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Crystal Structure of Iridium Trisilicide, $IrSi_3$

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Small single crystals of $IrSi_3$ were obtained from a polycrystalline sample that had been prepared by induction heating of the elements. The crystals are hexagonal, space group $P6_3mc$ with $a = 4.351 \pm 0.001$ Å, $c = 6.622 \pm 0.002$ Å, and $Z = 2$. The structure is an unusual one, consisting of infinite, planar, four-connected layers of silicon atoms perpendicular to the c axis, with each iridium atom spaced at unequal distances between two silicon layers. The irdium atoms each make nine almost equal contacts with silicon atoms. The silicon–silicon distances of 2.175 Å within each layer are distinctly shorter than the silicon–silicon elemental single bond distance.

During a study of the system iridium–silicon, we have prepared single crystals of composition $IrSi_3$. This phase has been made previously in polycrystalline form, and its crystal system and unit cell dimensions have been deduced.[1-3] In the present work the crystal structure has been determined from single-crystal X-ray data.

Experimental Section

Preparation and Physical Measurements.—Stoichiometric quantities of very coarse powders of iridium (>99.5%) and silicon (99.99%) were placed in an alumina boat and melted by induction heating (3 MHz) under an argon atmosphere. The compound was cooled slowly and although the polycrystalline sample adhered to the boat, small single-crystal fragments could be obtained. Rectangular polycrystalline samples were cut for electrical resistivity measurements: the room-temperature resistivity was 5×10^{-4} ohm cm and at 500° it was about 7×10^{-4} ohm cm.

X-Ray Measurements and Crystal Data.—The crystals were found to be hexagonal with Laue symmetry $6/mmm$ from $hk0$ and $hk1$ equiinclination Weissenberg photographs (λ 1.5405 Å, 25°). Accurate cell dimensions were obtained by a least-squares fit of back-reflection lines of the powder pattern, giving $a = 4.351 \pm 0.001$ Å, $c = 6.622 \pm 0.002$ Å. These cell constants and the details of the pattern itself agreed well with the previously published data.[2] The density calculated for two formula weights per unit cell is 8.455 g cm^{-3} compared to the reported value[2] of 8.64 g cm^{-3}. Systematic absences in the single-crystal Weissenberg data were hhl with l odd, indicating one of the three space groups $P6_3mc$, $P\bar{6}2c$, or $P6_3/mmc$.

For intensity measurements a very small crystal, almost cubic in shape and 0.025 mm on edge, was used. The reciprocal lattice layers $0kl$, $1kl$, $2kl$, and hhl were recorded using an equiinclination Weissenberg camera and Ni-filtered Cu Kα radiation. The multiple-film technique was used and intensities were estimated visually by comparison with a time-calibrated intensity strip. The separate layers were brought to a common scale by least-squares fit of the common reflections. Of 57 independent, nonzero reflections three were measured on three layers, forty on two layers, and the rest on only one layer. In view of the high absorption of the crystals ($\mu = 1298$ cm^{-1}) accurate absorption corrections were made using a modified Busing–Levy program.[4]

Structure Determination and Refinement.—The three-dimensional Patterson function showed an outstanding peak at $^1/_3$, $^2/_3$, $^1/_2$ corresponding to a vector between iridium atoms in the special positions $^1/_3$, $^2/_3$, $^1/_4$; $^2/_3$, $^1/_3$, $^3/_4$ of the space groups $P\bar{6}2c$ and $P6_3/mmc$ or the (b) positions $^1/_3$, $^2/_3$, z; $^2/_3$, $^1/_3$, $^1/_2 + z$ of the space group $P6_3mc$. Since this space group has no unique origin in the z direction, the z parameter could be taken as $^1/_4$. The only other two independent peaks of any height in the Patterson map were at $^1/_2$, $^1/_2$, 0.177 and $^1/_6$, $^5/_6$, 0.323. These two peaks were almost identical in height after normalizing for the different Patterson symmetries of the positions and were 23% of the normalized Ir–Ir peak. These peaks corresponded very well to vectors between the iridium atoms and silicon atoms in the (c) positions of the space group $P6_3mc$: $x, \bar{x}, z$; $x, 2x, z$; $2\bar{x}, \bar{x}, z$; $\bar{x}, x, {}^1/_2 + z$; $\bar{x}, 2\bar{x}, {}^1/_2 + z$; $2x, x, {}^1/_2 + z$ with $x = {}^5/_6$ and $z = 0.073$.

Using these coordinates, the structure was refined first by difference Fourier methods and then by full-matrix least squares, using a modified Busing–Martin–Levy program.[5] Three cycles of isotropic refinement converged to a conventional $R = 0.075$ and $wR = 0.095$. The isotropic B values were 1.53 (12) for Ir and 4.95 (67) for Si. Three further cycles using anisotropic temperature parameters for Ir and isotropic for Si gave $R = 0.072$ and $wR = 0.092$.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $IrSi_3$[a]

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
0 0 0	--	228.6	1 0 7	43.9	41.8	2 0 6	32.0	29.4	3 0 4	55.4	53.8	4 0 1	42.7	42.8
0 0 2	99.1	100.7	1 0 8	20.3	20.1	2 0 7	38.1	38.1	3 0 6	28.2	37.7	4 0 2	19.7	20.6
0 0 4	80.1	84.1	1 1 0	94.7	90.2	2 1 0	34.2	29.5	2 2 0	66.5	69.0	4 0 3	26.2	31.7
0 0 6	72.3	77.1	1 1 2	103.3	100.4	2 1 1	62.5	63.9	2 2 2	51.5	48.0	4 0 4	15.1	18.4
0 0 8	34.0	39.2	1 1 4	84.8	76.4	2 1 2	40.3	40.8	2 2 4	47.6	43.2	3 2 0	18.5	21.7
1 0 0	56.9	59.3	1 1 6	55.2	50.5	2 1 3	66.9	59.2	3 1 0	28.1	27.0	3 2 1	32.8	34.0
1 0 1	88.5	98.9	2 0 0	58.3	64.6	2 1 4	36.8	31.2	3 1 1	46.9	45.5	3 2 2	18.0	18.6
1 0 2	54.3	57.0	2 0 1	88.0	94.9	2 1 5	50.4	43.1	3 1 2	27.6	25.7	3 2 3	41.2	33.4
1 0 3	113.2	97.4	2 0 2	35.6	36.3	2 1 6	19.7	19.5	3 1 3	44.2	43.3	4 1 0	34.5	36.8
1 0 4	42.3	42.8	2 0 3	59.4	47.9	2 1 7	31.8	31.2	3 1 4	20.9	21.6	4 1 2	37.9	36.6
1 0 5	60.2	58.0	2 0 4	33.3	32.5	3 0 0	58.1	61.1	3 1 5	33.2	32.2			
1 0 6	28.7	29.2	2 0 5	65.2	59.3	3 0 2	63.2	67.2	4 0 0	25.0	27.0			

[a] Cu Kα radiation; F_c for contents of one unit cell.

TABLE II

STRUCTURAL PARAMETERS WITH STANDARD DEVIATIONS FOR $IrSi_3$[a]

Parameter	Ir	Si
x	$^1/_3$	0.818 (12)
y	$^2/_3$	0.182
z	$^1/_4$	0.083 (5)
$\beta(1,1)$	0.0497 (48)	5.14 (73)[b]
$\beta(2,2)$	0.0497	
$\beta(3,3)$	0.0075 (9)	
$\beta(1,2)$	0.0249	
$\beta(1,3)$	0.0	
$\beta(2,3)$	0.0	

[a] Temperature factor for Ir is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Value of B (Å^2) in the temperature factor $\exp[-(B \sin^2 \theta)/\lambda^2]$.

The corresponding observed and calculated structure factors are given in Table I, and the refined structural parameters, in Table II. According to Hamilton's test[6] the latter values of R and wR are significant at the 10% level. However, anisotropic refinement for the silicon atoms in addition brought no significant improvement. Since only one set of F_{hkl}, $F_{\bar{h}\bar{k}\bar{l}}$ were estimated, an attempt was made to distinguish these by refining both enantiomorphs of the noncentrosymmetric structure using the real and imaginary parts of the anomalous dispersion corrections.[7] The differences in the calculated structure factors were so small that both R and wR were identical in both refinements and the coordinates listed are arbitrarily assigned to correspond

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to F_{hkl}. All refinements were on the basis of F. An empirical weighting scheme was derived by plotting ΔF *vs.* F and in final refinement $\sigma F_o = 1.20 + 0.052F_o$. The form factors used are those given in ref 8. The thermal ellipsoids found for the iridium atoms are restricted by symmetry so that the axes within the *ab* plane are equal, and the short, unique axis is parallel to *c*. The axial ratio is 0.59.

Results and Discussion

The crystal structure of $IrSi_3$ is illustrated in Figure 1. The silicon atoms are arranged in infinite planar layers perpendicular to the *c* axis, with two such layers per unit cell. These layers are of the four-connected planar net type consisting of one-third hexagons and two-thirds triangles,[9] which is well known in alloy structures, *e.g.*, $CaCu_5$.[10] In addition to having four near neighbors within the layer, each silicon atom is in contact with three iridium atoms, two on one side and one on the other side of the layer. Each iridium atom, between two silicon layers, is in contact with nine silicon atoms. Of these, six form a hexagon in the nearer layer with Ir–Si = 2.44 ± 0.05 Å while three are in a triangle in the further layer with Ir–Si = 2.49 ± 0.04 Å.

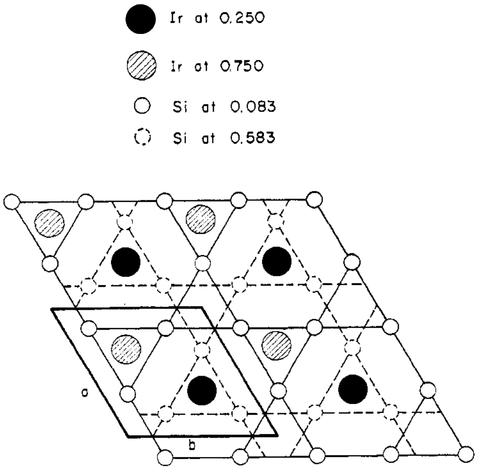

Figure 1.—Positions of the atoms in $IrSi_3$. The *z* coordinates (height above the plane of the diagram) are given in fractions of the *c* axis.

For the "ideal" value, $^5/_6$, for the silicon parameter all the close silicon–silicon distances would be equal. Taking the refined *x* value these distances would fall into two groups, with the distances in triangles in contact with iridium atoms being 1.98 ± 0.16 Å and the others 2.37 ± 0.16 Å. However the differences between the two sets is less than 3σ and may not be real. Regardless of the exact value of *x* it is clear that the Si–Si distances must average $a/2$ or 2.175 ± 0.001 Å which is considerably shorter than the elemental single-bond distance of 2.3516 ± 0.0001 Å for silicon.[11] In order to explain the higher observed bond order in $IrSi_3$ it is necessary to postulate electron transfer from the iridium atoms to the silicon layers. The 60° angles at each silicon atom would seem to favor a resonating structure giving partial double-bond character to essentially equal bonds rather than a nonresonating structure with bonds of appreciably different character.

The structure here described for $IrSi_3$ has identical iridium positions but quite different silicon positions from the structure proposed by Finnie[3] on the basis of powder data. He noted good agreement between the powder patterns of $IrSi_3$ and $HgMg_3$ (Na_3As type). However this agreement is due to domination of the X-ray intensities by the heavy atom in both cases. The three-dimensional Patterson map derived from the single-crystal data is quite incompatible with a structure similar to that of Na_3As and can only be interpreted by a structure containing planar networks of silicon atoms.

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A New Isomer of Diiodotetraphosphorus Trisulfide. The Preparation and Crystal Structure of β-$P_4S_3I_2$[1]

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β-$P_4S_3I_2$ is prepared by the reaction of P_4S_3 with I_2 in solution. The structure was determined from three-dimensional X-ray data collected by standard Weissenberg multiple-film techniques and refined with a data set collected by counter methods using Mo radiation. The compound crystallizes in the orthorhombic space group *Pnma* with $a = 9.399$ (2) Å, $b = 16.343$ (4) Å, $c = 6.657$ (9) Å, and four molecules per unit cell. The structure was refined with 259 observed reflections to a conventional residual of $R = 0.037$. The molecules lie on a crystallographic mirror plane, with one sulfur and two phosphorus atoms on the mirror. The P–S bond lengths range from 2.091 (16) to 2.145 (10) Å, the P–P bond length is 2.221 (10) Å, and the P–I bond length is 2.471 (8) Å. Evidence is presented to support the reaction sequence $P_4S_3 + I_2 \rightarrow \beta\text{-}P_4S_3I_2 \rightarrow \alpha\text{-}P_4S_3I_2$, where α-$P_4S_3I_2$ is a previously reported $P_4S_3I_2$ structure which has a P–S framework different from that of β-$P_4S_3I_2$.

Introduction

The phosphorus sulfides (P_4S_n, $n = 3, 5, 7, 9, 10$) constitute a series of molecules with cagelike structures unique in inorganic stereochemistry.[2,3] The compound $P_4S_3I_2$ is closely related to this series, and the

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