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Crystal structure of the new compound $Ce_3Pt_{23}Ge_{11}$

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Abstract

The crystal structure of the compound $Ce_3Pt_{23}Ge_{11}$ has been determined by X-ray analysis of a single crystal (Enraf–Nonius CAD-4 autodiffractometer, Mo Kα radiation, 276 independent reflections, R-factor 0.0735 in isotropic approximation). This structure has been found to belong to a new structural type: space group $F\bar{4}3m$, $a = 17.1833(9)$ Å, $Z = 8$. The coordination polyhedra of the cerium atoms are compressed cubes, those of platinum have eight or 10 apexes and those of germanium are either trigonal prisms with an additional atom or cubes. The magnetic properties of $Ce_3Pt_{23}Ge_{11}$ at low temperatures (4–100 K) were investigated. A diffuse magnetic phase transition at around 10 K was detected.

1. Introduction

The interaction of cerium with platinum and germanium has not been studied over the whole range of concentrations. The literature gives data on several ternary compounds of the Ce–Pt–Ge system: $CePt_2Ge_2$ (structural type $CeGa_2Al_2$) [1], $CePtGe_2$ (structural type $NdIrGe_2$) [2], CePtGe (structural type KHg_2) [3], $Ce_3Pt_4Ge_6$ (space group *Bmmb*) [4] and $Ce_2Pt_7Ge_4$ (space group Pnma) [5].

This paper presents data on the new ternary compound $Ce_3Pt_{23}Ge_{11}$ which has been found in the Ce–Pt–Ge system at 870 K; the determination of its structure and low temperature magnetic behaviour (in brief) is described.

2. Experimental details

A single crystal suitable for X-ray analysis was taken from an ingot of 1 g prepared by melting a starting mixture of composition $Ce_{7.5}Pt_{62.5}Ge_{30}$ in an arc furnace in an argon atmosphere followed by annealing at 870 K for 600 h. The purity of the starting metals was better than 99%.

The single crystal was examined photographically (RKV-86 and RGNS-2 cameras, Mo Kα and Cu Kα radiations) and then using an Enraf–Nonius CAD-4 autodiffractometer (Mo Kα radiation, flat graphite monochromator, θ–2θ scanning, $2\theta_{max} = 56°$). The lattice parameter was $a = 17.1833$ Å. Calculations using 276 independent reflections with $I \geqslant 2\sigma I$ were performed with CSD programmes [6] on an IBM PC AT286 computer.

The structure of the new compound was determined by direct methods to belong to the space group $F\bar{4}3m$. The atomic position parameters were refined in the isotropic approximation down to $R = 0.0735$ and the corresponding values are listed in Table 1. The interatomic distances are listed in Table 2.

The temperature dependence of the magnetic moment was measured in the temperature range 4–100 K with a "PARC" (USA) vibrating magnetometer to an accuracy of 10^{-5} in a magnetic field of 200 Oe.

3. Results and discussion

The projection of the unit cell of the structure on to the XY plane (for Z from 0 to $\frac{1}{2}$) and the coordination

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TABLE 1. Atomic position parameters of $Ce_3Pt_{23}Ge_{11}$

Atom	G (%)	x/a	y/b	z/c	B_i
Ce1	100	0.2482(11)	0	0	0.86(14)
Pt1	100	0.6219(3)	$\frac{1}{4}$	$\frac{1}{4}$	0.62(9)
Pt2	100	0.5598(4)	x	x	0.4(2)
Pt3	100	0.1639(3)	x	x	0.5(2)
Pt4	100	0.9427(5)	x	x	0.8(2)
Pt5	100	0.3287(3)	x	x	0.4(2)
Pt6	100	0.1659(3)	x	0.9979(4)	0.49(12)
Pt7[a]	100	0.1653(3)	x	0.5041(5)	0.72(13)
Ge1	100	0.0857(13)	x	x	0.9(5)
Ge2	100	0.4172(12)	x	x	0.4(6)
Ge3	100	0.8575(12)	x	x	1.3(6)
Ge4[a]	100	0.6462(8)	x	x	0.7(5)
Ge5	100	0.0785(9)	$\frac{1}{4}$	$\frac{1}{4}$	0.7(2)

[a] Occupation: Pt7, 0.78(3)Pt + 0.22(3)Ge; Ge4, 0.80(7)Ge + 0.20(7)Pt.

polyhedra of the atoms are given in Fig. 1. The coordination polyhedron of the cerium atoms has eight apexes, Ce1[Pt_8] (Fig. 1a), which is a rare phenomenon. The platinum atom polyhedra have eight or 10 apexes: Pt1[Pt_4Ge_4] (Fig. 1b), Pt2[Pt_6Ge_4] (Fig. 1c), Pt3[Pt_6Ge_4] (Fig. 1d), Pt4[Pt_6Ge_4] (Fig. 1e), Pt5[Pt_6Ge_4] (Fig. 1f), Pt6[$Ce_2Pt_5Ge_3$] (Fig. 1g) and Pt7[$Ce_2Pt_5Ge_3$] (Fig. 1h). Trigonal prisms with an additional atom are typical for the germanium atoms: Ge1[Pt_7] (Fig. 1i), Ge2[Pt_7] (Fig. 1j), Ge3[Pt_7] (Fig. 1k), Ge4[Pt_7] (Fig. 1l). The coordination polyhedron of Ge5 is a cube, Ge5[Pt_8] (Fig. 1m).

The interatomic distances in the structure of the new compound are in a range typical of this type of intermetallic (Table 2).

We have attempted to represent the crystal structure of $Ce_3Pt_{23}Ge_{11}$ using combinations of the coordination polyhedra of Ce1, Pt1 and Ge5. The coordination polyhedron of the Ce1 atom is a compressed cube (parallelepiped) with two square facets, Pt6–Pt6–Pt6–Pt6 and Pt7–Pt7–Pt7–Pt7. The coordination polyhedra of the Ge5 and Pt1 atoms are a cube and a distorted cube respectively. The relative location of these polyhedra in the layer from $Z = 0.142$ to 0.358 is shown in Fig. 2. In that layer (A) parallelepipeds are located at distances of ½*a*. We have marked the upper facets of the parallelepipeds by 6 or 7 in accordance with the squares that are visible, *i.e.* Pt6–Pt6–Pt6–Pt6 or Pt7–Pt7–Pt7–Pt7. The layer from $Z = 0.333$ to 0.667 is shown in Fig. 3 (to simplify the diagram, only the coordination polyhedra of the Ce1 atoms are shown). The upper apexes of two neighbouring parallelepipeds in layer A become the basis for the same perpendicularly oriented polyhedron. This layer of vertical parallelepipeds is termed the B layer. The next layer A′ is an inverted A layer. Thin lines in Fig.

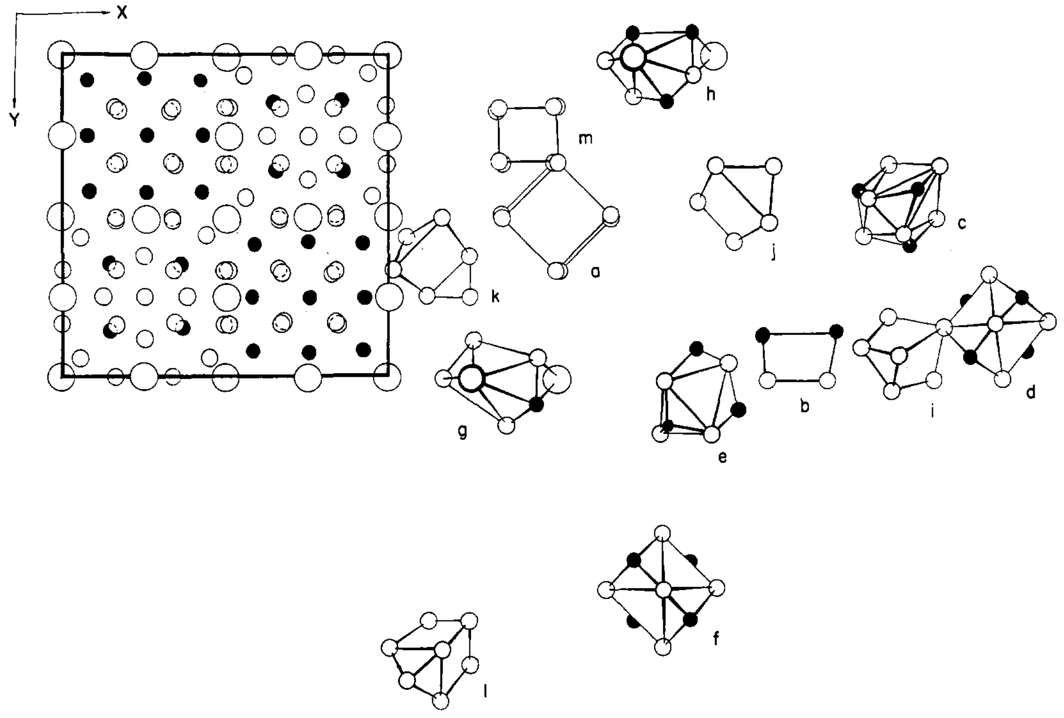

Fig. 1. Projection of $Ce_3Pt_{23}Ge_{11}$ unit cell on to XY plane (for Z from 0 to ½) and coordination polyhedra of cerium (a), platinum (b–h) and germanium (i–m) atoms.

TABLE 2. Interatomic distances

Atom	δ (Å)	Coordination number	Atom	δ (Å)	Coordination number
Ce1–4Pt6	3.182(10)	8	Pt7–Ge4	2.49(14)	10
4Pt7	3.206(11)		Ge2	2.50(2)	
			Ge5	2.501(11)	
Pt1–2Ge4	2.558(14)	8	Pt2	2.736(10)	
2Ge3	2.64(2)		Pt1	2.888(8)	
2Pt7	2.888(8)		2Pt6	2.902(8)	
2Pt6	2.901(7)		Pt5	3.017(10)	
			2Ce1	3.206(11)	
Pt2–3Ge2	2.51(2)	10			
1Ge4	2.570(15)		Ge1–Pt3	2.32(2)	7
3Pt7	2.736(10)		3Pt6	2.46(2)	
3Pt2	2.906(10)		3Pt4	2.55(2)	
Pt3–1Ge1	2.32(2)	10	Ge2–3Pt7	2.50(2)	7
3Ge5	2.556(10)		3Pt2	2.51(2)	
3Pt5	2.838(7)		Pt5	2.64(2)	
3Pt6	2.853(8)				
			Ge3–3Pt6	2.48(2)	7
Pt4–1Ge3	2.53(2)	10	Pt4	2.53(2)	
3Ge1	2.55(2)		3Pt1	2.64(2)	
3Pt4	2.787(12)				
3Pt6	2.803(10)		Ge4–3Pt7	2.49(2)	7
			3Pt1	2.558(14)	
Pt5–3Ge5	2.490(11)	10	Pt2	2.570(15)	
Ge2	2.64(2)				
3Pt3	2.838(7)		Ge5–2Pt6	2.470(10)	8
3Pt7	3.017(10)		2Pt5	2.490(11)	
			2Pt7	2.501(11)	
Pt6–Ge1	2.46(2)	10	2Pt3	2.556(10)	
Ge5	2.470(10)				
Ge3	2.48(2)				
Pt4	2.803(10)				
Pt3	2.853(8)				
Pt1	2.901(7)				
2Pt7	2.902(8)				
2Ce1	3.182(10)				

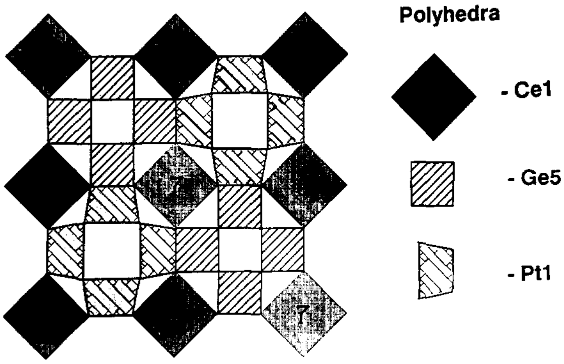

Fig. 2. Ce1, Pt1 and Ge5 coordination polyhedra packing in layer from $Z=0.142$ to 0.358 (layer A).

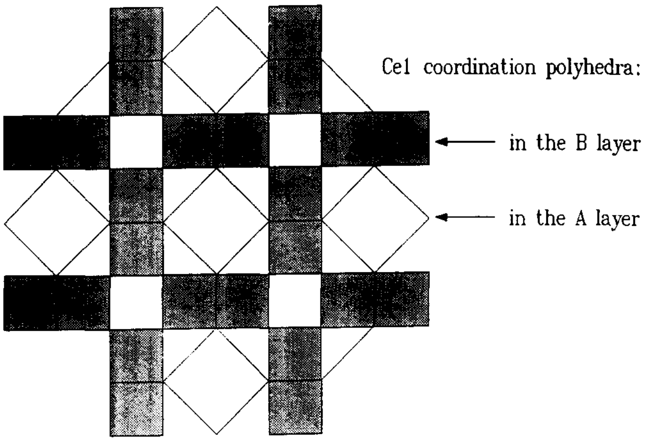

Fig. 3. Relative location of Ce1 coordination polyhedra in layers A and B.

3 give the contours of the Ce1 coordination polyhedra in the upper and lower layers A and A′. The complete structure may therefore be described by the sequence ...ABA′B′ABA′B′..., where B′ is an inverted B layer. Two parallelepipeds from layers A and A′ and four neighbouring parallelepipeds from layer B form a cubo-octahedron in which four Ge atoms and four Pt atoms are located. These eight atoms form two interlocking

tetrahedra. Our attempts to find closely related structures among other intermetallic compounds were unsuccessful. However, it should be mentioned that the coordination polyhedra of the Pt3 (Fig. 1d) and Pt5 (Fig. 1f) atoms are similar to those of the Ga atoms in $Ni_8Zn_{36}Ga_5$ [7]. We assume that the structure described here is a new structural type.

In the temperature dependence of the magnetic susceptibility a discontinuity occurs at 10 K. The shape of this magnetic anomaly is rather diffuse. The magnetic phase transition at 10 K is possibly due to a magnetic Ce ion interaction involving hybridization between 4f Ce ions and conduction s-electrons. Unfortunately, our data do not allow us to confirm the origin of this transition. At temperatures above 10 K we observed Curie–Weiss behaviour of the magnetic susceptibility.

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