

An XRay Investigation of the Structure of Lead Chromate

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Citation: [The Journal of Chemical Physics](#) **10**, 650 (1942); doi: 10.1063/1.1723634

View online: <http://dx.doi.org/10.1063/1.1723634>

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more, they can be compared roughly with values of the intermolecular energies as calculated from the second virial coefficient. Fowler¹⁰ has evaluated the coefficients λ and μ in the well-known expression

$$\varphi_1(r) = \lambda r^{-s} - \mu r^{-6} \quad (11)$$

for values of s ranging from 8 to 14 applying Eq. (11) to noble gases. Of the reactions given above that between the ammonium-ion-cyanate ion involves reactants which correspond reasonably well in molecular weight to argon. Using

¹⁰ R. H. Fowler, *Statistical Mechanics*, second edition (Cambridge, 1936), p. 306.

then, Fowler's constants for argon we obtain for $\varphi_1(r_0)$, with $r_0 = 2.5 \times 10^{-8}$ cm as determined from Eq. (1), values between 1.1 and 3.1×10^{-12} when s ranges from 8 to 14. Thus our value of 1.7×10^{-12} is of the same order of magnitude. The good agreement, however, must be considered as fortuitous, as Eq. (11) is very sensitive to a change in r . For this reason the other reactions studied above do not agree nearly as well with Fowler's values, since, for these reactions, Eq. (1) yields values of r_0 between 1.2 and 1.7×10^{-8} cm which are evidently somewhat small if consideration is taken of the large molecular weights of the reactants.

OCTOBER, 1942

JOURNAL OF CHEMICAL PHYSICS

VOLUME 10

An X-Ray Investigation of the Structure of Lead Chromate*

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(Received July 13, 1942)

An attempt to analyze the structure of lead chromate was undertaken, using the Weissenberg x-ray goniometer technique. Positions of the lead and chromium atoms were determined. Although the intensities were carefully corrected for absorption, accurate values of the oxygen parameters could not be determined from the data at hand. Further work is indicated. There is some discussion of the migration of ions in the photoblackening effect which lead chromate exhibits.

BRILL¹ and others^{2,3} have established that lead chromate (crocoite) is monoclinic with cell dimensions $a = 7.10\text{\AA}$, $b = 7.40\text{\AA}$, $c = 6.80\text{\AA}$, $\beta = 102^\circ 27'$. There are 4 molecules (PbCrO_4) per cell. The probable space group is $C_{2h}^5 - P2_1/n$. These data do not permit lead chromate to be classified with any of the previously determined structures in the oxyacid group of substances,⁴ so that a detailed x-ray investigation would seem to be of interest. In addition, a knowledge of the structure is important for an interpretation of

the photoblackening process which lead chromate exhibits.

Simple rotation and Weissenberg equi-inclination⁵ x-ray photographs were taken about the c and b axes. The indexing of these photographs verified the lattice and space group previously established. Unfiltered copper radiation was used throughout. Intensities were visually estimated. To aid in putting the intensities on a numerical

TABLE I.

Distance vector	Projection	u v w (fractions of cell translations)		
		u	v	w
$(2x \ 2y \ 2z)$	c face	0.43	0.30	0.80
	b face	0.45		
$(\frac{1}{2} \ \frac{1}{2} - 2y \ \frac{1}{2})$	c face	$\frac{1}{2}$	0.20	$\frac{1}{2}$
	b face	$\frac{1}{2}$		
$(\frac{1}{2} - 2x \ \frac{1}{2} \ \frac{1}{2} - 2z)$	c face	0.07	$\frac{1}{2}$	0.70
	b face	0.05		

* Submitted to the faculty of Bryn Mawr College in partial fulfillment of the requirements for the degree of doctor of philosophy. Gratitude is expressed to Dr. A. L. Patterson for his guidance and direction of the investigation. A grant made to Bryn Mawr College by the Elizabeth Thompson Science Fund made possible the purchase of much of the apparatus used.

¹ R. Brill, *Zeits. f. Krist.* **77**, 506 (1931).

² Gossner and Mussgnug, *Zeits. f. Krist.* **75**, 410 (1939).

³ S. von Glisczynski, *Zeits. f. Krist.* **101**, 1 (1939).

⁴ See R. W. G. Wyckoff, *The Structure of Crystals* (Chemical Catalogue Company, New York, 1931), second edition, Chap. 16.

⁵ M. J. Buerger, *Zeits. f. Krist.* **88**, 356 (1934).

scale, two exposures of different times were made at each setting. Use was also made of the relative intensity of reflections from the Cu $K\alpha$ and $K\beta$ components.

The extremely high absorption coefficient of lead chromate ($\mu = 1215/\text{cm}$ for the radiation used) makes it necessary to be very careful in correcting the intensities for absorption. In preliminary work, crystals were used in the form in which they occur in nature, and plane by plane absorption corrections based on the Hendershot⁶ method were applied. Even with refinements in the method of making the correction, inconsistencies in the results from these crystals indicated that the best natural crystals which could be found⁷ lacked the perfection of form required for a safe application of this method. The artificial crystals available were too small to give satisfactory photographs. It was therefore decided to prepare cylindrical specimens.

A few good single crystals of crocoite of sufficient size were selected. The crystal to be ground was mounted in a goniometer head and set along the appropriate axis with the aid of a two-circle goniometer. It was then transferred with little disturbance of the orientation to a rigid mount in the headstock of a small lathe. A small piece of sandpaper attached at one end to a tool blank and free at the other end served as a grinding tool. A high point on the sandpaper was the actual cutting tool. This paper is stiff enough to furnish the pressure required to cut the soft but brittle crystal, and flexible enough to prevent the frequent breakage attendant upon the use of a rigid tool. The finished cylinders were about $\frac{1}{2}$ mm in diameter and 1–2 mm long. Intensities of reflections from the cylindrical

TABLE II. Parameters in fractions of cell translations.

	x	y	z
Pb	0.220	0.150	0.400
Cr	.215	.150	.896

All values ± 0.004 .

⁶ O. P. Hendershot, Rev. Sci. Inst. **8**, 324 (1937). A discussion of the application of this method will appear shortly.

⁷ Crocoite from Tasmania, Brazil, and the Urals was generously supplied by Mr. George Vaux, Mr. Samuel Gordon, and Dr. E. H. Watson. Artificial crystals were obtained from Dr. S. C. Horning.

TABLE III. Observed and calculated structure factors.

hko	$ F_{\text{obs}} $	$F_{\text{Pb}} + F_{\text{Cr}}^*$	hkl	$ F_{\text{obs}} $	$F_{\text{Pb}} + F_{\text{Cr}}^{**}$
200	360	–340	200	390	–343
400	240	208	400	250	211
600	75	–89	600	85	–95
800	0	–5	800	0	2
110	38	46	101	125	–155
210	110	–114	101	90	95
310	90	–109	301	230	174
410	240	170	301	110	–19
510	175	133	501	160	–163
610	200	–183	501	0	–45
710	130	–129	701	90	133
810	110	168	701	35	84
020	73	–117	901	30	–106
120	315	–352	002	85	109
220	95	98	202	0	28
320	280	246	202	290	–224
420	0	–61	402	130	–127
520	175	–135	402	125	263
620	0	27	602	105	173
720	0	36	602	215	–244
820	0	17	802	80	–186
130	46	–63	802	130	201
230	45	–38	103	135	–171
330	145	158	103	320	328
430	29	61	303	110	116
530	210	–201	303	175	–182
630	34	–67	503	80	–57
730	165	202	503	120	135
830	22	62	703	20	3
040	243	–248	703	80	–83
140	190	175	903	30	33
240	240	217	004	250	–242
340	125	–135	204	260	264
440	130	–147	204	170	160
540	35	75	404	135	–232
640	30	66	404	90	–47
740	0	–22	604	65	175
840	0	4	604	25	–49
150	0	0	804	60	116
250	120	104	105	0	22
350	0	0	105	30	36
450	155	–172	305	35	–69
550	0	0	305	90	–87
650	135	199	505	45	102
750	0	0	505	80	117
060	215	208	705	65	–128
160	125	146	006	105	–190
260	205	–183	206	40	112
360	120	–125	206	235	235
460	70	126	406	0	–28
560	53	68	406	215	–230
660	1	–60	606	140	186
170	tr.	44	107	80	133
270	tr.	–27	107	80	–120
370	65	–118	307	60	–129
470	24	47	307	45	86
570	100	169	507	25	–42
670	1	–56	008	50	69
080	70	66	208	20	9
180	135	–201	408	20	–57
280	36	–59			
380	110	163			
480	31	43			
190	0	–21			
290	25	–63			

Parameters used in calculating: * Pb (x_1, y_1) = (0.219, 0.150), Cr (x_2, y_2) = (0.216, 0.150); ** Pb (x_1, z_1) = (0.220, 0.400), Cr (x_2, z_2) = (0.214, 0.896).

crystals, corrected for absorption by the method of Bradley⁸ were used in the main part of the work.

The general position of $P2_1/n$ is $(x\ y\ z)(\bar{x}\ \bar{y}\ \bar{z})$ $(\frac{1}{2}+x\ \frac{1}{2}-y\ \frac{1}{2}+z)$ $(\frac{1}{2}-x\ \frac{1}{2}+y\ \frac{1}{2}-z)$ and the symmetry of the F^2 series is $P2/m$. A set of atoms of atomic number Z in such a general position will produce an interatomic distance peak in the F^2 series⁹ of magnitude Z^2 at each of the general points 4: (o) $2x\ 2y\ 2z$ of the space group $P2/m$,¹⁰ and a peak of magnitude $2Z^2$ at each of the special points 2: (l) $\frac{1}{2}\ \frac{1}{2}+2y\ \frac{1}{2}$ and 2: (n) $\frac{1}{2}+2x\ \frac{1}{2}\ \frac{1}{2}+2z$ of the same group. If two general points $x_1y_1z_1$ and $x_2y_2z_2$ of $P2_1/n$ are occupied, peaks of equal magnitude are produced at the general points 4: (o) $S_xS_yS_z$, 4: (o) $D_xD_yD_z$, 4: (o) $\frac{1}{2}+S_x\ \frac{1}{2}+D_y\ \frac{1}{2}+S_z$, 4: (o) $\frac{1}{2}+D_x\ \frac{1}{2}+S_y\ \frac{1}{2}+D_z$ of $P2/m$, where $S_x=x_2+x_1$, $D_x=x_2-x_1$, etc.

Using the intensities of the $(hk0)$ and the $(h0l)$ reflections, properly corrected for polarization and absorption, the projections of the F^2 series on the b face and c face were computed and plotted. From these maps and from symmetry considerations it was concluded that all atoms must occupy general positions. The only reasonable interpretation of the strongest peaks, corresponding to the lead-lead distances, is given in Table I. This gives a unique set of parameters for the lead atoms, $x_1=0.22$, $y_1=0.15$, $z_1=0.40$.

Because of the high atomic number of lead it can be assumed that the signs of the structure factors are in the main determined by the contributions of the lead atoms, $F_{Pb}(hkl)$. The signs of the contributions $F_{Pb}(hk0)$ and $F_{Pb}(h0l)$ were accordingly determined from the above lead parameters. These signs were combined with the experimentally determined numerical values of the total structure factors and the set of trial F 's thus constructed was used in synthesizing the Fourier series for the projected density on the c and b faces. The chromium atoms were readily located on these maps. Parameters of the lead and chromium atoms obtained from the electron density maps are listed in Table II. The position of the lead atoms is identical with that

obtained from the F^2 maps. All peaks due to the lead-chromium distances appear in the right positions and orders of magnitude on the F^2 series maps. The structure factors calculated from these lead and chromium parameters are in good agreement with the observed magnitudes of the F 's (Table III). No sign changes are introduced by the contributions of the chromium atoms. Thus the assumption on which the calculation of the F series was based is justified.

No values are listed for the oxygen parameters since they cannot be located accurately from the data at hand. The maps give some indication of the positions of the oxygen atoms but the presence of spurious peaks on the maps, probably due to cutting off the Fourier series too soon, indicates that caution must be used in interpreting the weaker peaks. An extension of the data to higher order reflections would be desirable. Although plausible oxygen parameters can be obtained by adjusting the calculated structure factors, this procedure seems worthless without the support of direct evidence since the structure factors are very insensitive to large variations in the oxygen parameters. With the aid of a scale model attempts were made to find possible structures by packing nearly tetrahedral chromate groups about the lead ions. It is difficult to find adequate radii for the lead and chromate radicals in the literature and these attempts were inconclusive. From the lead and chromium positions and from indications of possible oxygen arrangements it seems that the structure is fairly close packed. The coordination number of oxygen atoms about lead is probably 8 or more.

In the light of these findings it would appear that the mechanism of photo-conductivity and photoblackening in lead chromate cannot depend on the migration of ions through a perfect lattice. Migration by means of holes due to lattice defects remains as a possibility. If any migration in a perfect lattice takes place it probably is accompanied by a breakdown of chromate groups and therefore of the lattice as a whole.¹¹

⁸ A. J. Bradley, Proc. Phys. Soc. **47**, 879 (1935).

⁹ A. L. Patterson, Zeits. f. Krist. **90**, 517 (1935).

¹⁰ Notation of *Int. Taf. zur Best. der Krist.*

¹¹ I am indebted to Dr. Frederick Seitz for a discussion of this interpretation. It was Dr. Seitz' interest in the problem which suggested the research reported here.