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Crystal structure of $R_{15}Ni_{96-x}Ga_x$ (R≡Sm, Y, Tb, Dy, Er, Tm, Yb, Lu)

L. O. Wasylechko, O. M. Sichewich and Yu. N. Grin
Institute of Inorganic Chemistry, Lvov University, Lvov (Ukraine)

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Abstract

The structure of the compound $Sm_{15}Ni_{52}Ga_{44}$ was investigated by means of single-crystal methods (autodiffractometer "Syntex" $P2_1$, Mo Kα, graphite monochromator): space group $P\bar{6}m2$, $a=8.771(1)$ Å; $c=25.061(4)$ Å, $Z=15$, $R_F=0.079$ for 391 reflections using the isotropic approximation for thermal parameters. The shortest interatomic distances are: Sm–Sm, 3.87; Sm–Ga, 2.76; Sm–Ni, 2.66; Ga–Ga, 2.20; Ni–Ni, 2.32; Ni–Ga, 2.30 Å. The coordination numbers for the atoms are: samarium, 18–20; nickel, 11, 12, 14; gallium, 11, 12, 14.

1. Introduction

Ternary compounds with isoconcentrations of about 13 at.% of rare earth metal (R) have been known for a long time in R–Ni–Ga systems; for example, the compound with probable composition $Ho_3Ni_8Ga_{11}$ existing in this range was first reported in 1980 [1]. The powder patterns of these phases are sufficiently complicated to make a structure determination from powder data impossible. The purpose of the present work was to determine the crystal structures of the phases found by means of single-crystal methods.

2. Experimental details

Details of the sample preparation were reported earlier [2]. Homogeneous annealing was carried out at 600 °C. A single crystal of prismatic shape was extracted from the $Sm_{13}Ni_{44}Ga_{43}$ alloy. Investigation of the single crystal by the Laue method indicated hexagonal $6/mmm$ symmetry. The unit cell parameters were determined by the rotation method followed by refinement on the autodiffractometer: $a=8.771(1)$ Å, $c=25.061(4)$ Å. A set of 1763 reflections was measured on the same diffractometer using the θ–2θ method. After elimination of the weak reflection and averaging of the symmetrical equivalents, 391 reflections with $I>2\sigma I$ remained in the set. Most reflections were compatible with the rhombohedral lattice ($h-k+l=3n$). However, there were about 10% weak reflections for which these extinctions were not valid. Further analysis indicated $P6/mmm$, $P\bar{6}m2$, $P\bar{6}2m$, $P6mm$ and $P622$ as possible space groups.

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3. Structure determination and description

The structure was solved in the $P\bar{6}m2$ space group. Atomic positions were defined by direct methods and refined by the least-squares method using the isotropic approximation for thermal parameters to $R_F = 0.079$. Final atomic coordinates are given in Table 1 and interatomic distances are given in Table 2. All calculations were carried out by means of program package CSD [3]. The projection of the structure $Sm_{15}Ni_{52}Ga_{44}$ on the XY plane is shown in Fig. 1. Only the atoms with $0 \leqslant z \leqslant \frac{1}{3}$ are presented.

The coordination polyhedra of Sm atoms are $CaCu_5$ like with 20 corners or derivatives thereof. Ga atoms are located in the centres of both icosahedra and trigonal prisms. Coordination polyhedra of icosahedron, cubo-octahedron and hexagonal antiprism type are characteristic for Ni atoms. The trigonal prisms in $Sm_{15}Ni_{52}Ga_{44}$ can be considered as defect icosahedra.

The structure of $Sm_{15}Ni_{52}Ga_{44}$ is the first representative of a new structure type. It can be referred to the structures with icosahedral coordination of the smallest atoms according to Kripjakevich [4].

TABLE 1

Atomic parameters for $Sm_{15}Ni_{52}Ga_{44}$

Atom	x/a	y/b	z/c	B (Å^2)
2Sm1	$\frac{2}{3}$	$\frac{1}{3}$	0.079(1)	1.5(2)
2Sm2	$\frac{2}{3}$	$\frac{1}{3}$	0.241(1)	1.4(2)
2Sm3	$\frac{2}{3}$	$\frac{1}{3}$	0.414(1)	1.0(2)
2Sm4	$\frac{1}{3}$	$\frac{2}{3}$	0.2549(8)	0.6(1)
2Sm5	$\frac{1}{3}$	$\frac{2}{3}$	0.4227(8)	1.1(2)
2Sm6	0	0	0.0835(9)	0.4(2)
2Sm7	0	0	0.3350(6)	1.1(1)
2Sm8	$\frac{1}{3}$	$\frac{2}{3}$	0	1.0(2)
12Ni1	0.302(3)	0.007(3)	0.4168(8)	1.4(2)
12Ni2	0.310(2)	0.009(3)	0.2504(9)	1.3(2)
6Ni3	0.175(2)	0.825(2)	0.343(2)	1.4(2)
6Ni4	0.493(3)	0.507(3)	0.327(1)	1.1(2)
6Ni5	0.808(5)	0.192(5)	0.329(1)	1.1(2)
3Ni6	0.170(4)	0.830(4)	$\frac{1}{2}$	1.7(2)
3Ni7	0.840(6)	0.160(6)	0	1.4(2)
2Ni8	0	0	0.204(2)	1.5(2)
2Ni9	0	0	0.453(2)	1.5(2)
12Ga1	0.050(2)	0.381(2)	0.0837(8)	0.8(1)
6Ga2	0.161(3)	0.839(3)	0.154(1)	2.1(2)
6Ga3	0.500(3)	0.500(3)	0.1729(9)	1.0(2)
6Ga4	0.830(5)	0.710(5)	0.1516(6)	0.7(2)
3Ga5	0.498(4)	0.502(4)	$\frac{1}{2}$	0.9(2)
3Ga6	0.850(5)	0.150(5)	$\frac{1}{2}$	1.0(2)
3Ga7	0.142(2)	0.858(2)	0	0.6(2)
3Ga8	0.515(2)	0.485(2)	0	0.6(2)
2Ga9	$\frac{1}{3}$	$\frac{2}{3}$	0.137(1)	0.5(2)

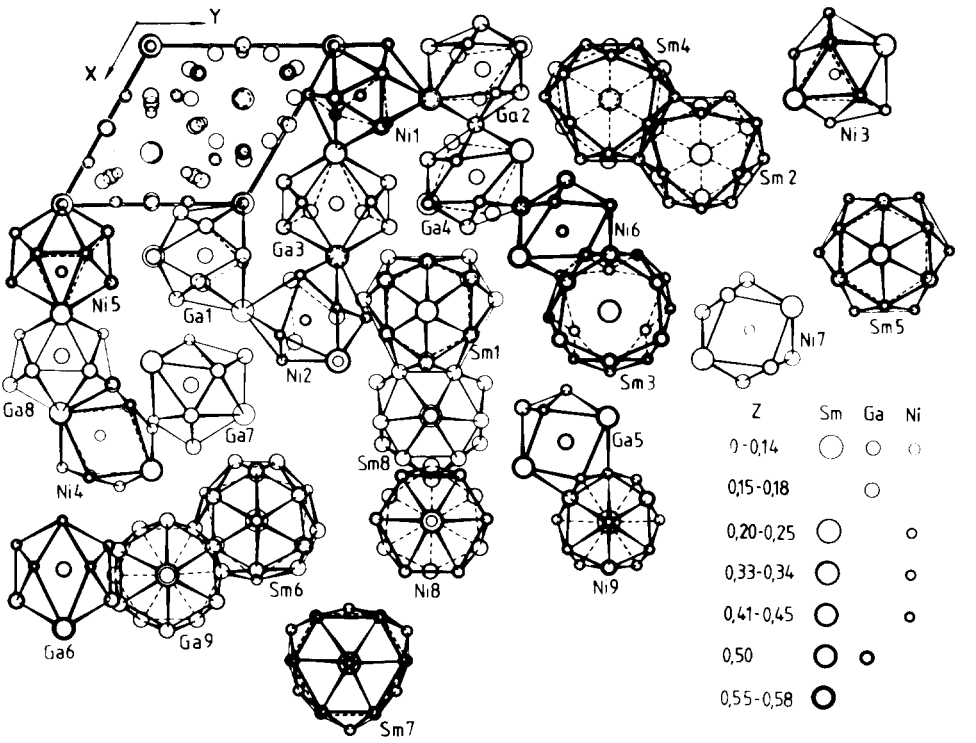

Fig. 1. Projection of $Sm_{15}Ni_{52}Ga_{44}$ structure on XY plane and coordination polyhedra for atoms.

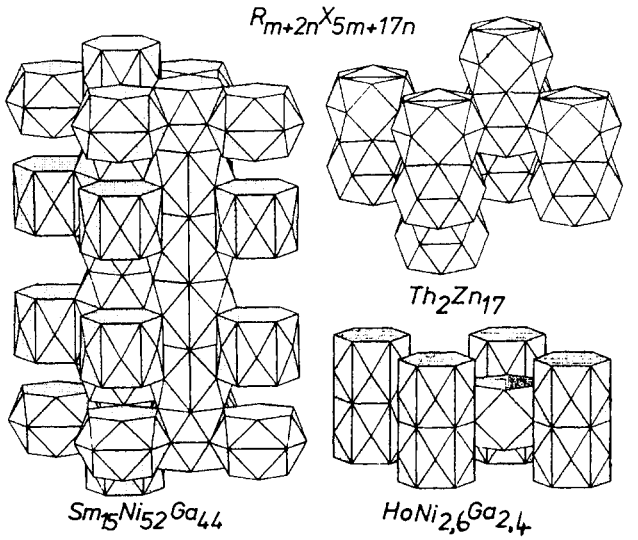

Fig. 2. $Sm_{15}Ni_{52}Ga_{44}$, Th_2Zn_{17} and $HoNi_{2.6}Ga_{2.4}$ structures as packing of polyhedra around R atoms.

TABLE 2

Interatomic distances (ångströms) for $Sm_{15}Ni_{52}Ga_{44}$

Atom	Distance	Atom	Distance	Atom	Distance
Sm1–3Ga8	3.03(3)	Sm2–6Ni2	3.00(2)	Sm3–3Ni5	3.03(4)
3Ga4	3.08(4)	3Ga3	3.06(4)	6Ni1	3.04(2)
6Ga1	3.17(2)	3Ni5	3.06(4)	3Ga5	3.34(6)
3Ni7	3.30(4)	3Ga4	3.35(3)	3Ni4	3.42(4)
3Ga3	3.46(4)	3Ni4	3.40(4)	3Ga6	3.51(4)
Sm1	3.95(4)	Sm1	4.07(4)		
Sm2	4.07(4)				
Sm4–Ga9	2.96(3)	Sm5–3Ni3	3.12(4)	Sm6–3Ga7	3.00(3)
3Ni4	3.03(4)	6Ni1	3.13(2)	Ni8	3.01(5)
6Ni2	3.11(2)	3Ni6	3.15(5)	3Ga2	3.01(4)
3Ga3	3.26(4)	3Ga5	3.17(6)	3Ga4	3.09(3)
3Ni3	3.27(4)	3Ni4	3.42(4)	6Ga1	3.15(2)
3Ga2	3.65(4)	Sm5	3.87(3)	3Ni7	3.20(4)
Sm7–3Ni3	2.66(3)	Sm8–3Ga8	2.76(3)	Ni1–Ni3	2.32(4)
3Ni5	2.93(4)	3Ga7	2.91(4)	Ga6	2.44(3)
Ni9	2.96(5)	12Ga1	3.26(2)	Ni6	2.51(4)
Ni8	3.29(5)	2Ga9	3.43(3)	Ni1	2.53(4)
6Ni1	3.33(3)			Ni5	2.63(3)
6Ni2	3.42(3)			Ni1	2.71(3)
				Ga5	2.73(4)
				Ni9	2.77(3)
				Ni4	2.87(4)
				Sm3	3.04(2)
				Sm5	3.13(2)
				Sm7	3.33(3)
Ni2–Ni5	2.41(3)	Ni3–2Ni1	2.32(4)	Ni4–2Ni5	2.42(3)
Ni2	2.56(4)	2Ni4	2.46(6)	2Ni3	2.46(6)
Ni4	2.57(4)	Sm7	2.66(3)	2Ni2	2.57(4)
Ga3	2.59(4)	2Ni2	2.75(4)	2Ni1	2.87(4)
Ni3	2.75(4)	2Ni5	2.83(5)	Sm4	3.03(4)
Ga4	2.80(3)	Sm5	3.12(4)	Sm2	3.40(4)
Ga2	2.80(4)	Sm4	3.27(4)	Sm5	3.42(4)
Ni2	2.80(3)			Sm3	3.42(4)
Ni8	2.93(3)				
Sm2	3.00(2)				
Sm4	3.11(2)				
Sm7	3.42(3)				
Ni5–2Ni2	2.41(3)	Ni6–2Ga6	2.45(7)	Ni7–2Ga7	2.30(6)
2Ni4	2.42(3)	2Ga5	2.49(10)	2Ga8	2.49(3)
2Ni1	2.63(3)	4Ni1	2.51(4)	4Ga1	2.83(4)
2Ni3	2.83(5)	2Ni9	2.84(6)	2Sm6	3.20(4)
Sm7	2.93(4)	2Sm5	3.15(5)	2Sm1	3.30(4)
Sm3	3.03(4)				
Sm2	3.06(4)				

(*continued*)

TABLE 2 (*continued*)

Atom	Distance	Atom	Distance	Atom	Distance
Ni8–3Ga2	2.74(4)	Ni9–Ni9	2.36(7)	Ga1–Ga2	2.20(4)
3Ga4	2.89(4)	3Ga6	2.57(4)	Ga1	2.47(3)
6Ni2	2.93(3)	6Ni1	2.77(3)	Ga1	2.52(3)
Sm6	3.01(5)	3Ni6	2.84(6)	Ga8	2.52(3)
Sm7	3.29(5)	Sm7	2.96(5)	Ga4	2.54(3)
				Ga7	2.55(3)
				Ga3	2.59(4)
				Ni7	2.83(4)
				Ga9	2.83(2)
				Sm6	3.15(2)
				Sm1	3.17(2)
				Sm8	3.26(2)
Ga2–2Ga1	2.20(4)	Ga3–2Ga4	2.57(5)	Ga4–2Ga2	2.51(5)
2Ga4	2.51(5)	2Ni2	2.59(4)	2Ga1	2.54(3)
2Ga3	2.62(6)	2Ga1	2.59(4)	2Ga3	2.57(5)
Ga9	2.66(4)	2Ga2	2.62(6)	2Ni2	2.80(3)
Ni8	2.74(4)	Ga9	2.69(4)	Ni8	2.89(4)
2Ni2	2.80(4)	Sm2	3.06(4)	Sm1	3.08(4)
Sm6	3.01(4)	Sm4	3.26(4)	Sm6	3.09(3)
Sm4	3.65(4)	Sm1	3.46(4)	Sm2	3.35(3)
Ga5–2Ni6	2.49(10)	Ga6–4Ni1	2.44(3)	Ga7–2Ni7	2.30(6)
2Ga6	2.68(7)	2Ni6	2.45(7)	4Ga1	2.55(3)
4Ni1	2.73(4)	2Ni9	2.57(4)	2Ga8	2.84(5)
2Sm5	3.17(6)	2Ga5	2.68(7)	Sm8	2.91(4)
2Sm3	3.34(6)	2Sm3	3.51(4)	2Sm6	3.00(3)
Ga8–2Ni7	2.49(6)	Ga9–3Ga2	2.66(4)		
4Ga1	2.52(3)	3Ga3	2.69(4)		
Sm8	2.76(3)	6Ga1	2.83(2)		
2Ga7	2.84(5)	Sm4	2.96(3)		
2Sm1	3.03(3)	Sm8	3.43(3)		

The availability of polyhedra which are characteristic for simpler structure types (Fig. 2) and also the fact that compounds having a structure of $Sm_{15}Ni_{52}Ga_{44}$ type are in equilibrium with ternary phases with structures of Th_2Zn_{17} and $HoNi_{2.6}Ga_{2.4}$ types in the phase diagrams allowed us to make a conclusion on the possible fragment building of the structure determined. The $Sm_{15}Ni_{52}Ga_{44}$ structure can be described as a linear stacking combination (intergrowth) of distorted flat fragments from Th_2Zn_{17} and $HoNi_{2.6}Ga_{2.4}$ structure types. The unit cell composition of the structures built in this way can be expressed by the formula $R_{3m+2n}X_{15m+17n}$, where m and n are amounts of $HoNi_{2.6}Ga_{2.4}$ and Th_2Zn_{17} fragments respectively. For $Sm_{15}Ni_{52}Ga_{44}$, $m=3$ and $n=3$ are valid.

Isotypic compounds were found in the systems with R≡Y, Tb, Dy, Er, Tm, Yb and Lu. Most of them have small ranges of homogeneity between $x=44$ and 57. Unexpected is the absence of a gadolinium phase.

TABLE 3

Crystallographic data of $R_{15}Ni_{96-x}Ga_x$ compounds

R	x	a (Å)	c (Å)	V (Å^3)
Sm	44	8.777(1)	25.061(4)	1670
Y	51–57	8.735(3)–8.758(3)	24.662(9)–24.63(2)	1630–1636
Tb	50–56	8.721(4)–8.771(5)	24.56(1)–24.68(1)	1618–1644
Dy	50	8.787(5)	24.79(3)	1658
Er	54	8.901(5)	24.82(2)	1703
Tm	49–56	8.690(4)–8.711(3)	24.51(1)–24.58(1)	1603–1615
Yb	46–52	8.708(3)–8.712(6)	24.30(1)–24.32(1)	1596–1597
Lu	52–56	8.710(3)–8.719(3)	24.86(1)–24.89(1)	1633–1639

Lattice parameters refined from the powder patterns (Cu, Kα) are shown in Table 3.

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