compound. A similar phenomenon was also observed in many of Ce-based compounds: e.g. RCo_5 (Velge and Buschow 1968), R_2Co_{17} (Buschow 1966) and $R_2Fe_{14}B$ (see, e.g., Strnat 1988) and RT_9Si_2 (Bodak and Hladyshevsky 1969). The reason is that Ce exhibits +IV or a mixture of +III and +IV oxidation states instead of the +III state for most other lanthanides.

Searching the IIIA and IVA elements for replacement for Si to form the 3:29:4:10 phase was carried out according to the $Nd_3Co_{29}M_4B_{10}$ ($M = Al, Ga, Ge$ and Sn) systems. For these

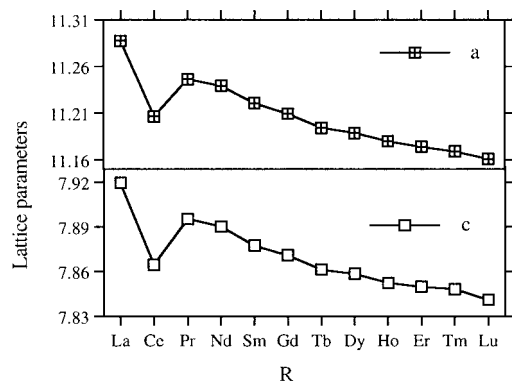


Figure 3. Lattice parameters of the $R_3Co_{29}Si_4B_{10}$ compounds.

Table 1. Lattice parameters of the $Nd_3Co_{29}M_4B_{10}$ compounds

$Nd_3Co_{29}M_4B_{10}$	M = Si	M = Ge	M = Al
a(Å)	11.241(5)	11.313(3)	11.329(4)
c(Å)	7.891(4)	7.950(3)	7.976(5)
c/a	0.702	0.703	0.704

elements of M, as shown in figure 4, Al and Ge can replace Si to form the dominant 3:29:4:10 phase. It seems that the valence of the M element is not the key factor for the formation of the 3:29:4:10 phase. 3-valent Al or 4-valent Si and Ge all can play the same key role to form the quaternary phase. The lattice parameters for the M = Al, Si and Ge and the c/a ratio are presented in table 1. The unit cell of Al- and Ge-type compounds clearly has expanded relative to the unit cell of Si-type compound (see table 1). However, the similar c/a ratio for the three kinds of compounds infers that the geometry of the unit cell for all compounds is similar.

From the above results, it is very encouraging that a novel group of $R_3Co_{29}M_4B_{10}$ quaternary compounds can form extensively for the whole investigated Ln group elements.

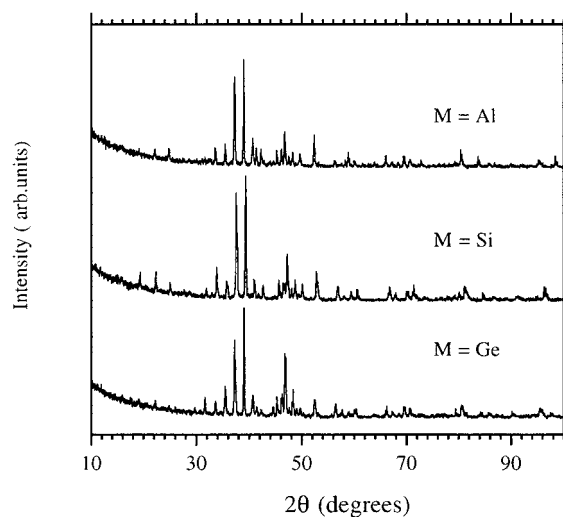


Figure 4. X-ray diffraction patterns of the $Nd_3Co_{29}M_4B_{10}$ compounds for M = Al, Si, Ge.

Table 2. Crystal structure and refinement parameters from the Rietveld refinement x-ray powder diffraction patterns of $R_3Co_{29}Si_4B_{10}$ (continued next page).

	R	La	Ce	Pr	Nd	Sm	Gd
Site							
R1	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(2b)	y/b	0.75	0.75	0.75	0.75	0.75	0.75
	z/c	0.5	0.5	0.5	0.5	0.5	0.5
R2	x/a	0	0	0	0	0	0
(4d)	y/b	0	0	0	0	0	0
	z/c	0	0	0	0	0	0
Si1	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(8i)	y/b	0.572(2)	0.561(2)	0.562(2)	0.564(3)	0.567(2)	0.567(3)
	z/c	0.197(4)	0.159(4)	0.172(3)	0.182(4)	0.163(4)	0.180(5)
Co1	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(2c)	y/b	0.25	0.25	0.25	0.25	0.25	0.25
	z/c	0.478(5)	0.466(5)	0.466(4)	0.470(4)	0.475(5)	0.470(5)
Co2	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(8i)	y/b	0.637(1)	0.642(1)	0.641(1)	0.637(1)	0.639(1)	0.639(1)
	z/c	0.889(2)	0.889(2)	0.892(2)	0.878(1)	0.891(2)	0.887(2)
Co3	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(8i)	y/b	0.018(1)	0.026(2)	0.021(1)	0.021(1)	0.022(2)	0.024(2)
	z/c	0.478(2)	0.473(2)	0.477(2)	0.474(2)	0.475(2)	0.471(2)
Co4	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(8i)	y/b	0.086(1)	0.090(2)	0.087(2)	0.083(2)	0.085(2)	0.080(2)
	z/c	-0.027(2)	-0.018(2)	-0.027(2)	-0.024(2)	-0.024(2)	-0.034(2)
Co5	x/a	0.133(1)	0.132(1)	0.134(1)	0.135(1)	0.132(1)	0.131(2)
(8j)	y/b	0.133(1)	0.132(1)	0.134(1)	0.135(1)	0.132(1)	0.131(2)
	z/c	0.253(2)	0.241(2)	0.248(2)	0.243(2)	0.249(2)	0.254(2)
Co6	x/a	0.140(1)	0.135(1)	0.144(1)	0.140(1)	0.142(1)	0.137(2)
(8j)	y/b	0.140(1)	0.135(1)	0.144(1)	0.140(1)	0.142(1)	0.137(2)
	z/c	0.700(2)	0.694(2)	0.704(2)	0.705(2)	0.708(2)	0.701(2)
Co7	x/a	0.077(1)	0.078(1)	0.078(1)	0.075(1)	0.077(1)	0.074(1)
(16k)	y/b	0.590(1)	0.588(1)	0.590(1)	0.588(1)	0.588(1)	0.588(1)
	z/c	0.339(1)	0.335(1)	0.334(1)	0.335(1)	0.331(1)	0.339(2)
B1*	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(2c)	y/b	0.25	0.25	0.25	0.25	0.25	0.25
	z/c	0.024(3)	0.24(3)	0.08(3)	0.10(3)	0.06(3)	0.04(4)
B2*	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(2c)	y/b	0.25	0.25	0.25	0.25	0.25	0.25
	z/c	0.82(1)	0.90(1)	0.79(1)	0.85(1)	0.80(1)	0.81(2)
B3*	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(8i)	y/b	-0.055(9)	0.01(1)	-0.01(1)	-0.02(1)	0.02(9)	0.02(1)
	z/c	0.7(1)	0.75(2)	0.75(1)	0.69(1)	0.76(2)	0.75(2)
B4*	x/a	0.070(5)	0.051(5)	0.047(5)	0.060(5)	0.051(7)	0.060(6)
(8j)	y/b	0.070(5)	0.051(5)	0.047(5)	0.060(5)	0.051(7)	0.060(6)
	z/c	0.473(3)	0.485(4)	0.459(3)	0.487(3)	0.460(3)	0.487(5)
a (Å)		11.2870(8)	11.206(1)	11.2456(9)	11.2405(8)	11.2201(9)	11.209(1)
c (Å)		7.9193(6)	7.8641(9)	7.8912(7)	7.8905(6)	7.8772(7)	7.8709(9)
V (Å ³)		1008.9(2)	987.5(2)	997.9(2)	997.0(2)	991.7(2)	988.9(3)
B _R		0.5(1)	0.8(1)	1.1(1)	0.9(1)	1.2(1)	0.6(1)
B _{Si}		0.4(5)	0.3(6)	-0.5(4)	1.2(6)	0.8(5)	1.0(6)
B _{Co}		1.0(1)	0.7(1)	1.0(1)	0.7(1)	1.1(1)	0.3(1)
*B _B		1.0	1.0	1.0	1.0	1.0	1.0
R _p		0.1139	0.1192	0.1093	0.1114	0.1095	0.1082
R _{wp}		0.1631	0.1624	0.1458	0.1506	0.1470	0.1465
R _{exp}		0.1059	0.0939	0.1034	0.1061	0.1081	0.1039
R _B		0.0743	0.0810	0.0593	0.0608	0.0588	0.0575
GOF		1.54	1.73	1.41	1.42	1.36	1.41

	R	Tb	Dy	Ho	Er	Tm	Lu
Site							
R1	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(2b)	y/b	0.75	0.75	0.75	0.75	0.75	0.75
	z/c	0.5	0.5	0.5	0.5	0.5	0.5
R2	x/a	0	0	0	0	0	0
(4d)	y/b	0	0	0	0	0	0
	z/c	0	0	0	0	0	0
Si	x/a	0.25	0.25	.25	0.25	0.25	0.25
(8i)	y/b	0.569(3)	0.565(3)	0.563(4)	0.566(3)	0.560(3)	0.563(4)
	z/c	0.179(4)	0.175(5)	0.177(7)	0.190(5)	0.185(5)	0.176(6)
Co1	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(2c)	y/b	0.25	0.25	0.25	0.25	0.25	0.25
	z/c	0.463(4)	0.462(4)	0.461(6)	0.464(4)	0.471(6)	0.473(5)
Co2	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(8i)	y/b	0.639(1)	0.639(1)	0.641(2)	0.638(1)	0.636(2)	0.639(1)
	z/c	0.890(2)	0.890(2)	0.884(3)	0.895(2)	0.888(3)	0.889(2)
Co3	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(8i)	y/b	0.017(2)	0.015(2)	0.019(2)	0.025(2)	0.024(2)	0.019(2)
	z/c	0.474(3)	0.474(2)	0.477(3)	0.475(3)	0.471(3)	0.475(3)
Co4	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(8i)	y/b	0.086(2)	0.083(2)	0.083(2)	0.086(2)	0.080(2)	0.083(2)
	z/c	-0.032(2)	-0.029(2)	-0.029(3)	-0.025(3)	-0.025(3)	-0.028(3)
Co5	x/a	0.133(1)	0.136(1)	0.136(2)	0.136(1)	0.130(1)	0.128(1)
(8j)	y/b	0.133(1)	0.136(1)	0.136(2)	0.136(1)	0.130(1)	0.128(1)
	z/c	0.244(2)	0.246(2)	0.247(3)	0.240(2)	0.241(3)	0.240(2)
Co6	x/a	0.143(1)	0.140(1)	0.135(2)	0.139(1)	0.141(2)	0.141(1)
(8j)	y/b	0.143(1)	0.140(1)	0.135(2)	0.139(1)	0.141(2)	0.141(1)
	z/c	0.703(2)	0.700(2)	0.700(3)	0.697(2)	0.698(3)	0.701(3)
Co7	x/a	0.076(1)	0.080(1)	0.075(1)	0.075(1)	0.078(2)	0.072(1)
(16k)	y/b	0.587(1)	0.594(1)	0.598(1)	0.592(1)	0.589(2)	0.586(2)
	z/c	0.334(2)	0.333(2)	0.336(2)	0.337(2)	0.337(2)	0.336(2)
B1*	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(2c)	y/b	0.25	0.25	0.25	0.25	0.25	0.25
	z/c	0.11(4)	0.08(4)	0.25(6)	0.11(4)	0.06(4)	0.11(4)
B2*	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(2c)	y/b	0.25	0.25	0.25	0.25	0.25	0.25
	z/c	0.90(1)	0.80(2)	0.80(2)	0.78(2)	0.85(2)	0.80(2)
B3*	x/a	0.25	0.25	0.25	0.25	0.25	0.25
(8i)	y/b	-0.02(1)	-0.06(1)	-0.08(2)	-0.03(1)	0.00(1)	-0.01(1)
	z/c	0.64(2)	0.81(2)	0.85(4)	0.65(2)	0.73(2)	0.72(2)
B4*	x/a	0.043(6)	0.059(7)	0.034(9)	0.065(7)	0.054(7)	0.075(7)
(8j)	y/b	0.043(6)	0.059(7)	0.034(9)	0.065(7)	0.054(7)	0.075(7)
	z/c	0.474(4)	0.502(5)	0.520(8)	0.453(4)	0.473(6)	0.458(6)
a (≈)		11.1944(9)	11.1893(7)	11.182(1)	11.175(1)	11.172(1)	11.164(1)
c (≈)		7.8615(7)	7.8581(6)	7.853(1)	7.851(1)	7.850(1)	7.843(1)
V(≈ ³)		985.2(2)	983.8(2)	981.9(3)	980.4(3)	979.8(3)	977.5(3)
B _R		0.9(1)	3.0(1)	4.1(2)	1.2(1)	0.4(1)	0.7(1)
B _{Si}		0.6(6)	0.0(5)	-0.8(8)	1.6(7)	-1.0(5)	0.9(7)
B _{Co}		0.7	-0.7(1)	-1.6(1)	0.3(1)	0.7(1)	0.4(1)
*B _B		1.0	1.0	1.0	1.0	1.0	1.0
R _p		0.116	0.123	0.1322	0.1087	0.1115	0.1147
R _{wp}		0.1561	0.1661	0.1816	0.1429	0.1453	0.1536
R _{cxp}		0.0976	0.0923	0.0080	0.0928	0.0914	0.0937
R _g		0.084	0.0982	0.1221	0.0577	0.092	0.0578
GOF		1.6	1.8	2.26	1.54	1.58	1.64

* All the parameters regarding boron only for reference, as such light element cannot be determined accurately by X-ray powder diffraction data.

It also can form for M = Si, Al and Ge etc. IIIA and IVA elements. According to the thermodynamic consideration in the work (Zhang et al 1999), the above conclusions should also be applied to the corresponding Ni-matrix systems. Hence, immediately, the rare-earth intermetallics family can increase by more than 70 quaternary 3d-rich rare earth R₃Ti₂₉M₄B₁₀

compounds. The discovery of this new class of rare-earth compounds is an important approach to understanding and exploring quaternary rare-earth intermetallic compound family. Through the study of this compound series, it is expected to lead to a better understanding and more knowledge regarding the phase, structure and magnetic behaviour for rare-earth quaternaries. Consequentially, it will contribute to the further exploration of rare-earth intermetallic magnetic materials.

Considering that isostructural compounds can form for the $R_3T_{29}Si_4B_{10}$ series, we applied the tetragonal structure model of $Nd_3Ni_{29}Si_4B_{10}$ (space group $P4/nmm$) (Zhang et al 1998) to refine the x-ray powder diffraction patterns for all the $R_3Co_{29}Si_4B_{10}$ series compounds. We found that in all cases, the calculated patterns can match very well with the measured patterns. The refinement results are summarized in the table 2. These reasonably good fit results further indicate the reliability of the $Nd_3Ni_{29}Si_4B_{10}$ structure model and that all the $R_3Co_{29}Si_4B_{10}$ are isostructural compounds with $Nd_3Ni_{29}Si_4B_{10}$.

4. Conclusions

This investigation has proved that the $R_3Co_{29}Si_4B_{10}$ phase can be formed for the whole investigated Ln group elements ($R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er$ and Lu). All of the formed compounds are isostructural and are the predominant phase in the investigated systems. In addition, the group IVA element Ge and group IIIA element Al can replace Si to form the corresponding 3:29:4:10 phase. This further expands the range of the quaternary compound, with a group of rare-earth quaternary intermetallics having entered the rare-earth compound family.

The $Nd_3Ni_{29}Si_4B_{10}$ structure model has been applied to refinement of the x-ray powder diffraction data for $R_3Co_{29}Si_4B_{10}$ series. Rietveld refinements of room temperature x-ray powder diffraction patterns on the $R_3Co_{29}Si_4B_{10}$ samples have proved that the $R_3Co_{29}Si_4B_{10}$ compounds have a tetragonal structure with space group $P4/nmm$. The good refinement results obtained for all of the quaternary series indicate that the $R_3Co_{29}Si_4B_{10}$ series are isostructural with $Nd_3Ni_{29}Si_4B_{10}$.

This work is supported by grants from the Australian Research Council leading to the award of Research Scholarship (HZ). This project is also supported in part by grants from the Australian Institute of Nuclear Science and Engineering.

References

- Bodak O I and Hladyshesky E I 1969 *Dopovidi Akademii Nauk Ukrain's'Koi Rsr, Seriya: Fiziko-Tekhnichni Ta Matematichni Nauki* **5** 452
- Bulcock S R, Zhang H, Wu E, Campbell S J 1998 *J. Mater. Sci. Lett.* **17** 1791
- Buschow K H J 1966 *J. Less-Common Metals* **16** 45
- Buschow K H J 1988 *Ferromagnetic Materials* vol 4, ed E P Wohlfarth and K H J Buschow (Amsterdam: North-Holland) p 1
- Buschow K H J 1991 *Rep. Prog. Phys.* **54** 1123
- Coe J M D and Sun H 1990 *J. Magn. Magn. Mater.* **87** L521
- Franse J J M and Radwanski R J 1993 *Handbook of Magnetic Materials* vol 7, ed K H J Buschow (Amsterdam: North-Holland) p 307
- Howard C J and Hunter B 1995 *Internal Report of the Australian Atomic Energy Commission* (Lucas Heights)
- Li Hong-Shuo and Coey J M D 1991 *Handbook of Magnetic Materials* vol 6, ed K H J Buschow (Amsterdam: North-Holland) p 1
- Sagawa M, Fujimura S, Togawa M and Maitssura Y 1984 *J. Appl. Phys.* **55** 2083

- Strnat K J 1988 in *Ferromagnetic Materials* vol 4, ed E P Wohlfarth and K H J Buschow (Amsterdam: North-Holland) p 131
- Velge W A J J and Buschow K H J 1968 *J. Appl. Phys.* **39** 1717
- Wu E 1989 *J. Appl. Crystallogr.* **22** 506
- Wu E, Wantenaar G H J, Campbell S J and Li Hong-Shuo 1993 *J. Phys.: Condens. Matter* **5** 1154
- Zhang Heng, Wu E, Campbell S J, Kennedy S J, Li H-S, Studer A J, Bulcock S R and Rae A D 1998 *J. Alloys Compounds* **278** 239
- Zhang Heng, Campbell S J, Li H-S and Wu E 1999 *J. Alloys Compounds* **284** 155