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The structure of the orthorhombic modification of lead chromate $PbCrO_4$.

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In the course of an investigation on the phase transition from the orthorhombic to the monoclinic modification occurring in precipitated lead chromate, first reported by Quittner, Sapgir & Rassudowa (1932), we thought it desirable to undertake a study of the crystal structure of the orthorhombic form. Samples of orthorhombic lead chromate were prepared by mixing at 25 °C. 0·1*M* solutions of K_2CrO_4 and $Pb(NO_3)_2$. The crystals obtained were too small for single crystal work. Diffraction patterns of polycrystalline samples were obtained by means of a Norelco diffractometer using Cu *Kα* radiation. The cell dimensions as determined by Lipson's method (1949) are:

$$a = 8{\cdot}67 \pm 0{\cdot}03,\ b = 5{\cdot}59 \pm 0{\cdot}01,\ c = 7{\cdot}13 \pm 0{\cdot}02\ \text{Å}\ .$$

The most probable space group, after indexing all the reflexions and taking into account the isomorphism with $PbSO_4$ (Quittner, Sapgir & Rassudowa, 1932) is *Pnma*. With four formula units per cell the calculated density is 6·22 g.cm.$^{-3}$, which compares fairly satisfactorily with the experimental pycnometric value of 5·8 g.cm.$^{-3}$.

Only reflexions contained within half the radius of the reciprocal sphere were recorded; therefore, in view of strong series termination effects, it was not possible to rely on the use of Fourier projections for the structure determination. A method based on trials and errors was used. 4 Pb atoms and 4 Cr atoms were placed in special positions while the oxygen atoms were placed at the corners of regular tetrahedrons with chromium atoms at the centers. The following atomic coordinates gave the best agreement between observed and calculated intensities:

4 Pb in 4(*c*),	$x = 0{\cdot}185$,	$y = \frac{1}{4}$,	$z = 0{\cdot}165$
4 Cr in 4(*c*),	$x = 0{\cdot}085$,	$y = \frac{1}{4}$,	$z = 0{\cdot}690$
4 O in 4(*c*),	$x = 0{\cdot}24$,	$y = \frac{1}{4}$,	$z = 0{\cdot}56$
4 O in 4(*c*),	$x = 0{\cdot}93$,	$y = \frac{1}{4}$,	$z = 0{\cdot}56$
8 O in 8(*d*),	$x = 0{\cdot}085$,	$y = 0{\cdot}01$,	$z = 0{\cdot}82$.

The reliability index $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ has the value 0·16 when all the non observed reflexions are included, and becomes 0·11 if only observed reflexions are considered. The values of $\sin^2 \theta_0$, $\sin^2 \theta_c$, $|F_o|$, $|F_c|$ (corrected for a thermal factor) are listed in Table 1. The Cr–O distance is 1·65 Å; twelve O atoms surround each Pb atom as follows: 1 at 2·64 Å, 2 at 2·71 Å, 1 at 2·83 Å, 2 at 2·91 Å, 2 at 2·96 Å, 2 at 3·57 Å; the average value of the Pb–Cr distances is 3·63 Å. The rather short Cr–O distance might be taken as an evidence for multiple bonding in the CrO_4^{-2} ion (Pauling, 1948, and Jaffé, 1954). The O–O distance (2·70 Å) corresponds to the theoretical one, while in the SO_4^{-2} ions the observed distance is only 2·45 Å (James, 1925). This difference may well be accounted for by the different size of the coordinating atom.

Unfortunately it is not possible to compare the above distances with those of monoclinic $PbCrO_4$, because the coordinates of the O atoms in this structure are not available (Brody, 1942).

Table 1. *X-ray data*

hkl	$\sin^2 \theta_o$	$\sin^2 \theta_c$	$\|F_o\|$	$\|F_c\|$
101	—	0·0196	—	33
011	0·0306	0·0307	148	166
200	0·0315	0·0316	161	155
111	0·0384	0·0386	109	112
201	0·0431	0·0433	102	103
002	0·0466	0·0468	180	195
210	0·0505	0·0506	256	268
102	0·0546	0·0547	257	250
211	0·0621	0·0623	226	201
112	0·0735	0·0737	165	150
020	0·0758	0·0761	370	344
202	—	0·0784	—	44
301	0·0827	0·0829	129	128
121	—	0·0957	—	4
212	0·0974	0·0974	99	145
311	—	0·1019	—	29
220	0·1078	0·1077	143	155
103	0·1133	0·1131	83	90
302	0·1175	0·1179	123	85
221	0·1192	0·1194	147	124
022	0·1227	0·1228	113	107
013	—	0·1242	—	—
400	0·1265	0·1265	56	53
122	0·1310	0·1307	217	233
113	0·1324	0·1321	210	192
203	interf.	0·1368	—	—
312	interf.	0·1369	—	—
401	interf.	0·1382	—	—
410	0·1454	0·1455	156	196
222	0·1535*	0·1545	81	62
213	—	0·1558	—	11
321	0·1590	0·1589	76	105
402	0·1735*	0·1732	265	242
303	0·1768*	0·1763		
031	0·1829	0·1829	140	122
004	—	0·1870	—	109
123	interf.	0·1892	122	134
131	interf.	0·1908		
322	interf.	0·1940		
104	interf.	0·1950	—	—
313	interf.	0·1953	—	—
230	0·2031	0·2028	198	172

* Marked values are subject to a larger error.

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References

Brody, S. B. (1942). *J. Chem. Phys.* **10**, 650.

International Tables for X-ray Crystallography (1952). Vol. I, p. 151. Birmingham: Kynoch Press.

James, R. W. (1925). *Proc. Roy. Soc.* A, **189**, 598.

Jaffé, H. H. (1954). *J. Phys. Chem.* **58**, 185.

Lipson, H. (1949). *Acta Cryst.* **2**, 43.

Pauling, L. (1948). *Nature of the Chemical Bond.* Ithaca: Cornell University Press.

Quittner, F., Sapgir, J. & Rassudowa, N. (1932). *Z. anorg. Chem.* **204**, 315.

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