REFINEMENT OF THE CRYSTAL STRUCTURES OF $AuSn_4$ AND $PdSn_4$

R. KUBIAK and M. WOŁCYRZ

Institute for Low Temperature and Structure Research, Polish Academy of Sciences, pl. Katedralny 1, 50-950 Wroclaw (Poland)

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Summary

The crystal structures of $AuSn_4$ and $PdSn_4$ were investigated using single-crystal samples. Unit cell parameters were measured, and the positional parameters and atomic temperature factors were determined in the structure refinement process. It was revealed that the structures investigated depart from the model proposed for $PtSn_4$. The results explain the existence of the glide effect observed earlier for $AuSn_4$.

1. Introduction

In 1950 Schubert and Roesler [1] published the results of a structure refinement of $PtSn_4$. They also reported powder data for $AuSn_4$ and $PdSn_4$ and suggested that both these compounds were isomorphous with $PtSn_4$. We have found that thermal and mechanical treatment of $AuSn_4$ samples has a marked effect on the crystal structure [2]. Partial disorder appears very easily and is related to gliding of the monatomic layers perpendicular to the [001] direction by the vector $\frac{1}{2}(\pm a \pm b)$.

The present studies of $PtSn_4$-type structures were undertaken to obtain an explanation of the glide effect. In addition, we were able to use the single-crystal data to correct the previous models of the $AuSn_4$ and $PdSn_4$ crystal structures.

2. Experimental details

2.1. Crystal growth

Homogeneous polycrystalline $AuSn_4$ and $PdSn_4$ samples were obtained by melting mixtures of pure metals. The samples were heated for about 3 days at temperatures of 490 K and 575 K respectively. Attempts to obtain spherical single crystals from the alloys were made using the method described in refs. 3 and 4. Drops of the molten alloys were cooled at various rates ranging from 1 to

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5 K min^{-1}. A spherical single crystal of $AuSn_4$ of diameter 0.2 mm which was obtained using this procedure was selected for further study. Attempts to obtain spherical single crystals of $PdSn_4$ were unsuccessful. Therefore a portion of the polycrystalline homogeneous $PdSn_4$ sample was remelted, cooled rapidly and then heated at 525 K for 2 weeks. The sample obtained in this way was crystalline and very fragile, and we were able to extract a parallelepipedic single crystal of dimensions 0.3 mm × 0.2 mm × 0.1 mm.

2.2. Data collection and processing

The unit cell dimensions of both crystals were measured using a diffractometer of the Bond type with copper radiation (λ = 1.540 56 Å).

The intensity data for $AuSn_4$ were collected using a Stadi-2 two-circle diffractometer with graphite-filtered Cu Kα radiation. The ω–2θ scan technique was employed up to $2\theta = 120°$. The intensities of the reflections from layers from ($hk0$) to ($hk5$) were measured, and 101 non-equivalent reflections were used for the structure refinement. The data were corrected for Lorentz and polarization factors. The absorption correction for a sphere was introduced. The structure was refined using the LSQ program of the XRAY system [5]. Because of the relatively small number of measured reflections, the atomic temperature factors were assumed to be isotropic in the refinement.

The intensity data for $PdSn_4$ were collected up to $2\theta = 120°$ using a Syntex $P2_1$ four-circle diffractometer with graphite-filtered Mo Kα radiation. 873 independent reflections were used in the structure refinement. The data were corrected for Lorentz and polarization factors. An empirical absorption correction was introduced (ψ scan method). The structure was refined using the LSQ method of the Syntex XTL structure determination system [6].

The atomic scattering factors and the anomalous dispersion correction for gold, palladium and tin were taken from ref. 7.

3. Results and discussion

The structures of $AuSn_4$ and $PdSn_4$ were refined in the space group $Aab2$ [1]. The unit cell parameters for both crystals are given in Table 1.

Figure 1 shows the $PtSn_4$-type structure. For easy comparison of our results with those for $PtSn_4$ we use a similar structure presentation and atomic numbering as in ref. 1. The unit cell contains three non-equivalent atoms located as follows (the Wyckoff notation is used): platinum in the 4a position; Sn(I) and

TABLE 1

The unit cell parameters of $AuSn_4$ and $PdSn_4$ at room temperature (298 K)

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
$AuSn_4$	6.5124(1)	6.5162(1)	11.7065(1)	496.778(12)
$PdSn_4$	6.3888(1)	6.4415(1)	11.4462(2)	471.051(18)

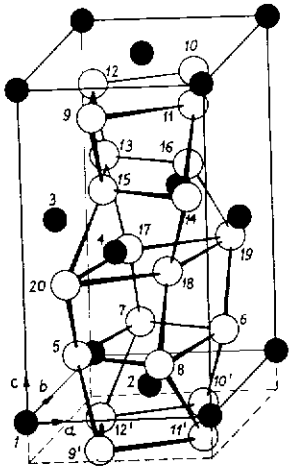

Fig. 1. $PtSn_4$-type crystal structure: ●, gold or palladium; ○, tin.

Sn(II) in the 8b position. The structures belonging to this family are composed of alternate layers of tin atoms and platinum, gold or palladium atoms. Moreover, the positional parameters for Sn(I) and Sn(II) in $PtSn_4$ are related to each other as follows [1]:

$$x_{Sn(I)} = y_{Sn(II)} \qquad y_{Sn(I)} = x_{Sn(II)} \qquad z_{Sn(I)} = -z_{Sn(II)}$$

The final positional and thermal parameters with the standard deviations in parentheses are given in Tables 2 and 3. For comparison parameters for $PtSn_4$ taken from ref. 1 are also given in Table 2.

The results presented indicate that the layers of tin atoms in $AuSn_4$ and $PdSn_4$ are not exactly antisymmetric. As a consequence, the layers of Sn(I) and Sn(II) atoms are not identically strongly bound with the layers of gold or palladium atoms. The layers which are more weakly bound (Sn(II) for $AuSn_4$ and

TABLE 2

The positional parameters of the atoms and the discrepancy factors for $PtSn_4$ [1], $AuSn_4$ and $PdSn_4$

Compound	*Non-equivalent atom*	*x*	*y*	*z*	*R* (%)
$PtSn_4$	Pt	0	0	0	—
	Sn(I)	0.173(5)	0.327(5)	0.125(5)	
	Sn(II)	0.327(5)	0.173(5)	−0.125(5)	
$AuSn_4$	Au	0	0	0	3.9
	Sn(I)	0.1639(1)	0.3395(1)	0.1205(3)	
	Sn(II)	0.3312(2)	0.1642(2)	−0.1409(2)	
$PdSn_4$	Pd	0	0	0	8.7
	Sn(I)	0.1702(7)	0.3281(5)	0.1311(5)	
	Sn(II)	0.3303(6)	0.1662(5)	−0.1224(5)	

Sn(I) for $PdSn_4$) show a higher temperature factor (*cf.* Tables 3 and 4). The distance between the Sn(I)–Sn(II) layers for both $AuSn_4$ and $PdSn_4$ is less than 0.25*c*, while the distance between the Sn(II)–Au–Sn(I) or Sn(II)–Pd–Sn(I) layers is greater than 0.25*c*. It is assumed that the differences in these values, compared with $PtSn_4$, are caused not only by the different atomic radii of gold, palladium and platinum but also by the influence of the atomic bond. Therefore it seems to be reasonable to undertake the $PtSn_4$ structure refinement process again.

TABLE 3

Thermal parameters

Compound	*Atom*	U_{11} (U) (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
$AuSn_4$	Au	1.33(1)	—	—	—	—	—
	Sn(I)	1.02(3)	—	—	—	—	—
	Sn(II)	1.85(3)	—	—	—	—	—
$PdSn_4$	Pd	0.56(4)	0.54(5)	0.29(5)	−0.05(16)	0.00(0)	0.00(0)
	Sn(I)	1.32(10)	0.84(9)	0.48(6)	−0.30(9)	0.13(8)	0.11(6)
	Sn(II)	0.66(6)	0.80(8)	0.72(8)	−0.06(8)	0.09(8)	0.16(6)

The anisotropic temperature factor is defined as $\exp(-2\pi^2\Sigma_{ij}h_ih_ja_i^*a_j^*U_{ij})$.

TABLE 4

A comparison of the bond lengths for $AuSn_4$ and $PdSn_4$

Atoms	*Numbers*	*Bond length* (Å)	
		$AuSn_4$	*$PdSn_4$*
Au(Pd)—Sn(I)	2—5	2.806(2)	2.814(4)
	2—7	2.833(2)	2.811(4)
Au(Pd)—Sn(II)	2—9′	2.952(2)	2.786(4)
	2—11′	2.918(2)	2.750(4)
Sn(I)—Sn(I)	5—6″	2.988(1)	3.105(5)
	5—7	3.446(1)	3.378(4)
	5—8	3.459(1)	3.349(6)
Sn(I)—Sn(II)	5—9′	3.443(4)	3.249(7)
	5—11″	3.749(4)	3.625(7)
	5—12′	3.720(4)	3.628(7)
	5—17	3.670(3)	3.708(7)
	5—20	3.018(4)	3.008(7)
Sn(II)—Sn(II)	9—10″	3.068(1)	3.047(5)
	9—11	3.443(2)	3.372(5)
	9—12″	3.426(1)	3.380(4)

The atoms are numbered according to Fig. 1. The primes and double primes denote atoms outside the unit cell.

The results obtained explain the existence of the glide effect and allow us to conclude that the interlayer glide observed for $AuSn_4$ can occur most easily between the atomic layers of gold and Sn(II).

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