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Note on the Crystal Structures of Ru_5Si_3 and PdSi

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During the continued investigations of platinum metal silicides at this Institute the structure of a new ruthenium silicide, Ru_5Si_3, has been established from X-ray powder data, and the atomic parameters for PdSi have been refined from single crystal X-ray data.

Ru_5Si_3. Alloys were prepared by arc melting ruthenium powder (Heraeus, claimed purity 99.9 %) and silicon (Pechiney, claimed purity 99.9 %). By examining the powder photographs of the alloys the presence of a new intermediate phase was observed. The composition of the phase was found to be intermediate between Ru_2Si [1] and Ru_4Si_3.[2] A comparison of the powder diffraction pattern of the new phase and that of Rh_5Si_3 [3] showed fairly good agreement and it was possible to index the pattern on the basis of an orthorhombic unit cell. The striking similarity between the intensities of equivalent diffraction lines for Rh_5Si_3 and the new phase as well as the correspondence of the unit cells implies that the two phases are isostructural.

The unit cell dimensions of Ru_5Si_3 were evaluated from measurements of a powder pattern recorded in a Guinier-Hägg focusing camera using Cu$K\alpha_1$ radiation. Silicon ($a=5.43054$ Å) was incorporated in the powder specimen as an internal calibration standard. A least-squares refinement of the unit cell dimensions was made (see the list of programmes in Ref. 2).

Crystallographic data for Ru_5Si_3: Structure type: Rh_5Ge_3. $Z=2$. $a=5.246(2)$ Å, $b=9.815(2)$ Å, $c=4.023(1)$ Å, $U=207.14$ Å^3.

PdSi. An alloy of the equi-atomic stoichiometry was prepared by arc melting palladium powder (Heraeus, claimed purity 99.9 %) and silicon (Pechiney, claimed purity 99.9 %). The X-ray powder analysis of the alloy showed the presence of one phase, PdSi. The unit cell dimensions of PdSi (Table 1) were determined in an analogous way to those of Ru_5Si_3 (see above). The lattice constants are uniformly about 0.3 % less than those found in an earlier investigation.[4]

The single crystal investigation was carried out in an equi-inclination Weissenberg camera using zirconium-filtered MoK radiation and the multiple film technique. The crystal was rotated about the b axis and the intensities of the $h0l$ reflexions were recorded. The intensities were estimated by visual comparison with a calibrated intensity scale. Nothing was found during the work that contradicted the correctness of the space group, *Pnma*, proposed earlier.[4]

Starting with the approximate atomic parameters given in Ref. 4 the structure of PdSi was refined by the method of least squares. The refinement was based on 128 $h0l$ reflexions. Four positional parameters, two individual temperature factors, and one scale factor were allowed to vary during the refinement. The weighting scheme according to Cruickshank *et al.*[5] $w=1/(a+|F_o|+c|F_o|^2)$, was used where the constants a and c were given the values 28.0 and 0.014, respectively. The atomic scattering factors for palladium and silicon were obtained from Ref. 6 together with the real and imaginary dispersion corrections. The computational work was carried out utilizing the various

programmes listed in Ref. 2. The final result of the refinement is given in Table 1 and the interatomic distances are listed in Table 2.

(The estimated standard deviations for lattice parameters and atomic co-ordinates are given in parenthesis and refer to the last decimal place of the respective values.)

Table 1. Final structure data for PdSi. Space group: *Pnma*. Structure type: MnP (*B* 31). $Z=4$. $a=5.6173(10)$ Å, $b=3.3909(6)$ Å, $c=6.1534(12)$ Å, $U=117.21$ Å^3.

		Position parameters		Individual isotr. temp., factors
Atom	Position	x	z	B
Pd	4(c)	0.0043(3)	0.1906(3)	0.27(3)
Si	4(c)	0.1770(14)	0.5722(15)	0.33(9)

Final R value = 0.12.

Table 2. Interatomic distances in PdSi. (Distances shorter than 4.0 Å are listed).

Pd	−2	Pd: 2.895(3)
	−2	Pd: 2.902(1)
	−2	Pd: 3.391(1)
	−	Si: 2.449(9)
	−2	Si: 2.458(7)
	−	Si: 2.541(9)
	−2	Si: 2.571(6)
	−	Si: 3.927(10)
Si	−	Pd: 2.449(9)
	−2	Pd: 2.458(7)
	−	Pd: 2.541(9)
	−2	Pd: 2.571(6)
	−	Pd: 3.927(10)
	−2	Si: 2.760(13)
	−2	Si: 3.391(1)
	−2	Si: 3.560(12)
	−4	Si: 3.607(4)

The interesting structural feature of the MnP-type structure is the occurrence of zigzag chains of non-metal atoms parallel to the shortest crystallographic axis. The main purpose of this refinement of the structure of PdSi was to obtain a more accurate distance between the silicon atoms which form these chains. As is evident from Table 2 the distance is 2.76 Å and about 0.1 Å shorter than the one obtained earlier.[4] The average Pd−Pd as well as the average Pd−Si distances are roughly the same as those given in Ref. 4.

In order to make a comparison of the Si−Si distances in PdSi and NiSi [7] the atomic parameters of the latter were refined by the method of least squares. The refinement was based on the F_o values given in Ref. 7 and significant changes of the atomic positions were obtained. ($x_{Ni}=0.0061$, $z_{Ni}=0.1873$, $x_{Si}=0.1741$, and $z_{Si}=0.5844$. R values = 0.11). The interatomic distances showed individual deviations from those given in Ref. 7, but the average Ni−Ni and Ni−Si distances are about the same. The largest deviation appeared in the distance between the silicon atoms which form the zigzag chains. The distance given earlier, 2.58 Å, changed to 2.64 Å.

The difference between the shortest Si−Si distances in PdSi and NiSi is thus about 0.1 Å. In a recent investigation of RhSi (MnP type) [8] the corresponding Si−Si distance was found to be 2.65 Å. In spite of the fairly large difference in atomic radii for rhodium and nickel the interaction between the silicon atoms is about the same in their MnP-type silicides. It might be mentioned that there is a striking difference between the metal-metal distances RhSi and PdSi. Whereas the metal atoms in PdSi are surrounded by four metal atoms, all situated at a distance of 2.90 Å, the conditions are different in RhSi (MnP). In the latter structure the metal atoms are surrounded by six metal atoms at 2.84(2), 3.00(2), and 3.07(2) Å. The distance mentioned last is identical with the length of the *b* axis.

In a comparison of the silicides and phosphides [9] of the MnP-type structure it is found that the distance between the non-metal atoms which form the zigzag chain is about 25 % larger than the covalent single bond distance in the phosphides, whereas the corresponding value is roughly 15 % for the silicides.

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Derivatives of Hydrazine

IX. Conclusive Nuclear Magnetic Resonance Evidence for the Cyclic Structure of Isopropylidenediselenocarbazic Acids

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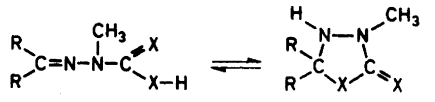
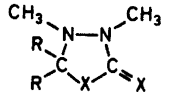
In a recent paper from this laboratory,[1] it was shown that the attempted preparation of isopropylidene-methyldithiocarbazic acid (I) gave a product which, according to ^{1}H NMR and IR spectroscopic evidence, has the tautomeric 3,5,5-trimethyl-1,3,4-thiadiazolidine-2-thione structure (III), both in the solid state and in solution. This conclusion was reached by comparing the spectra with those of 3,4,5,5-tetramethyl-1,3,4-thiadiazolidine-2-thione (VI) for which the alternative open-chain dipolar form is highly improbable.



I : X=S, R=CH$_3$
II: X=Se, R=CH$_3$

III: X=S, R=CH$_3$
IV: X=Se, R=CH$_3$
V : X=Se, R=H



VI : X=S, R=CH$_3$
VII : X=Se, R=CH$_3$
VIII: X=Se, R=H

The reaction between acetone and the hydrazinium salts of 2-methyl- or 2,3-dimethyldiselenocarbazic acid furnished the corresponding selenium compounds, IV, and VII, respectively. When recording the ^{1}H NMR spectra of these compounds (Table 1), it was noted that, in addition to peaks analogous to those observed for III and VI, two small satellites were always present grouped symmetrically around the $(CH_3)_2C$ signal (mutual separation varying between 7.7 and 8.2 Hz, depending on the solvent). An estimate of the intensities of the satellites based upon their heights compared with that of the main signal showed that each corresponds to *ca.* 3.5 %. This shows that the satellites are due to coupling with ^{77}Se (natural abundance). The corresponding coupling constant for diethylselenide is 10.8 Hz,[2] and values around 7 Hz have been found for 2-alkylamino-5-methyl-1,3,4-selenadiazoles.[3] Provided that a ^{77}Se long range coupling can be excluded these observations are only consistent with a cyclic structure for IV and VII. Since such long range coupling was not observed for the methyl ester of the open-chain form II (*cf.* experimental part), the ^{1}H NMR spectra furnish conclusive evidence for the cyclic structure IV (and VII). The solvent shifts of IV and VII closely parallel the results obtained for the sulfur analogues and the previous conclusions concerning the cyclic structure of III (and VI) are therefore strongly reinforced.

The product (VIII) from the reaction between formaldehyde and 1,2-dimethyl-