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The new structure type $Ce_5Co_4Ge_{13}$

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The crystal structure of $Ce_5Co_4Ge_{13}$ was refined from single-crystal X-ray diffraction data. This new orthorhombic structure type (space group *Cmmm*, *a* = 4.265(1), *b* = 45.175(9), *c* = 4.293(1) Å) is a filled-up derivative of the Nb_5Ga_{13} type and contains AlB_2-, $BaNiSn_3$- and $AuCu_3$-type slabs intergrown along [010]. The "interstitial" Co atoms are characterized by bicapped square-antiprismatic [Ce_5Ge_5] coordination.

Cerium / Cobalt / Germanium / Intermetallic compound / Crystal structure

Introduction

The isothermal section at 670/870 K of the phase diagram of the Ce-Co-Ge system was found to contain eleven ternary intermetallic phases, four of which were reported with unknown structure and approximate composition [1]. The compound $Ce_5Co_4Ge_{13}$ investigated here probably corresponds to the phase ~Ce_3CoGe_6.

Experimental details

Single crystals were found in a sample of nominal composition $Ce_{20}Co_{20}Ge_{60}$, which had been prepared from Ce (99.99%), Co (99.99%), and Ge (99.9999%) by induction melting under an Ar atmosphere.

Integrated intensities were measured with graphite monochromatized Mo Kα radiation on an Xcalibur CCD diffractometer. The cell parameters were refined from 6332 reflections. The crystal data and other parameters for the data collection and refinement are shown in Table 1. The intensity of the reflections was corrected for Lorentz and polarization effects. The structure was solved from Patterson maps and refined by the full-matrix least-squares method on F^2 using SHELX-97 [2]. The atomic positional parameters were standardized with the program STRUCTURE TIDY [3].

Table 1 Crystal data and details of the data collection and structural refinement for the $Ce_5Co_4Ge_{13}$ compound.

Crystal data	Data collection	Refinement
M_r = 1879.99	Xcalibur diffractometer	R = 0.0413
Orthorhombic	CCD detector, ω-scan	wR = 0.0829
Space group *Cmmm*	Mo Kα radiation	S = 1.082
a = 4.265(1) Å	T = 295(2) K	728 reflections with $I > 2\sigma(I)$
b = 45.175(9) Å	Analytical absorption correction	48 parameters
c = 4.293(1) Å	T_{min} = 0.045, T_{max} = 0.342	$w = 1/[\sigma^2F_o^2+(0.0224P)^2+$
V = 827.1(3) Å^3	6332 measured reflections	$50.2126P]$, $P = (F_o^2+2F_c^2)/3$
Z = 2	971 independent reflections	$(\Delta/\sigma)_{max} < 0.0001$
D_x = 7.548 Mg m^{-3}	R_{int} = 0.0478	$\Delta\rho_{max}$ = +8.19 e Å^{-3}
μ = 40.496 mm^{-1}	θ_{max} = 33.72°	$\Delta\rho_{min}$ = -3.15 e Å^{-3}
F(000) = 1628	$-6 \le h \le 4$, $-70 \le k \le 60$, $-6 \le l \le 5$	Extinction coefficient
Metallic gray platelet,		(SHELXL): 0.00016(7)
0.110×0.070×0.028 mm^3		

Table 2 Atomic positional and displacement parameters (Å^2) for $Ce_5Co_4Ge_{13}$ (space group *Cmmm*).

Atom	WP	*x*	*y*	*z*	U_{eq}	U_{11}[a]	U_{22}	U_{33}
Ce1	4*j*	0	0.39371(2)	1/2	0.0072(2)	0.0068(3)	0.0076(3)	0.0071(3)
Ce2	4*i*	0	0.21248(2)	0	0.0072(2)	0.0067(3)	0.0078(3)	0.0072(4)
Ce3	2*a*	0	0	0	0.0068(2)	0.0066(4)	0.0066(4)	0.0072(5)
Co1	4*j*	0	0.31950(4)	1/2	0.0061(3)	0.0053(7)	0.0069(8)	0.0061(8)
Co2	4*i*	0	0.07067(5)	0	0.0115(4)	0.0111(9)	0.0113(9)	0.0121(9)
Ge1	4*j*	0	0.04975(4)	1/2	0.0125(3)	0.0163(8)	0.0124(8)	0.0088(7)
Ge2	4*j*	0	0.15874(3)	1/2	0.0078(3)	0.0047(6)	0.0091(7)	0.0096(7)
Ge3	4*j*	0	0.26692(3)	1/2	0.0072(3)	0.0059(6)	0.0059(6)	0.0096(7)
Ge4	4*i*	0	0.12104(4)	0	0.0107(3)	0.0083(6)	0.0141(7)	0.0099(7)
Ge5	4*i*	0	0.34110(3)	0	0.0079(3)	0.0094(7)	0.0087(7)	0.0058(7)
Ge6	4*i*	0	0.45018(4)	0	0.0141(3)	0.0093(7)	0.0151(8)	0. 0178(8)
Ge7	2*c*	1/2	0	1/2	0.0260(7)	0.0104(11)	0.057(2)	0.0111(12)

[a] $U_{12} = U_{13} = U_{23} = 0$.

Results and discussion

Cell parameters, final positional parameters and displacement parameters of $Ce_5Co_4Ge_{13}$ are listed in Tables 1 and 2. A projection of the unit-cell content along [001] and the coordination polyhedra of the atoms in the asymmetric unit are shown in Figs. 1 and 2, respectively.

The new structure type represented by $Ce_5Co_4Ge_{13}$, Pearson symbol *oS*44 and Wyckoff sequence *Cmmm*–j^5i^5ca (#65), can be obtained considering the insertion of additional atoms (Co atoms) into the orthorhombic structure type Nb_5Ga_{13} ("Ce_5Ge_{13}"), *oS*36, *Cmmm*–j^4i^4ca (#65), *a* = 3.778, *b* = 40.335, *c* = 3.778 Å [4]. The parent type Nb_5Ga_{13}, Gd_3Sn_7 [5], Ce_3Sn_7, and Ce_2Sn_5 [6] are members of a homologous structural series based on an intergrowth of slabs characteristic of the simple structure types AlB_2, $AuCu_3$, and CaF_2 [3]. The structure of $Ce_5Co_4Ge_{13}$ contains slabs of the types AlB_2, $BaAl_4$ (or its ternary variant $BaNiSn_3$), and $AuCu_3$ (Fig. 1). The first two structure types have representatives in the Ce-Co-Ge system: $CeCo_{0.5}Ge_{1.5}$ and $CeCoGe_3$ [1]. Similar segments are also present in the orthorhombic structures of $La_3Co_2Sn_7$ [7] and $Ho_3Co_2Si_7$ [8], in monoclinic $Lu_5Co_4Si_{14}$ [9], and in tetragonal $Sc_5Co_4Si_{10}$ [10]. In the structure of $Ce_5Co_4Ge_{13}$, the Co and Ge atoms are characterized by square-antiprismatic, cubooctahedral, and trigonal-prismatic coordinations (Table 3, Fig. 2).

High residual electron densities (+8.19 and -7.06 e Å^{-3}) were observed at (0 0.1054 0) and (1/2 0.0370 1/2). These positions are located between the site Co2 in the mixed $BaNiSn_3$-$AuCu_3$ slab and its nearest neighbor Ge4 in the $BaNiSn_3$ slab, and on both sides of the Ge7 site at the interface of two neighboring $BaNiSn_3$-$AuCu_3$ slabs. A refinement considering partial replacement of pairs Co2-Ge4 by single Ge atoms, related to a partial replacement of single atoms Ge7 by Co-Co pairs, improved the agreement with the observed intensities (*R* = 0.0295, *wR* = 0.0544, *S* = 1.090, $\Delta\rho_{max}$ = +2.59 e Å^{-3}, $\Delta\rho_{min}$ = -2.20 e Å^{-3}, extinction coefficient: 0.00051(7)).

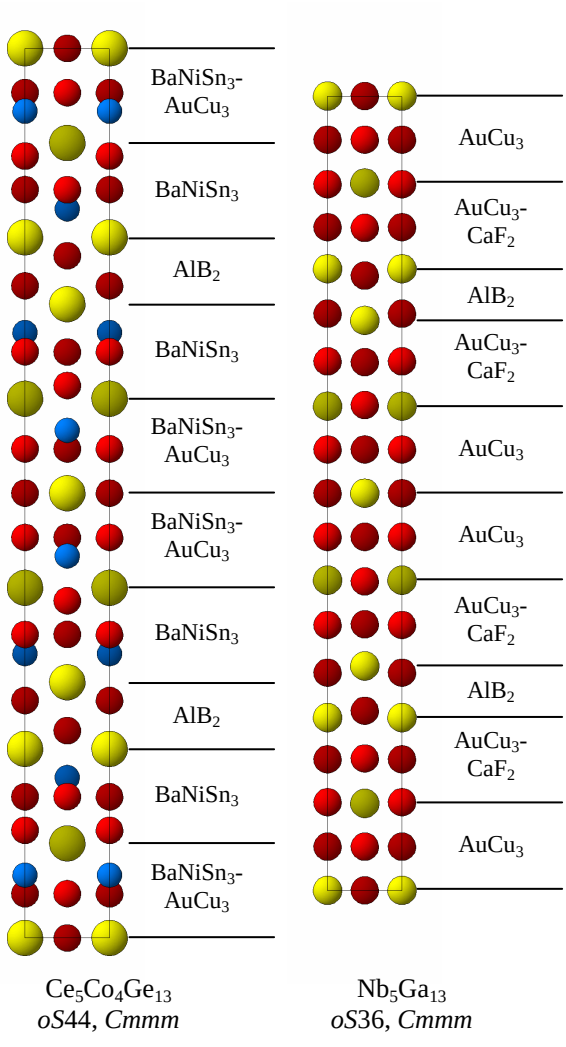

Fig. 1 Projections of the structures of $Ce_5Co_4Ge_{13}$ and Nb_5Ga_{13} along [001]. The segments of simple structure types intergrown along [010] are outlined; Ce atoms: large light spheres, Co atoms: small spheres, Ge and Ga atoms: medium dark spheres, Nb atoms: medium light spheres.

Table 3 Interatomic distances (Å) in $Ce_5Co_4Ge_{13}$.

Atoms		δ	Atoms		δ	Atoms		δ
Ce1	4Ge4	3.098(1)	Co1	2Ge2	2.348(1)	Ge3	1Co1	2.375(3)
	2Ge2	3.188(1)		2Ge5	2.358(1)		2Ge3	2.624(2)
	2Ge5	3.202(1)		1Ge3	2.375(3)		4Ce2	3.166(1)
	2Ge1	3.327(2)		1Ce1	3.352(2)		2Ce2	3.264(1)
	2Ge6	3.334(2)		4Ce2	3.353(1)	Ge4	1Co2	2.276(3)
	1Co1	3.352(2)	Co2	1Ge4	2.276(3)		2Ge5	2.734(2)
	4Co2	3.427(1)		2Ge6	2.331(1)		2Ge2	2.740(2)
	2Ce1	4.265(1)		2Ge1	2.345(1)		4Ce1	3.098(1)
	2Ce1	4.293(1)		1Ce3	3.193(2)	Ge5	2Co1	2.358(1)
Ce2	4Ge3	3.166(1)		4Ce1	3.427(1)		2Ge4	2.734(2)
	2Ge5	3.226(1)	Ge1	2Co2	2.345(1)		4Ge2	3.026(1)
	2Ge2	3.240(1)		4Ge6	3.026(1)		2Ce1	3.202(1)
	2Ge2	3.240(1)		4Ge6	3.026(1)		2Ce1	3.202(1)
	2Ge3	3.264(1)		2Ge7	3.098(1)		2Ce2	3.226(1)
	4Co1	3.353(1)		2Ce3	3.108(1)	Ge6	2Co2	2.331(1)
	2Ce2	4.005(1)		2Ce1	3.327(2)		4Ge1	3.026(1)
	2Ce2	4.265(1)	Ge2	2Co1	2.348(1)		2Ce3	3.100(1)
	2Ce2	4.293(1)		2Ge4	2.740(2)		2Ge7	3.110(1)
Ce3	4Ge7	3.026(1)		4Ge5	3.026(1)		2Ce1	3.334(2)
	4Ge6	3.100(1)		2Ce1	3.188(1)	Ge7	4Ce3	3.026(1)
	4Ge1	3.108(1)		2Ce2	3.240(1)		4Ge1	3.098(1)
	2Co2	3.193(2)					4Ge6	3.110(1)
	2Ce3	4.265(1)						
	2Ce3	4.293(1)						

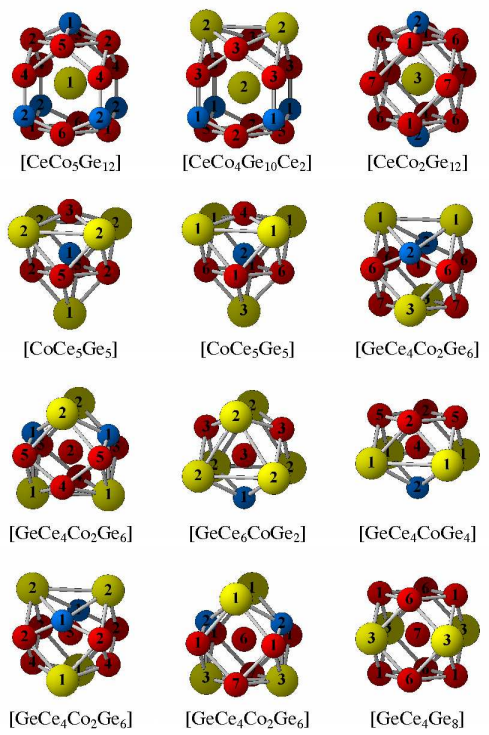

Fig. 2 Coordination polyhedra of the atoms in $Ce_5Co_4Ge_{13}$. Ce atoms: large light spheres, Co atoms: small spheres, and Ge atoms: medium dark spheres; the numbers inside the spheres correspond to the labels used in Table 2.

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