Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Neutron diffraction investigation of orthorhombic lead(II) fluoride.* By P. Boldrini and B. O. Loopstra, *Reactor Centrum Nederland, Petten (N.H.), The Netherlands*

Neutron diffraction has been used to check the structure of polycrystalline orthorhombic lead(II) fluoride. The X-ray work of Byström has been confirmed, and more accurate interatomic distances have been found.

From an X-ray powder investigation Byström (1947) found that orthorhombic lead(II) fluoride has the lead(II) chloride structure. As the fluorine positions were derived from packing considerations only, some doubt has been expressed recently with regard to the correctness of this determination (van den Berg, 1964). Because of this, a neutron powder study was undertaken, the neutron scattering lengths of 0·96 and 0·55 × 10^{-12} cm for lead and fluorine, respectively, being very favourable for a direct localization of fluorine.

A polycrystalline sample was prepared by slowly adding PbO to concentrated hydrofluoric acid (39 % by weight) and drying the residue at 80–100 °C in an inert atmosphere. An X-ray investigation showed the sample to be free from contamination by the cubic form of PbF_2.

Three different neutron diffraction patterns were obtained, all of which were used independently for refining the structure. For all three patterns monochromatic radiation was obtained from the 111 reflexion of copper; the other experimental details have been collected in Table 1. With the space group *Pnma*, the cell constants are: $a = 6·440$, $b = 3·899$, $c = 7·651$ Å (Sauka, 1951).

The structure was refined by means of a full-matrix least-squares program described by Rietveld (1966), taking the

Table 1. *Experimental details*

α_1 is the angular divergence of the collimator between the reactor and the monochromator, α_3 that of the collimator in front of the BF_3 detector; λ is the wavelength used and $(\sin \theta)/\lambda$ the range of observation.

Pattern	α_1	α_3	λ	$(\sin\theta)/\lambda$
A	10'	10'	1·169 Å	0·43
B	5·5	10	1·181	0·46
C	10	10	2·561	0·34

atomic coordinates of Byström (1947) as initial parameters. Unobserved intensities were introduced as one-third of the minium observable value and given a weight corresponding to 0·05 times the background; the other reflexions were

Table 3. *Observed and calculated structure factors in barns per unit cell*

hkl	jF_c^2	ΣjF_o^2 A	ΣjF_o^2 B	ΣjF_o^2 C	hkl	jF_c^2	ΣjF_o^2 A	ΣjF_o^2 B
101	0.0	<0.1	<0.2	<0.3	223	20.4		
002	5.8	5.6	5.6	5.5	115	60.1		
011	7.3	7.9	7.4	6.9	412	7.2		
102	16.9	17.6	16.4	15.3	205	22.2	⎤125.2	⎤118.4
200	9.2	7.7	8.2	8.7	024	72.8		
111	24.0	19.4	19.7	20.0	403	4.4	⎦	⎦70.3
201	0.1	<0.2	<0.4	<0.8	327	190.8		
112	62.2	⎤	65.1	60.2	314	46.2		
210	36.5			38.3	124	2.5	⎤313.0	⎤214.8
202	13.8	⎦112.7	⎦51.2	14.1	215	25.1	19.4	26.8
103	24.6	⎤	⎤		413	12.1		
211	122.0	⎦153.7	⎦158.9	⎦146.7	031	6.1		
013	91.0	94.7	99.9	94.5	006	8.2		
212	10.2	⎤	⎤	11.0	501	6.8	⎦29.2	⎦35.8
301	22.2	⎦34.6	⎦37.0	24.9	224	22.3		
113	44.7	44.1	49.0	47.1	131	20.2		
203	12.4	15.4	16.2	14.8	323	4.4		
020	114.9	110.9	120.1	114.1	106	37.5		
004	42.5	45.0	47.8	45.1	305	0.2		
302	111.4	107.5	108.8	100.8	420	30.4		
104	1.3			<1.7	404	52.7		
311	76.9	⎦80.7		76.7	421	15.7		
121	0.0	<0.5	⎦79.0	<1.7	502	32.7		⎦240.3
213	126.3	124.0	131.9	122.6	132	41.7		
022	9.9	12.6	12.5	10.8	511	187.9		
312	1.6	⎤	⎤	<1.8	230	24.7	⎦459.0	⎦241.9
122	31.1			29.4	116	0.0		
220	17.0	⎦46.7	⎦46.6	16.5	231	88.6		
114	0.0	<0.6	<0.8	<1.8	315	107.5		
204	12.2	⎤	⎤		206	58.7		
303	2.7	⎦17.0	⎦15.8	⎦17.4	125	2.9		
221	0.2	<0.6	<0.8	<1.8	422	3.8	⎦266.5	⎦262.0
400	17.1	15.9	16.4	13.0	414	4.3	<1.1	<1.5
401	9.5	8.1	7.9	13.4	512	0.0		
222	23.5		20.3	23.6	033	67.2		
214	3.9	⎤	⎤		324	25.4		
313	0.1			⎦<1.8	503	1.7		
123	40.3	⎦62.2	⎦39.4	41.4	232	6.9		⎦105.7
105	1.8	⎤	⎤		133	32.5		
410	1.3				216	3.3		
402	2.5	⎦6.6	⎦6.2	⎦5.5	225	36.4		⎦59.6
411	1.2	<0.8	<1.0	<1.8	423	7.3		<1.6
304	14.6	⎤	⎤		405	2.4		
015	36.9				513	32.3		
321	36.3	⎦94.4	⎦84.2		331	58.4		
					306	16.9		⎦99.6
					233	94.8		87.3

Table 2. *Atomic coordinates as fractions of cell edges*

	Final coordinates (this work)*			Byström's (1947) values		
	x/a	y/b	z/c	x/a	y/b	z/c
Pb	0·2527 (13)	0·2500	0·1042 (7)	0·244	0·250	0·103
F(1)	0·8623 (21)	0·2500	0·0631 (15)	0·858	0·250	0·085
F(2)	0·4662 (20)	0·2500	0·8457 (17)	0·449	0·250	0·814

* The figures in brackets indicate $\sigma \times 10^{-4}$.

weighted according to Rietveld (1966). Observed values can be expressed as ΣjF_o^2, where j is the multiplicity factor and the summation extends over the reflexions comprised in one observed peak. These were brought to an absolute scale by comparison with their calculated values.

Five refinement cycles were performed, until the maxium shift of all coordinates was smaller than one-third of their standard deviations. Isotropic temperature coefficients were taken to be:

$$B_{Pb} = 1 \cdot 0 \text{ and } B_F = 1 \cdot 5 \text{ Å}^2 \text{ for all diagrams}.$$

As the three sets of coordinates were found to be in good agreement, they were averaged according to:

$$\bar{x} = (\Sigma w_i x_i)/\Sigma w_i$$

and similarly for z. Here w_i is the reciprocal of the variance of x_i. The standard deviations of the averaged coordinates were computed as $\sigma(\bar{x}) = (\Sigma w_i)^{-\frac{1}{2}}$. In no case did the difference between the coordinates of the original three sets and the averaged values exceed $1 \cdot 5\sigma$. The agreement indices computed from the final coordinates and defined by Rietveld (1966), were: $4 \cdot 4\%$ for pattern A, $7 \cdot 4\%$ for pattern B and $5 \cdot 1\%$ for pattern C.

Table 4. *Interatomic distances and their standard deviations (in brackets)*

Pb–F(1)	2·64 (1) Å	Pb–F(2)	2·41 (2) Å
	2·53 (2)		2·69 (1)
	2·45 (1)		3·03 (1)

In Table 2 the final coordinates have been listed together with those derived by Byström. It is seen that his structure has been fully confirmed. Table 3 gives the observed and calculated values of jF_o^2, while in Table 4 Pb–F distances and their standard deviations have been collected. The minimum fluorine–fluorine separation is $2 \cdot 81 \pm 0 \cdot 02$ Å.

References

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Some C11 b-type compounds of Sc, Y and the lanthanides with Cu, Ag and Au.
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The C11b (MoSi$_2$ type) structure has been studied in twenty compounds of AB$_2$ stoichiometry. The A elements are Sc, Y and the lanthanide elements Gd through Lu. The B elements are Cu, Ag and Au. Unit-cell constants are given.

Introduction

Several crystal structure types exist in AB$_2$ compounds in which A is an element from a group to the left of the Mn group in the periodic table and B is an element from either the Mn group or a group lying to the right. Nearly all AB$_2$ compounds can be classified into three families, as follows: (1) Laves phases, of the MgCu$_2$, MgZn$_2$, and MgNi$_2$ types, (2) AlB$_2$ type and its variant CeCu$_2$ type, (3) MoSi$_2$ type and its variant MoPt$_2$ type. In AB$_2$ compounds where A is a member of the Sc group (including the lanthanides), and B is a member of the Cu group, there is a competition between the second and third families, *i.e.* CeCu$_2$ type and MoSi$_2$ type. The present paper reports crystal structure data for the b.c. tetragonal MoSi$_2$-type compounds.

Experimental technique

Alloys were made by arc melting on a water-cooled copper hearth under an argon atmosphere. Sc, Y and lanthanide elements were 99·0% pure, while the copper, silver and gold were 99·9% pure. Weight losses were usually less than 2% of the initial weight for silver alloys and less than 1% for gold and copper alloys. Arc-melted buttons of the alloys were homogenized in evacuated capsules at temperatures from 600 to 900 °C. Powder specimens obtained by crushing

the homogenized buttons were then heat treated briefly at the same temperature as the homogenization temperature before X-ray diffraction. Some powder specimens were furnace cooled, others were given a water quench. No differences in the resolution of lines, or in the presence of a second phase, could be attributed to the cooling rate.

X-ray powder photographs were taken with Co $K\alpha$ radiation and a Straumanis-type Debye–Scherrer powder camera (114·6 mm diameter). The patterns were identified as tetragonal by use of a Bunn chart, and as body-centered from the observation that $h + k + l = 2n$. The stronger lines on the pattern were those for which $l = 3n$. The presence of numerous weaker lines, including 002, 101, 004 and 112, for which $l \neq 3n$, required a unit cell containing six atoms, rather than the smaller cell containing two atoms. The observed lattice parameters, extinctions and intensities all indicated that the b.c. tetragonal structure was the C11b, of which MoSi$_2$ is the prototype. Lattice parameters were calculated on the IBM 704 and CDC 3600 computers by the method described by Mueller, Heaton & Miller (1960). The α_1 and α_2 lines of the 226, 323, 109, 400 and 316 reflections were used in computer solutions.

Results

Table 1 lists unit cell constants and volume ratios for twenty examples of the MoSi$_2$-type structures. Eight of these