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Structures of Ce_2Sn_5 and Ce_3Sn_7, Two Superstructures of $CeSn_3$

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Abstract

Ce_2Sn_5 and Ce_3Sn_7 crystallize in two new structures which are superstructures of cubic $CeSn_3$ ($AuCu_3$ type). They are orthorhombic with space group *Cmmm*. Their lattice parameters are related to that of $CeSn_3$ with $b(Ce_2Sn_5) \simeq 7a(CeSn_3)$ and $b(Ce_3Sn_7) \simeq 5a(CeSn_3)$. These superstructures are deduced from the cubic $CeSn_3$ structure by ordered atomic substitutions. In both cases these substitutions induce two crystallographic sites for the Ce atoms: one which has practically the same environment as that of Ce in $CeSn_3$, with only Sn atoms as first neighbours, and one with two Ce atoms among the first neighbours. Crystal data: Ce_2Sn_5, $a = 4{\cdot}559\ (6)$, $b = 35{\cdot}014\ (39)$, $c = 4{\cdot}619(4)$ Å, $R = 0{\cdot}048$ for 303 independent reflections; Ce_3Sn_7, $a = 4{\cdot}524(1)$, $b = 25{\cdot}742(11)$, $c = 4{\cdot}610\ (2)$ Å, $R = 0{\cdot}077$ for 191 independent reflections.

Introduction

The intermetallic compound $CeSn_3$, which crystallizes in the cubic $AuCu_3$($L1_2$ type) structure, is considered to be a typical intermediate-valence compound. Therefore, the low-temperature magnetic susceptibility has been carefully studied by a large number of authors [see references given in Gschneidner, Dhar, Stierman, Tsang & McMasters (1985) and Boucherle, Fillion, Flouquet, Givord, Lejay & Schweizer (1986)] with particular attention to the increase of susceptibility at very low temperature ($T < 20$ K). Some of the authors consider this increase to be a result of the intermediate-valence character of cerium in this compound, but others attribute it to impurities and possibly to other phases of the Ce–Sn system.

To clarify this point, we have investigated the Ce–Sn compounds which can occur as impurities in $CeSn_3$. As the $AuCu_3$-type compounds may deviate from the $L1_2$

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ideal structure and present periodic antiphases (Watanabe & Fisher, 1965), we have focused our research on the neighbouring phases which could be superstructures of $CeSn_3$.

Two neighbouring compounds are quoted in the literature: Ce_2Sn_5 and Ce_3Sn_7 (Iandelli & Palenzona, 1966). We have prepared single crystals of these two phases and determined their crystal structures by neutron diffraction. We present here these experiments and explain how these two new structures are related to $CeSn_3$.

Experimental

Small single crystals (size $\simeq 0{\cdot}1$ mm) of Ce_2Sn_5 and Ce_3Sn_7 were extracted from polycrystalline ingots prepared by melting in a cold crucible. The starting materials were 99·99% pure Ce and 99·999% pure Sn. The crystals were sealed under an argon atmosphere in Lindemann glass tubes. X-ray diffraction on a Weissenberg camera showed that both compounds crystallize as superstructures of $CeSn_3$ and determined approximate unit-cell parameters. However, no reliable collection of intensities could be achieved on an X-ray four-circle diffractometer: the measured intensities of the standard reflections kept decreasing during the experiment owing to oxidation of the crystals, in spite of the inert atmosphere.

Therefore, we performed neutron-scattering experiments on larger samples to suppress the oxidation effects. Large single crystals of Ce_2Sn_5 and Ce_3Sn_7 were prepared by the Bridgman method in tantalum crucibles. Ce_2Sn_5 was annealed at 1363 K for 5 days and Ce_3Sn_7 at 1323 K for 4 days. Parallelepipeds were cut parallel to the crystallographic axes. The crystals were mounted on the four-circle diffractometer of reactor Siloe (CEN, Grenoble), which is equipped with a low-temperature device. The neutron wavelength is $\lambda = 1{\cdot}175$ (2) Å. The experimental conditions are summarized in Table 1.

The two compounds are orthorhombic and their cell parameters are reported in Table 1. Because of the large value of parameter *b*, overlapping of different Bragg reflections sometimes occurred. Most of the reflections affected by overlap were removed by performing ω and ω–2θ scans to collect the intensities and then comparing the two profiles. 950 and 605 reflections were measured on Ce_2Sn_5 and Ce_3Sn_7. After elimination of the biased reflections and reduction of the symmetry-equivalent reflections, 472 and 255 reflections remained for the two crystals.

A complementary experiment was carried out on a smaller Ce_2Sn_5 sample (2·3 × 1·7 × 0·8 mm) cut from the same crystal, to determine the extinction parameter *g*. For this purpose, the intensities of 12 low-angle strong reflections and 25 weak reflections were measured.

Table 1. *Experimental conditions, lattice parameters [for comparison with the cell parameter of cubic* $CeSn_3$ *at* 300 K, $a_0 = 4{\cdot}721$ (2) Å] *and conditions of the structure refinement*

	Ce_2Sn_5	Ce_3Sn_7
Annealing conditions	5 days at 1363 K	4 days at 1323 K
Sample dimensions (mm)	3·80 × 3·80 × 4·50	3·95 × 4·85 × 3·70
Temperature (K)	10	100
Wavelength (Å)	1·175 (2)	1·175 (2)
$\lambda/2$ contribution	0·00301 (14)	0·00301 (14)
a (Å)	4·559 (6)	4·524 (1)
b (Å)	35·014 (39)	25·742 (11)
c (Å)	4·619 (4)	4·610 (2)
No. of reflections used for cell parameter determination	17	17
Angular zone (°)	$12 \leq \theta \leq 26$	$12 \leq \theta \leq 26$
No. of measured reflections	950	605
No. of reflections after elimination of overlapped biased reflections	628	380
No. of independent reflections	303	191
$R_{\rm merge}$ (%)	1·8	0·7
θ range (°)	$1 \leq \theta \leq 50$	$1 \leq \theta \leq 31{\cdot}5$
Range of *h,k,l*	$-3 \leq h \leq 0$	$-5 \leq h \leq 5$
	$0 \leq k \leq 45$	$0 \leq k \leq 26$
	$-3 \leq l \leq 3$	$0 \leq l \leq 5$
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0·65	0·44
Standard reflection	002	002
Deviation of intensity ($R_{\rm merge}$) (%)	0·80	0·35
Extinction parameter *g*	100 (150)	730 (300)
R	0·048	0·077
Ratio of max. LS shift to e.s.d.	0·073	0·028
wR	0·059	0·104

Structure solution and refinement

Comparison of the lattice parameters of $CeSn_3$, Ce_2Sn_5 and Ce_3Sn_7 leads to the conclusion that the Ce_2Sn_5 and Ce_3Sn_7 structures are obtained by stacking of $CeSn_3$ cells along the **b** axis with some ordered modifications. The frequency of these modifications yields the values of $b(Ce_2Sn_5) \simeq 7a(CeSn_3)$ and $b(Ce_3Sn_7) \simeq 5a(CeSn_3)$.

A large number of the measured reflections, at least at lower angles, are weak (superstructure reflections). Nevertheless, it appeared that after correcting for the $\lambda/2$ contribution, systematic absences exist for $h+k = 2n+1$, with no extra condition. 303 and 191 allowed and independent reflections remained for the two compounds. The only possible space groups are then *Amm*2 ($\sim$*Cm*2*m*), *C*222, *Cmm*2 and *Cmmm*.

Various kinds of modifications were searched for. The simple substitution of one Sn atom by one Ce atom every seventh (or fifth) cell for Ce_2Sn_5 (or Ce_3Sn_7) was rejected because it led to a *P* space group. Other substitutions were therefore considered, following those in the $ErSn_2$ structure (Iandelli & Palenzona, 1966): $CeSn_3$ cells are stacked along the **b** axis and one plane of Sn atoms is removed, involving an **a**/2 glide between the cells on both sides of the missing plane (Fig. 1). The frequency of the substitutions determines the stoichiometry of the compounds according to:

$$4CeSn_3 - 2Sn \rightarrow 2Ce_2Sn_5$$
$$3CeSn_3 - 2Sn \rightarrow Ce_3Sn_7.$$

There are two such substitutions per cell of Ce_2Sn_5 and per cell of Ce_3Sn_7 and their arrangement leads to the space group *Cmmm*, in contrast to $ErSn_2$ for which the space group is *Cmcm*. Schematic representations of the unit cells are shown in Fig. 2. After refinement, this model was found to fit the measured data.

In both structures all the atoms belong to one of the four following positions: 2(*a*) (0,0,0), 2(*c*) ($\frac{1}{2}$,0,$\frac{1}{2}$), 4(*i*) (0,*y*,0; 0,$\bar{y}$,0) and 4(*j*) (0,*y*,$\frac{1}{2}$; 0,$\bar{y}$,$\frac{1}{2}$). The atomic parameters were refined on a Prime computer using the program *ORXFLS*3 (Busing, Martin & Levy, 1971). Refinement was on F^2 with isotropic thermal parameters. The individual reflection weights were $1/[\sigma(F^2_{\rm obs})]^2$. The atomic scattering factors used were b(Ce) = 4·84 fm (Atoji, 1961) and b(Sn) = 6·228 fm (Bauspiess, Bonse & Rauch, 1978).

The extinction parameter g [$= 1/(2\pi^{1/2}\eta)$, where η is the mosaicity of the crystal] was determined for Ce_2Sn_5 by two different methods. First, it was deducted from a comparison between the measured intensities for the small and large single crystals. It has also been deduced by measuring the flipping ratios of the large crystal with polarized neutrons at different wavelengths (Boucherle, Givord, Lejay, Schweizer & Stunault, 1988). The two determinations were in good agreement. The determination of g by the first method gave a large correlation with the thermal parameters. The parameter determined from the polarized neutron experiment was then chosen. The extinction parameter of Ce_3Sn_7 was obtained from a polarized neutron experiment (Boucherle *et al.*, 1988).

Table 2. *Final atomic coordinates for* Ce_2Sn_5

The temperature factor is given by $\exp(-B\sin^2\theta/\lambda^2)$.

Site	Position	x	y	z	B(Å^2)
Ce(1)	4(*i*)	0	0·43206 (3)	0	0·32 (25)
Ce(2)	4(*i*)	0	0·29764 (3)	0	0·30 (25)
Sn(1)	2(*a*)	0	0	0	0·31 (25)
Sn(2)	2(*c*)	$\frac{1}{2}$	0	$\frac{1}{2}$	0·28 (25)
Sn(3)	4(*i*)	0	0·13661 (3)	0	0·26 (25)
Sn(4)	4(*j*)	0	0·36298 (3)	$\frac{1}{2}$	0·25 (25)
Sn(5)	4(*j*)	0	0·07102 (3)	$\frac{1}{2}$	0·36 (25)
Sn(6)	4(*j*)	0	0·22147 (2)	$\frac{1}{2}$	0·29 (25)

Table 3. *Final atomic coordinates for* Ce_3Sn_7

The temperature factor is given by $\exp(-B\sin^2\theta/\lambda^2)$.

Site	Position	x	y	z	B(Å^2)
Ce(1)	2(*a*)	0	0	0	0·33 (8)
Ce(2)	4(*i*)	0	0·18424 (11)	0	0·31 (7)
Sn(1)	2(*c*)	$\frac{1}{2}$	0	$\frac{1}{2}$	0·48 (7)
Sn(2)	4(*i*)	0	0·40612 (8)	0	0·36 (6)
Sn(3)	4(*j*)	0	0·09440 (8)	$\frac{1}{2}$	0·33 (6)
Sn(4)	4(*j*)	0	0·28872 (9)	$\frac{1}{2}$	0·40 (6)

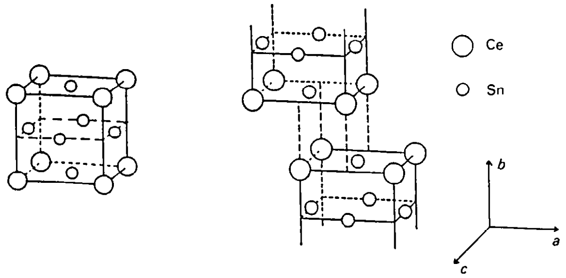

Fig. 1. Unit cell of $CeSn_3$ and substitution zone in its superstructures: Ce_2Sn_5 and Ce_3Sn_7.

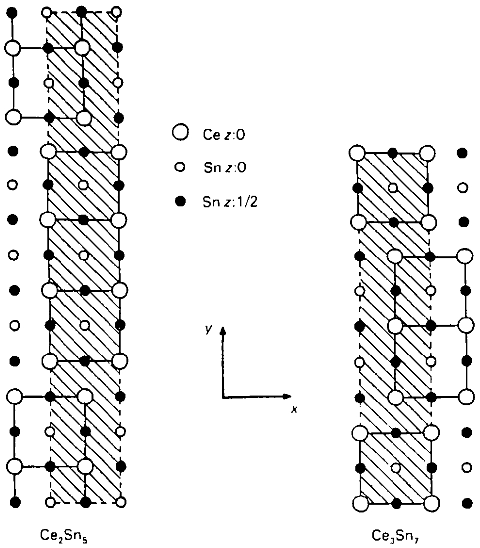

Fig. 2. Schematic representation of the unit cells of Ce_2Sn_5 and Ce_3Sn_7 (projection along **c**).

The results of the two refinements are reported in Tables 2 and 3.* The agreements between observed and calculated intensities are good: $R = 0{\cdot}048$ for Ce_2Sn_5 and $R = 0{\cdot}077$ for Ce_3Sn_7. This confirms the validity of the model. The two structures are shown in Fig. 3.

These structures are characterized by two different sites for cerium (Fig. 4): the Ce(1) site, with twelve Sn atoms as nearest neighbours, has practically the same environment as in $CeSn_3$. The Ce(2) site in the substitution zone, with ten Sn atoms and two Ce atoms as nearest neighbours, has a completely different environment. The shortest distances are reported in Tables 4 and 5.

Concluding remarks

The two compounds Ce_2Sn_5 and Ce_3Sn_7 crystallize in two new structures which can be deduced from $CeSn_3$ by ordered substitutions of atoms. The frequency of the substitutions determines the stoichiometry Ce_2Sn_5 or Ce_3Sn_7.

In both compounds there are two types of Ce sites: one, the unperturbed site, which is very close to the Ce site in $CeSn_3$ with no Ce atoms as first neighbours, and

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44858 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

another, the substitution site, with two Ce atoms among the first neighbours. One can expect very different magnetic behaviour for these two cerium sites, particularly the behaviour of the magnetic moments and the magnetic anisotropy.

The same type of substitution which, when ordered, gives rise to the structures Ce_2Sn_5 or Ce_3Sn_7 may certainly exist simply as stacking faults, without order, in a $CeSn_3$ crystal. Coming back to the magnetic properties of $CeSn_3$ samples, any analysis must take into account the possible existence of well characterized impurities as Ce_2Sn_5 or even Ce_3Sn_7, or simply of the stacking faults which also implies different cerium environments (Boucherle *et al.*, 1986).

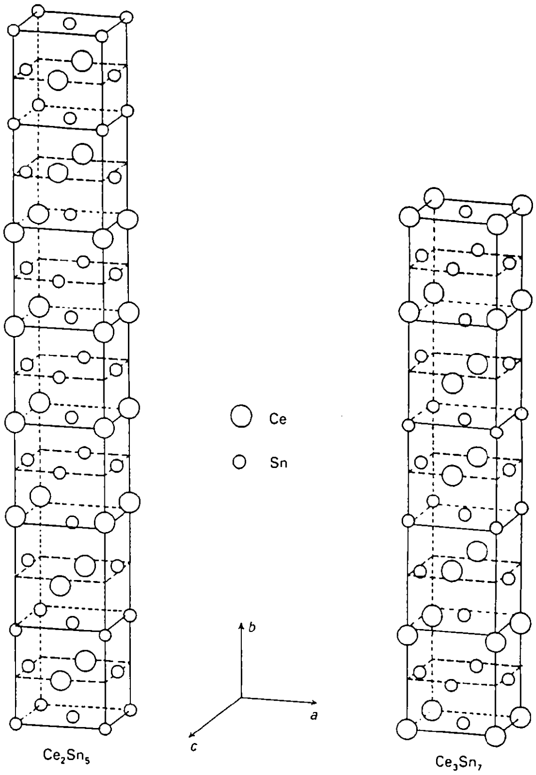

Fig. 3. Ce_2Sn_5 and Ce_3Sn_7 crystallographic cells.

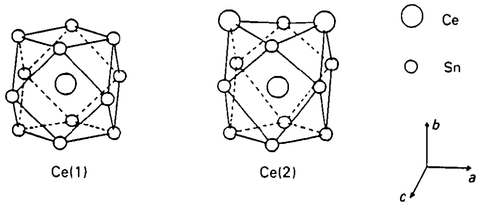

Fig. 4. Environments of the two Ce sites.

Table 4. *Interatomic distances* (Å) *in* Ce_2Sn_5

Ce(1)–Sn(5) ×4	3·247 (3)	Sn(1)–Sn(2) ×4	3·245 (3)
Sn(1) ×2	3·295 (3)	Sn(5) ×4	3·394 (3)
Sn(3) ×2	3·313 (3)		
Sn(2) ×2	3·316 (3)	Sn(2)–Sn(5) ×4	3·373 (3)
Sn(4) ×2	3·344 (3)		
		Sn(3)–Sn(4) ×4	3·245 (3)
Ce(2)–Sn(3) ×2	3·240 (3)	Sn(5) ×2	3·257 (3)
Sn(4) ×2	3·251 (3)	Sn(6) ×2	3·763 (3)
Sn(6) ×4	3·313 (3)		
Sn(6) ×2	3·528 (3)	Sn(4)–Sn(5) ×2	3·246 (3)
Ce(2) ×2	4·041 (4)	Sn(6) ×2	3·734 (4)
		Sn(6)–Sn(6) ×2	3·031 (3)

Table 5. *Interatomic distances* (Å) *in* Ce_3Sn_7

Ce(1)–Sn(2) ×4	3·310 (2)	Sn(1)–Sn(3) ×4	3·320 (2)
Sn(1) ×4	3·229 (1)	Sn(2) ×4	3·340 (2)
Sn(3) ×4	3·349 (2)		
		Sn(2)–Sn(3) ×4	3·229 (1)
Ce(2)–Sn(2) ×2	3·245 (3)	Sn(4) ×2	3·801 (3)
Sn(3) ×2	3·265 (3)		
Sn(4) ×4	3·304 (1)	Sn(3)–Sn(4) ×2	3·764 (3)
Sn(4) ×2	3·542 (3)		
Ce(2) ×2	4·072 (4)	Sn(4)–Sn(4) ×2	3·015 (3)

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