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The Crystal Structures of $IrAs_3$ and $IrSb_3$

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The compounds $IrAs_3$ and $IrSb_3$ have the $CoAs_3$-type structure (space group $Im3$) with

$$IrAs_3:\ a=8{\cdot}4691\ \text{Å},\ y=0{\cdot}350\pm0{\cdot}002,\ z=0{\cdot}146\pm0{\cdot}002,\ \text{density}=9{\cdot}03\ \text{g.cm.}^{-3},$$
$$IrSb_3:\ a=9{\cdot}2495\ \text{Å},\ y=0{\cdot}343\pm0{\cdot}001,\ z=0{\cdot}157\pm0{\cdot}001,\ \text{density}=9{\cdot}26\ \text{g.cm.}^{-3}.$$

The shortest interatomic distances are

$$\text{Ir–6As}=2{\cdot}445\pm0{\cdot}012,\ \text{As–As}=2{\cdot}473\pm0{\cdot}034\ \text{and}\ 2{\cdot}541\pm0{\cdot}034\ \text{Å},$$
$$\text{Ir–6Sb}=2{\cdot}613\pm0{\cdot}006,\ \text{Sb–Sb}=2{\cdot}904\pm0{\cdot}018\ \text{Å}.$$

The compounds have almost zero magnetic susceptibility.

The structure parameters have been refined by a trial-and-error method. Three different reliability indices R_1, R_2 and R_3 have been calculated to check the agreement between I_o and I_c for every shift of the atoms. Systematic improvement of the coordinates is discussed on the basis of $R(y, z)$ maps.

Introduction

In recent studies of the iridium antimonides (Žuravlev & Ždanov, 1956; Kuzmin *et al.*, 1957) a compound $IrSb_3$, was identified by means of X-ray and metallographic methods. According to Žuravlev & Ždanov the structure is of the skutterudite, $CoAs_3$, type, and in making their structure determination they used Oftedal's (1928) parameter values for $CoAs_3$. Oftedal's values were based on the postulated relation $y+z=\frac{1}{2}$ between the independent parameters y and z, which makes all distances between immediately coordinating arsenic atoms equal. This relation has also been used by Rosenqvist (1953) for $CoSb_3$ and by Žuravlev & Ždanov (1956) for $CoSb_3$ and $RhSb_3$. In order to check this assumption a reinvestigation of $IrSb_3$ was carried out. As a preliminary study of the iridium–arsenic system indicated the existence of an isostructural compound $IrAs_3$, this compound was also investigated.

The $IrAs_3$ and $IrSb_3$ samples were made by heating weighed quantities of iridium and arsenic or antimony at about 850 °C. in pure alumina crucibles placed inside silica tubes which were evacuated and sealed. The samples were heated at this temperature for one month and cooled slowly to room temperature. Heat treatment at temperatures above 1200 °C. indicates that $IrAs_3$ and $IrSb_3$ are formed peritectically. For $IrSb_3$ this is in agreement with the result by Kuzmin *et al.* (1957), who found that this compound has a peritectic temperature between 800 and 950 °C.

Crystallographic data

Powder photographs of $IrAs_3$ and $IrSb_3$ were taken with filtered Cu K-radiation ($\lambda_{\alpha_1}=1{\cdot}54050$ Å) in cameras with 114·6 mm. effective diameter and indexed on the basis of a cubic unit cell, *cf.* Tables 1 and 2. The extrapolated lattice constants (Nelson & Riley, 1945) of $IrAs_3$ and $IrSb_3$ are listed in Table 3, together with the lattice constant for $IrSb_3$ determined by Žuravlev & Ždanov (1956). The agreement between this value and the new one is very satisfactory.

On the basis of the observed densities at 25·00 °C., *cf.* Table 3, the unit cell contains 8 AB_3-groups ($Z_c=7{\cdot}92$ for $IrAs_3$ and $Z_c=7{\cdot}91$ for $IrSb_3$).

The systematic missing reflections were of the type (hkl) absent when $h^2+k^2+l^2=2n+1$. This condition also characterized the possible space groups of $CoAs_3$ (Oftedal, 1928). According to Oftedal the atomic arrangement in the skutterudite, $CoAs_3$, structure in terms of the space group $Im3(T_h^5)$ is as follows:

8 Co	in (e)	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ etc.
24 As	in (g)	$0, y, z$ etc.

Table 1. *Powder photograph data of* $IrAs_3$ *taken with* Cu *K-radiation*

α_2 and β lines omitted. Calculated intensities for $y=0{\cdot}350$ and $z=0{\cdot}146$

$\sin^2\theta\times10^4$	$h^2+k^2+l^2$	I_o	I_c
166	2	10·7	9·5
330	4	73·7	73·5
496	6	9·0	6·7
663	8	59·3	58·4
828	10	64·2	57·0
993	12	31·0	28·6
1159	14	17·9	13·5
1326	16	11·0	9·4
1491	18	5·3	4·2
1657	20	82·6	88·2
1822	22	4·8	4·4
1991	24	52·5	54·1
2153	26	23·9	20·5
—	30*	0·0	0·2
2653	32	4·7	4·7
2816	34	6·1	5·1
2982	36	6·3	6·1
—	38*	0·0	0·3
3314	40	18·1	19·0
3482	42*	1·4	1·1
3642	44	16·5	17·2
3810	46	6·3	5·6
3973	48	12·0	12·3
4141	50	2·3	2·0
4307	52	15·9	16·6
4472	54	3·1	2·3
4637	56	10·7	11·3
4805	58	5·8	5·4
5137	62	3·9	3·3
5302	64	6·1	5·6
5469	66*	1·5	1·1
5632	68	18·7	19·2
5799	70*	1·7	1·1
5963	72	17·2	18·6
6130	74	9·7	9·5
6291	76	6·0	6·7
—	78*	0·0	0·1
6625	80	4·2	3·9
6789	82	2·2	1·7
6954	84	15·0	17·7
7121	86*	1·2	1·1
7282	88	4·1	4·4
7447	90	1·7	1·9
7778	94	6·4	7·1
7941	96	7·6	9·1
8110	98	4·2	3·3
8274	100	5·5	6·6
8439	102	1·5	1·5
8605·4	104	19·0	25·7
8768	106	2·2	1·9
8935·6	108	6·0	8·0
9100·6	110	7·7	11·4
9429	114	2·9	4·0
9595·9	116*	51·0	98·0
9760	118*	4·0	3·2
9926·0	120*	51·5	199·5

Table 2. *Powder photograph data of* $IrSb_3$ *taken with* Cu *K-radiation*

α_2 and β lines omitted. Calculated intensities for $y=0{\cdot}343$ and $z=0{\cdot}157$

$\sin^2\theta\times10^4$	$h^2+k^2+l^2$	I_o	I_c
139	2	22·0	23·2
277	4	89·5	94·7
416	6	22·0	12·8
555	8	39·4	40·1
693	10	163·4	187·9
832	12	23·0	22·2
973	14	63·4	58·0
1111	16	13·0	12·7
1251	18	19·4	17·1
1391	20	125·8	147·7
1527	22	20·1	20·9
1667	24	88·7	101·1
1805	26	56·5	50·9
2085	30*	1·7	0·9
2225	32*	3·4	3·4
2360	34	34·4	26·2
2498	36	9·5	7·2
2640	38	5·2	5·5
2780	40	27·5	26·0
2921	42*	2·0	0·9
3057	44	32·5	33·1
3195	46	31·1	29·8
3334	48	17·1	18·5
3470	50	10·1	9·6
3612	52	19·7	21·3
3747	54	9·3	6·6
3887	56	7·2	7·2
4027	58	18·2	16·6
4302	62	12·3	9·7
4441	64	7·7	6·1
4580	66	3·3	2·0
4719	68	37·1	35·3
4862	70	11·5	8·8
5002	72	38·4	41·9
5137	74	23·8	17·2
5276	76	8·2	6·8
—	78*	0·0	0·5
5557	80*	2·8	2·5
5693	82	8·9	9·3
5831	84	10·5	9·9
5968	86	5·8	4·6
6110	88	4·3	4·1
6248	90	2·7	3·3
6525	94	22·7	23·8
6663	96	13·6	13·3
6801	98	9·7	7·7
6940	100	6·7	6·0
7081	102*	1·9	1·6
7217	104	11·1	10·5
7352	106	11·0	7·9
7494	108	3·0	2·8
7632	110	18·5	17·4
7908	114	4·7	2·8
8048	116	61·1	59·0
8184	118	18·7	17·1
8324	120	58·9	61·2
8461	122	13·4	11·3
8737	126	6·4	7·6
8878	128	5·0	5·5
9016·4	130	19·4	18·8
9153	132	14·8	13·4
9293·4	134	24·2	27·6
9431·9	136	42·9	41·8
9570	138	4·2	3·9
9708·9	140*	85·8	108·5
9847	142*	16·3	24·4

Table 3. *Lattice constants and observed densities of* $IrAs_3$ *and* $IrSb_3$

Compound	*a* (Å)	*d* (g.cm.$^{-3}$)	Reference
$IrAs_3$	8·4691	9·03	Present
$IrSb_3$	9·2495	9·26	Present
$IrSb_3$	9·248 ± 0·002	8·9	Žuravlev & Ždanov

While the positions of the cobalt atoms are fixed, two parameters, y and z, are necessary to establish the positions of the arsenic atoms. A projection of the $CoAs_3$-type structure is shown in Fig. 1, where the postulated relation $y+z=\frac{1}{2}$ is indicated by the broken line.

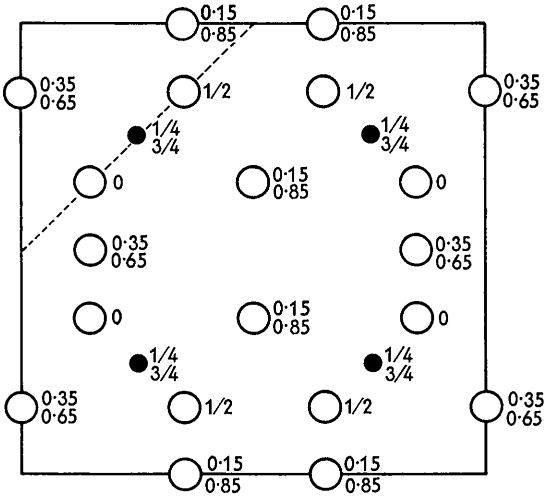

Fig. 1. Projection of one unit cell of the $CoAs_3$-type structure, with $y=0·35$ and $z=0·15$. Filled circles represent metal atoms and open circles metalloid atoms. Figures give the x-parameters of the atoms. The broken line indicates $y+z=\frac{1}{2}$.

Determination of the parameters

The relative intensities of the reflections on the powder photographs of $IrAs_3$ and $IrSb_3$ were determined from photometer recordings of the films. Multiple-film photographs were used to avoid errors in the estimation of the highest and weakest intensities on the photographs.

The intensities of the reflections were calculated using the formula

$$I_c = 10^{-6} \times |F|^2 \times Lp \times v\ .$$

Thus no corrections for absorption and temperature factors were used. The calculation of the F-values was made in terms of the atomic arrangement for the skutterudite structure. The observed intensities were referred to a relative, absolute scale by making the sums of I_o and I_c equal.

The parameters of the metalloid atoms were refined by a trial-and-error method. A set of I_c was prepared for the different values of y and z listed in Tables 4 and 5. To check the agreement between each set of

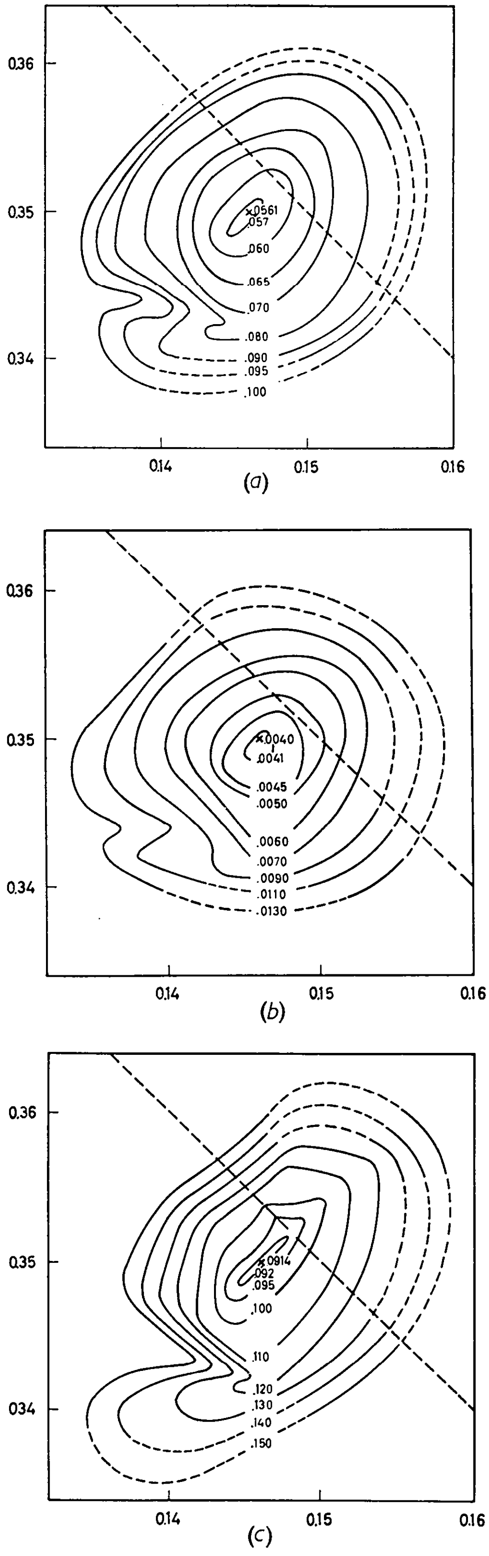

Fig. 2. Projection on y, z-plane of $R(y,z)$ for $IrAs_3$. Contours are drawn at constant values of R. (*a*) R_1, (*b*) R_2 and (*c*) R_3.

I_c and I_o, statistical tests were applied. Three different reliability indices

$$R_1 = \Sigma|\sqrt{(I_c)} - \sqrt{(I_o)}|/\Sigma\sqrt{(I_o)}$$
$$R_2 = \Sigma|\sqrt{(I_c)} - \sqrt{(I_o)}|^2/\Sigma I_o$$
$$R_3 = \Sigma|I_c - I_o|/\Sigma I_o$$

were calculated and the values noted in Tables 4 and 5. $R(y, z)$ maps, *cf.* Figs. 2(*a*), (*b*), (*c*) and 3(*a*), (*b*), (*c*), are drawn on the basis of these values. As seen from the figures, the R_1, R_2 and R_3 maps turned out to be similar for each compound. Furthermore, for each compound, minima in the different R maps are found at the same y, z-values. In agreement with convention the final parameters are taken equal to the y, z-values for the absolute minimum in the R-factors. The best agreement is thus obtained with the following parameters:

$IrAs_3$	$y = 0{\cdot}350 \pm 0{\cdot}002$	$z = 0{\cdot}146 \pm 0{\cdot}002$
$IrSb_3$	$y = 0{\cdot}343 \pm 0{\cdot}001$	$z = 0{\cdot}157 \pm 0{\cdot}001$.

The probable errors in the parameters, indicated by the limits, are estimated from the curvature of the R-surfaces on the $R(y, z)$ maps. Despite the fact that the minima in Figs. 2(*a*), (*b*), (*c*) are not found on the line $y + z = \frac{1}{2}$, Oftedal's (1928) relation is satisfied within the limited accuracy.

The I_o and I_c values are listed in Tables 1 and 2. The observed intensities of the strong, high-angle reflections with $\theta \geqq 78{\cdot}4°$ are considerably lower than calculated, probably because of systematic errors, and are not taken into account in the statistical R-tests. In addition, the observed intensities of the weakest reflections are supposedly evaluated more incorrectly than the other reflections and are not used in the calculations of the various R-factors. It should be noted, however, that the $R(y, z)$ maps are only slightly changed when these reflections, marked by asterisks in Tables 1 and 2, are taken into account. The minima are still found at the same y, z-values.

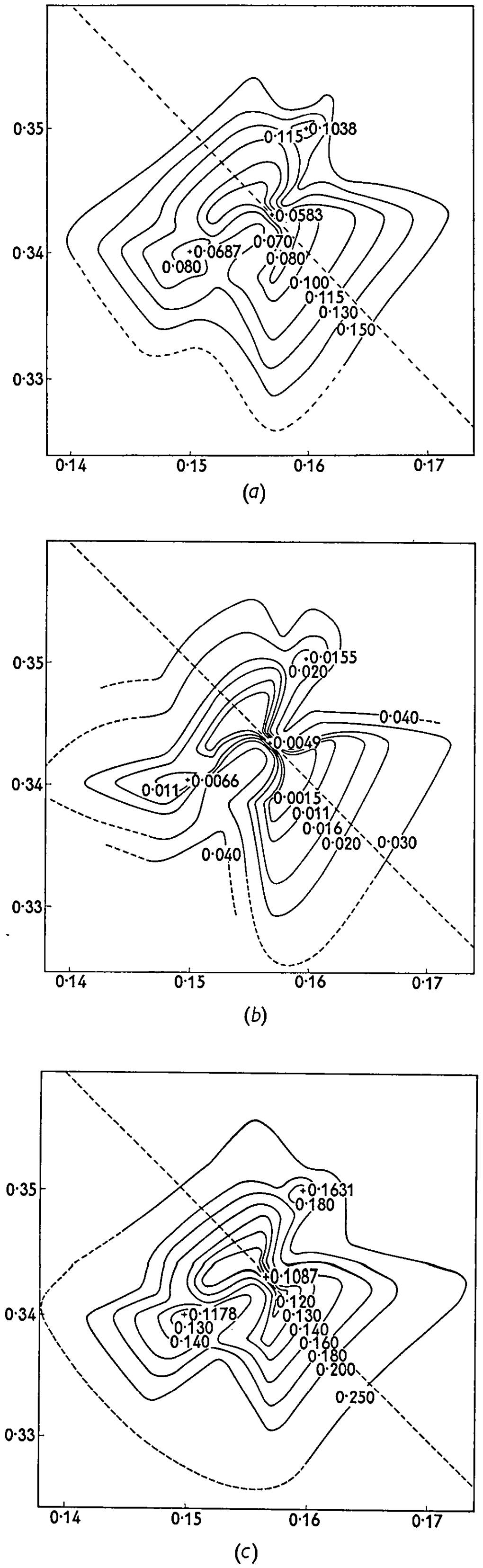

Fig. 3. Projection on y, z-plane of $R(y, z)$ for $IrSb_3$. Contours are drawn at constant values of R. (*a*) R_1, (*b*) R_2 and (*c*) R_3.

Discussion of the refinement method

Although the calculations are carried out according to a trial-and-error method, the refinement method using the R-maps is closely related to systematic methods (Vand *et al.*, 1960). The curvature and form of the R-surface are of fundamental importance in systematic refinement methods. Especial interest is connected with the R_2-surface because of the close relation between the R_2-function and the $R^* = \Sigma w(|F_c| - |F_o|)^2$ function for least-squares refinement.

It is convenient to represent the normal equations of the method of least-squares (Templeton, 1960) as follows:

$$\mathbf{ME} = \mathbf{D},\ \mathbf{E} = \mathbf{M}^{-1}\mathbf{D}\ .$$

The elements of the column matrix $\mathbf{E}$ are the shifts e_i of the parameters x_i. The elements of the column matrix $\mathbf{D}$ are:

Table 4. *Calculated values of* R_1, R_2 *and* R_3 *for* $\mathrm{IrAs_3}$ *with different parameter values* y, z

z	y	R_1	R_2	R_3
0·134	0·344	0·1073	0·0145	0·1655
0·134	0·350	0·1037	0·0132	0·1730
0·137	0·340	0·0989	0·0143	0·1399
0·137	0·357	0·1222	0·0188	0·1974
0·138	0·342	0·0934	0·0111	0·1454
0·138	0·348	0·0839	0·0087	0·1403
0·140	0·344	0·0979	0·0114	0·1628
0·140	0·354	0·0852	0·0088	0·1433
0·142	0·346	0·0687	0·0070	0·1083
0·143	0·352	0·0645	0·0054	0·1043
0·144	0·348	0·0573	0·0042	0·0922
0·144	0·358	0·0927	0·0103	0·1537
0·146	0·342	0·0724	0·0063	0·1152
0·146	0·350	0·0561	0·0040	0·0914
0·146	0·354	0·0645	0·0056	0·1017
0·147	0·351	0·0572	0·0042	0·0916
0·147	0·353	0·0601	0·0050	0·0943
0·148	0·347	0·0615	0·0044	0·1047
0·148	0·352	0·0577	0·0046	0·0921
0·148	0·357	0·0730	0·0079	0·1122
0·150	0·350	0·0616	0·0047	0·1037
0·150	0·354	0·0666	0·0060	0·0988
0·151	0·355	0·0704	0·0068	0·1068
0·152	0·344	0·0800	0·0079	0·1315
0·153	0·340	0·1045	0·0133	0·1723
0·153	0·352	0·0756	0·0069	0·1162
0·153	0·357	0·0860	0·0112	0·1196
0·156	0·358	0·0986	0·0151	0·1413

Table 5. *Calculated values of* R_1, R_2 *and* R_3 *for* $\mathrm{IrSb_3}$ *with different parameter values of* y, z

z	y	R_1	R_2	R_3
0·140	0·340	0·1493	0·0218	0·2230
0·142	0·343	0·1436	0·0225	0·2248
0·147	0·333	0·1394	0·0419	0·2003
0·147	0·353	0·2087	0·0530	0·3218
0·148	0·338	0·0930	0·0163	0·1456
0·148	0·342	0·1079	0·0195	0·1790
0·148	0·346	0·1287	0·0323	0·2059
0·150	0·340	0·0687	0·0066	0·1178
0·152	0·338	0·1111	0·0387	0·1668
0·152	0·340	0·1159	0·0398	0·1956
0·152	0·341	0·0815	0·0157	0·1412
0·152	0·343	0·0628	0·0060	0·1109
0·153	0·336	0·1227	0·0393	0·2097
0·154	0·346	0·0756	0·0071	0·1326
0·154	0·352	0·1398	0·0302	0·2270
0·156	0·342	0·1077	0·0388	0·1530
0·156	0·344	0·0599	0·0050	0·1102
0·157	0·328	0·1336	0·0214	0·2276
0·157	0·338	0·0674	0·0064	0·1247
0·157	0·343	0·0583	0·0049	0·1087
0·157	0·348	0·0843	0·0099	0·1402
0·157	0·358	0·1695	0·0378	0·2616
0·158	0·342	0·0616	0·0055	0·1148
0·158	0·344	0·1218	0·0402	0·1774
0·158	0·350	0·1178	0·0240	0·1920
0·158	0·352	0·1563	0·0423	0·2375
0·160	0·330	0·1336	0·0207	0·2295
0·160	0·340	0·0786	0·0082	0·1402
0·160	0·346	0·1356	0·0450	0·2245
0·160	0·350	0·1038	0·0155	0·1631
0·162	0·343	0·0873	0·0103	0·1503
0·162	0·348	0·1515	0·0501	0·2274
0·162	0·352	0·1472	0·0346	0·2604
0·164	0·346	0·1557	0·0473	0·2563
0·167	0·333	0·1693	0·0316	0·2902
0·167	0·353	0·2130	0·0731	0·3023
0·170	0·340	0·1464	0·0289	0·2369
0·172	0·343	0·1493	0·0301	0·2410

$$d_i = \Sigma w \frac{\partial |F_c|}{\partial x_i} (|F_c| - |F_o|) = \frac{\partial R^*}{\partial x_i} \,.$$

The elements of the square matrix **M** are:

$$m_{ij} = \Sigma w \frac{\partial |F_c|}{\partial x_i} \frac{\partial |F_c|}{\partial x_j} \,.$$

The elements of the inverse matrix $\mathbf{M}^{-1}$ are proportional to the variances and covariances of the parameters. (Most of the programs for least-squares refinement of atomic coordinates for ordinary digital computers neglect off-diagonal terms in **M**.)

As the geometrical interpretation of **D** is a vector equal to the gradient along the R^*-surface, the successive improvement of the parameters x_i according to the method of least-squares terminates in a minimum value on the R^*-surface. The existence of secondary minima on the R^*-surface (*cf.* the R_2-surface Fig. 3(*b*)) is of fundamental importance, since with the method of least-squares one is unable to separate the absolute minimum from a secondary one. Thus the possibility of wrong solutions for the parameters is introduced and wrong bond distances might be obtained.

Between two minima, e.g. on the R_2-surface in Fig. 3(*b*), curves corresponding to the geographical 'watersheds' might be drawn. Using the method of least-squares one is probably not able to cross from one side of a 'watershed' to another.† Thus the starting point seems to be of importance for the final parameters. If secondary minima on the R^*-surface are supposed to be common for structures with two and more parameters, a disagreement between the parameters from two different X-ray (or between X-ray and neutron parameters) studies might be found. To avoid this error, different starting points for the least-squares improvement should be tried to check whether the final parameters are changed or not.

The contours for constant values of R, *cf.* Figs. 2–3, around the absolute minimum are far from circular‡. The minimum value is more sharply determined in some directions than in others. A set of parameters with low R-value might well be found at a larger distance from the parameters of the absolute minimum than a set with higher R-value. Thus one R-value is

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† An attempt to solve the differential equations for the 'watersheds' will be the outlines for further work.

‡ A detailed recalculation covering a larger area in the yz plane is in progress.

Table 6. *Comparison of observed and calculated interatomic distances*

	Metal–metalloid distance (Å)				Metalloid–metalloid distance (Å)			
Compound	Observed	Covalent	Metallic	Ionic	Observed	Covalent	Metallic	Ionic
$IrAs_3$	$2{\cdot}445 \pm 0{\cdot}012$	2·50	2·475	'2·54'	$2{\cdot}473 \pm 0{\cdot}034$ $2{\cdot}541 \pm 0{\cdot}034$	2·36	2·601	'2·98'
$IrSb_3$	$2{\cdot}613 \pm 0{\cdot}006$	2·68	2·656	'2·70'	$2{\cdot}904 \pm 0{\cdot}018$	2·72	2·963	'3·30'

Table 7. *Magnetic susceptibility of* $IrAs_3$ *and* $IrSb_3$ *measured by the Gouy method*

The $\chi_g \times 10^6$ values are mean values of the results at $H_{\text{max.}} = 4015$, 4700 and 5110Ø

	Temperature °C.						
Compound	−183	−78	20	150	300	450	Induced diamagnetism
$IrAs_3$	−0·21	−0·21	−0·21	−0·23	−0·26	−0·26	−0·56
$IrSb_3$	−0·16	−0·16	−0·16	−0·19	−0·24	−0·27	−0·58

not a significant measure for the correctness of the reliability of a particular structure determination.

Discussion of the structures

The coordination in the $CoAs_3$-type structure is seen from Fig. 1. Each metal atom has six metalloid neighbours octahedrally arranged. Each metalloid atom has two metalloid neighbours and two metal neighbours, the four forming a tetrahedral arrangement. The shortest interatomic distances are listed in Table 6, together with the values expected from the covalent, metallic and ionic models of the chemical bond.

In applying the covalent valence-bond description (Pauling, 1960) the iridium (IrIII) atom probably can be said to form d^2sp^3 bonds and the arsenic and antimony atoms to form sp^3 bonds. This gives larger metal–metalloid distances and smaller metalloid–metalloid distances than the observed values. Better agreement is obtained by using the metallic radii of the elements (Pauling, 1960). An ionic description of the skutterudite structure, would probably correspond to the ions Ir^{3+} and $(As_4)^{4-}$ or $(Sb_4)^{4-}$, respectively (Rosenqvist, 1953). The radius of the Ir^{3+} ion as well as the radii of arsenic and antimony in $(As_4)^{4-}$ and $(Sb_4)^{4-}$ ions are difficult to stipulate. The distances listed in Table 6 are the radii sums according to Rabinowitsch & Thilo (1929). Real ionic distances are expected to be still higher, i.e., definitely larger than the observed distances.

Further support for a covalent or metallic model is obtained from the magnetic criterion for bond types. The measured susceptibilities, *cf.* Table 7, are exceedingly low and almost balanced by the diamagnetism induced in the compounds. The diamagnetic corrections are $-40{\cdot}1 \times 10^{-6}$ per mole Ir° according to Søvold (1954), $-64{\cdot}6 \times 10^{-6}$ per mole As^{3-} and $-94{\cdot}4$ per mole Sb^{3-} according to Angus (1932). They are given per gram of the compounds in the far column of Table 7. By subtracting these values from the measured susceptibilities, the susceptibilities of the paramagnetic ions are obtained. The effective magnetic moments, which range from 0·32 to 1·00 Bohr magnetons, show that the compounds are of an essentially covalent or metallic type. In case the bond had been of ionic type, the 'spin only' theory demands a magnetic moment of $4{\cdot}90\,\mu B$ for compounds containing the Ir^{3+} ion.

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