quoted in the literature. The average value for the Al–F distances is 1·80 Å, with 1·772 as minimum and 1·822 Å as maximum. The angular values F–Al–F are not far from 90° and 180°.

The coordination around the Na may be referred to a distorted triangular prism having six F lying at the corners, and there are two more F atoms beyond two of the prism faces. The distances Na–F range from 2·321 to 2·654 Å with an average of 2·46 Å.

The unusual number (eight) of F atoms neighbouring Na, which is usually 6 or 7, together with some unusually high Na–F distances, implies that Na is contained in the coordination polyhedron by electrostatic forces which are weaker than usual. This assumption may be confirmed by the Na thermal parameter (2·8 Å^2), which is the highest of the whole structure.

The structure on the whole may be described thus: Ca polyhedra are linked by F [F(1), F(2), F(3), F(4)] to four Al octahedra forming undulating sheets at $\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$ and $\frac{7}{8}$ *c* nearly parallel to (001) (Fig. 2). Within these sheets lie the strong Ca–F bonds, so determining the perfect cleavage of the mineral and its somewhat pearly luster on {001}.

Ca polyhedra also form chains with the F(5) and F(6) of the same Al octahedra which develop nearly parallel to the *c* axis at about $\frac{3}{4}$ and $\frac{1}{4}$ *b*, close to $\frac{1}{4}$ and $\frac{3}{4}$ *a* respectively. The chains in two adjoining cells are connected by a Ca–F bond for each Ca and by pairs of oxygen atoms around the center at 0,$\frac{1}{2}$,0. Such chains yield the distinct cleavage {110}.

On the whole the thomsenolite structure is not very compact and the distribution of its atoms in the cell is rather homogeneous, so giving a clear explanation of its low hardness ($H=2$) and low birefringence.

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The Crystal Structures of the Spodiosite Analogs, Ca_2CrO_4Cl and Ca_2PO_4Cl*†

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(*Received* 11 *July* 1966)

Both calcium chromate(V) chloride (Ca_2CrO_4Cl) and calcium phosphate chloride (Ca_2PO_4Cl) crystallize in the orthorhombic system, space group *Pbcm*, with four molecules per unit cell. The dimensions of the unit cell are: $a=6{\cdot}259\pm0{\cdot}005$, $b=7{\cdot}124\pm0{\cdot}005$, $c=10{\cdot}990\pm0{\cdot}005$ Å for $CaCrO_4Cl$, and $a=6{\cdot}185\pm0{\cdot}002$, $b=6{\cdot}983\pm0{\cdot}002$, $c=10{\cdot}816\pm0{\cdot}004$ Å for $CaPO_4Cl$. The crystal structures of both compounds have been determined from full data in three dimensions. X-ray reflection intensities were measured with scintillation counters. Refinement of the atomic coordinates was carried out by full-matrix least-squares procedures. The structures are made up of discrete CrO_4^{3-} and PO_4^{3-} tetrahedra which appear to be held together primarily by calcium ions. The indicated distortion of the CrO_4^{3-} tetrahedra is considerably greater than that of the PO_4^{3-} tetrahedra. This is in agreement with measurements of infrared absorption which show substantially more splitting of vibrational bands of the chromate compound than of the phosphate.

Introduction

Recently the syntheses of compounds of composition Ca_2CrO_4Cl and Ca_2PO_4Cl, as well as their strontium analogs, have been reported (Banks & Jaunarajs, 1965). X-ray diffractometric studies indicated that the dimensions of the unit cells of these phases were close to those of chlorospodiosite (ideally Ca_2PO_4Cl) (Palache, Berman & Frondel, 1951). The Ca_2CrO_4Cl compound is of particular interest, since in it the chromium appears to be in the 5+ state.

The analysis of the crystal structures of Ca_2CrO_4Cl and Ca_2PO_4Cl was undertaken to make possible detailed comparisons of the atomic parameters in the two

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* Abstracted in part from a dissertation submitted by Martha Greenblatt to the Polytechnic Institute of Brooklyn in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

† Supported in part by contract DA-31-124-ARO(D)-70.

structures, to establish whether the chromium was indeed present in the 5+ state in the chromate compound and to permit comparisons of the results of the X-ray analyses with corresponding results of optical measurements of these compounds.

Experimental

Single crystals of $\mathrm{Ca_2CrO_4Cl}$ and $\mathrm{Ca_2PO_4Cl}$ were grown from the melt, using excess $\mathrm{CaCl_2}$ as flux. The preparations were carried out in platinum crucibles; the starting materials were thoroughly mixed, fired overnight at 900 °C in a nitrogen atmosphere and cooled at 3° per hour to 300–400 °C.

Well-formed dark green, needle-like crystals of $\mathrm{Ca_2CrO_4Cl}$ were obtained in this way. The needle axis corresponded to the *b* axis of the unit cell. Crystals of $\mathrm{Ca_2PO_4Cl}$ were obtained in a similar fashion, in the form of well-shaped needles; these, however, are colorless and the needle axis corresponds to the crystallographic *c* axis.

Single-crystal photographic studies with precession and Weissenberg cameras indicated that reflections of the type $0kl$ with k odd, and $h0l$ with l odd, were systematically absent from X-ray patterns of both compounds. The space group is therefore either *Pbc*2 or *Pbcm*. Efforts to detect a piezoelectric effect, using relatively large single crystals of both phases, were unsuccessful and it was concluded that the most probable space group is *Pbcm*. The choice of space group was subsequently confirmed by single-crystal X-ray diffraction analyses of both phases.

Crystal data for both compounds are listed in Table 1.

Single crystals of both phases were ground to spherical form (the radius of the $\mathrm{Ca_2CrO_4Cl}$ crystal was 0·13 mm, the $\mathrm{Ca_2PO_4Cl}$ 0·18 mm). Data were collected by means of a General Electric single-crystal orienter with zirconium-filtered molybdenum *K* radiation. A scintillation crystal was used as detector. The stationary-crystal stationary-counter method was used. The take-off angle of the X-ray beam was 5°. Background corrections were made by measuring the intensity on either side of the peak, averaging, and subtracting from the total intensity. The intensities were corrected in the usual way for Lorentz polarization and absorption effects. Three hundred and sixty-three $\mathrm{Ca_2CrO_4Cl}$ and seven hundred and seventy $\mathrm{Ca_2PO_4Cl}$ reflections were measured and used.

Determination of the crystal structure of $\mathrm{Ca_2CrO_4Cl}$

Approximate positions of the heavy atoms were readily determined from peak locations on a three-dimensional Patterson map. All the heavy atoms are situated in fourfold positions 4(*c*) or 4(*d*) of *Pbcm* (*International Tables for X-ray Crystallography*, 1952). The eight calcium atoms are situated in two independent sets of fourfold positions, 4(*d*) and 4(*c*); the chromium atoms are in 4(*c*) and the chlorine atoms in 4(*d*). Oxygen atoms are in the eightfold general positions.

Signs of coefficients of structure factors were computed based on contributions from the heavy atoms alone (*i.e.* all except the oxygen atoms); a difference electron density map using $(F_{\text{obs}}-F_{\text{heavy atoms}})$ as coefficients of the Fourier series was computed. Approximate oxygen positions were obtained from this map. The structure was then refined by least-squares procedures using the Brookhaven National Laboratories version of the least-squares program of Busing, Martin & Levy (1962*a*). After several cycles of least-squares refinement in which individual atomic isotropic temperature factors were used and in which the scattering factors of the heavy atoms were corrected for dispersion effects, R, $(R=\Sigma\,||F_{\text{obs}}|-s|F_{\text{cal}}||/\Sigma\,|F_{\text{obs}}|)$ the discrepancy coefficient, was 10·0%. Anisotropic temperature factors were then introduced and, in addition, a weighting scheme in which $w=1$ for F_{obs} less than or equal to $4F_{\text{min}}$ and $w=16F^2_{\text{min}}/F^2_{\text{obs}}$ for F_{obs} greater than $4F_{\text{min}}$ was used. Other weighting schemes gave no improvement over this one. Initially 67 unobserved reflections were included at approximately half the appropriate minimum observable intensity values. They

Table 2. *Atomic positional coordinates in* $\mathrm{Ca_2CrO_4Cl}$

Estimated standard deviations are given in parentheses.

	Position	x	y	z
Ca(1)	4(*c*)	0·6202(3)	0·2500	0·0000
Ca(2)	4(*d*)	0·1395(3)	0·4702(2)	0·2500
Cl	4(*c*)	0·4791(4)	0·1781(3)	0·2500
Cr	4(*c*)	0·1243(2)	0·2500	0·0000
O(1)	8(*e*)	0·0422(7)	0·7351(5)	0·3767(3)
O(2)	8(*e*)	0·7110(6)	0·5693(5)	0·5313(3)

Table 1. *Crystal data*

	$\mathrm{Ca_2CrO_4Cl}$	$\mathrm{Ca_2PO_4Cl}$
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbcm*	*Pbcm*
a	6·259 ± 0·005 Å	6·185 ± 0·002 Å
b	7·124 ± 0·005	6·983 ± 0·002
c	10·99 ± 0·005	10·816 ± 0·004
Density (measured)	3·14 g.cm^{-3} (Wilhelmi, 1965)	2·995 g.cm^{-3}
Density (X-ray)	3·14 g.cm^{-3}	2·993 g.cm^{-3}
Number of molecules per unit cell	4	4
Color	Dark-green	Colorless
Habit	Needles, elongated along **b**	Needles, elongated along **c**

were omitted as the refinement progressed since they clearly introduced relatively large errors. In the very last cycles of refinement, 13 strong reflections which appeared to suffer strongly from extinction effects (*i.e.* F_{obs} was much less than F_{calc}) were also omitted from the calculations. The final discrepancy coefficient was 4·1%.

The atomic parameters and their standard deviations for all atoms are listed in Tables 2 and 3. Calculated and observed structure factors are listed in Table 4.

The refinement of the crystal structure of Ca_2PO_4Cl proceeded in much the same way. The atomic coordinates determined for Ca_2CrO_4Cl were used as a starting point. The final least-squares refinement yielded a value of $R = 4{\cdot}3\%$.

The atomic parameters are listed in Tables 5 and 6. Calculated and observed structure factors are listed in Table 7.

Originally the crystal structure of Ca_2PO_4Cl had been determined from film data obtained with precession

Table 3. *Atomic thermal parameters in* Ca_2CrO_4Cl

Estimated standard deviations are given in parentheses

A. Anisotropic thermal factors

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca(1)	0·0049(7)	0·0033(3)	0·0024(1)	0·0000	0·0000	0·0006(1)
Ca(2)	0·0058(6)	0·0032(2)	0·0015(1)	0·0005(1)	0·0000	0·0000
Cl	0·0075(7)	0·0084(3)	0·0019(1)	0·0034(4)	0·0000	0·0000
Cr	0·0043(6)	0·0029(3)	0·0011(1)	0·0000	0·0000	−0·0001(1)
O(1)	0·0046(10)	0·0053(6)	0·0016(2)	0·0013(7)	0·0002(6)	0·0003(3)
O(2)	0·0051(11)	0·0035(6)	0·0023(3)	0·0000	0·0000	0·0002(3)

B. R.M.S. displacement along principal axes of thermal ellipsoids (Å)

	1	2	3
Ca(1)	0·088(4)	0·098(7)	0·125(3)
Ca(2)	0·088(4)	0·095(3)	0·109(5)
Cl	0·100(6)	0·107(3)	0·163(4)
Cr	0·081(3)	0·087(3)	0·092(6)
O(1)	0·088(11)	0·098(7)	0·124(7)
O(2)	0·095(8)	0·100(11)	0·118(7)

Table 4. *Calculated and observed structure factors*: Ca_2CrO_4Cl

L	FOBS	FCAL
(H = 0)		
(K = 0)		
2	743	824
6	389	332
12	804	823
16	724	732
(K = 2)		
1	193	178
3	317	294
4	400	414
5	163	145
6	1000	1122
7	332	335
8	842	887
10	834	856
11	179	147
12	369	365
14	590	588
15	117	77
16	421	424
(K = 4)		
1	765	816
2	723	758
3	383	388
4	847	915
5	685	696
6	594	601
7	362	351
8	979	1045
9	597	599
10	467	468
11	235	232
12	532	534
13	325	325
14	302	306
15	275	272
16	541	534
(K = 6)		
0	746	768
1	162	158
3	222	211
4	351	343
5	322	321
6	938	1003
8	406	402
9	185	176
10	704	721
11	131	120
12	115	85
13	182	192
14	477	481
16	177	167
(K = 8)		
0	427	419
1	235	233
2	577	586
3	170	153
4	267	260
6	589	571
7	255	253
8	456	428
9	156	146
10	548	542
11	119	127
12	286	286
14	420	425
15	139	149
16	302	311
(K = 10)		
0	580	568
1	231	233
2	443	434
3	384	380
4	451	441
5	252	255
6	375	372
7	278	282
8	444	448
9	131	144
10	305	304
11	277	285
12	272	285
13	179	194
14	208	215
15	104	128
16	241	263
(H = 1)		
(K = 0)		
0	401	385
2	161	153
4	533	496
6	114	129
8	277	268
10	174	172
12	83	85
14	97	109
16	153	142
(K = 1)		
0	403	393
1	568	579
2	185	177
3	180	184
4	483	497
5	613	620
7	81	71
8	138	130
9	404	407
11	108	93
12	136	139
13	214	215
15	151	131
(K = 2)		
1	470	458
2	774	838
3	591	584
4	752	779
5	396	390
6	551	568
7	367	353
8	106	91
9	225	217
10	407	413
11	287	283
12	337	343
13	207	196
14	265	267
15	157	159
(K = 3)		
0	602	586
1	414	407
2	60	19
3	345	336
4	231	239
5	404	407
6	195	178
7	200	203
8	96	93
9	281	274
(K = 4)		
0	661	687
1	80	68
2	197	183
3	169	162
4	134	119
5	208	212
6	171	162
8	428	428
9	79	77
(K = 5)		
0	448	451
1	145	145
2	64	58
3	212	208
4	443	454
7	236	232
8	191	191
(K = 6)		
0	308	295
1	231	217
2	99	88
3	378	366
5	298	292
6	59	66
7	223	215
8	262	248
9	153	144
15	118	123
(H = 2)		
(K = 0)		
0	454	431
2	672	697
4	256	222
6	341	339
8	439	432
10	91	93
12	136	131
(K = 1)		
0	877	1032
1	592	610
3	643	663
5	382	373
6	874	963
7	523	524
8	676	687
9	290	275
(K = 2)		
0	896	1004
1	477	476
2	120	90
3	157	155
4	226	188
5	423	425
6	206	188
7	129	124
8	414	417
9	345	344
(K = 3)		
0	792	859
1	280	267
3	349	341
4	889	993
5	259	249
6	1002	1103
7	228	228
8	462	455
9	156	145
(K = 4)		
0	188	180
1	269	261
2	196	193
3	309	299
4	255	249
6	119	121
7	389	386
9	84	74
(K = 5)		
0	927	1012
1	303	305
2	416	404
3	180	179
4	1024	1128
5	253	248
6	398	380
7	186	177
8	787	801
9	237	240
(K = 6)		
0	173	168
1	236	224
2	84	68
4	352	348
5	157	142
6	136	120
7	115	110
9	200	195
(H = 3)		
(K = 0)		
0	419	439
2	828	902
6	546	563
4	818	919
8	498	493
(K = 1)		
0	140	124
1	143	134
2	215	202
3	289	267
4	383	385
6	76	79
7	274	269
(K = 2)		
0	151	125
1	119	115
2	404	409
4	248	243
5	239	230
6	279	280
8	149	135
9	143	141
(K = 3)		
1	267	260
2	352	347
3	361	349
4	264	272
5	264	258
6	220	210
7	237	232
8	131	123
9	176	161
(K = 4)		
0	161	164
1	416	410
2	73	63
3	579	587
4	415	418
5	366	360
7	447	445
8	118	120
9	242	233
(K = 5)		
0	146	149
1	107	99
2	110	114
4	152	136
9	87	93
(K = 6)		
0	398	399
1	172	175
2	262	261
3	142	129
4	174	173
6	291	288
7	210	206
8	223	222
(H = 4)		
(K = 0)		
0	755	789
2	689	709
4	910	996
6	649	651
8	649	641
(K = 1)		
0	255	264
2	312	311
3	195	185
4	169	167
5	75	71
6	228	226
7	176	169
8	232	229
(K = 2)		
0	392	372
1	335	338
3	358	358
4	530	521
5	212	206
7	341	342
8	208	186
9	187	187
(K = 3)		
1	277	277
2	186	181
3	238	228
4	168	160
5	161	156
7	251	256
9	163	168
(K = 4)		
0	888	969
2	521	507
3	81	82
4	955	1040
6	443	420
8	690	709
(K = 5)		
2	145	145
5	85	84
7	106	102
(K = 6)		
0	540	524
1	327	334
2	520	509
3	299	290
4	598	611
5	229	233
6	496	483
7	317	309
8	476	465
9	234	238
(H = 5)		
(K = 0)		
0	534	534
2	97	93
4	513	528
6	179	174
8	255	257
(K = 1)		
0	201	201
1	366	368
2	169	166
3	408	426
4	169	186
5	315	313
6	189	146
7	347	353
8	158	154
9	236	234
(K = 2)		
0	91	93
1	89	81
2	102	103
3	200	198
7	184	187
(K = 3)		
0	150	159
1	129	129
2	303	318
4	189	187
6	230	237
7	110	114
9	89	88
(K = 4)		
1	256	248
3	150	156
4	108	94
5	341	341
9	262	267
(K = 5)		
0	472	459
1	178	185
2	258	257
3	241	246
4	220	213
5	277	256
6	216	214
7	140	137
8	395	398
9	142	152
(K = 6)		
2	271	271
6	196	196
8	113	114
9	73	39

and Weissenberg cameras. The intensities were estimated visually by comparison with timed exposures of representative reflections. Using 290 independent reflections the crystal structure was refined by least-squares methods until the value of R was just under 10%.

Table 5. *Atomic positional coordinates in* Ca_2PO_4Cl

Estimated standard deviations are given in parentheses.

	Position	x	y	z
Ca(1)	4(*c*)	0·6336$_{(1)}$	0·2500	0·0000
Ca(2)	4(*d*)	0·1286$_{(2)}$	0·4720$_{(1)}$	0·2500
Cl	4(*c*)	0·5185$_{(2)}$	0·2173$_{(2)}$	0·2500
P	4(*c*)	0·1381$_{(2)}$	0·2500	0·0000
O(1)	8(*e*)	0.0105$_{(4)}$	0·7277$_{(3)}$	0·3855$_{(1)}$
O(2)	8(*e*)	0·7160$_{(4)}$	0·5764$_{(3)}$	0·5233$_{(2)}$

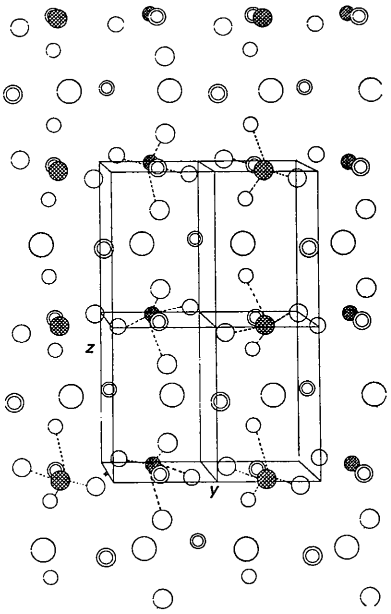

Fig. 1. The unit-cell contents of Ca_2CrO_4Cl projected along **a**. Large open circles, Cl; atoms shaded up and down. Cr; double circles, Ca; smaller open circles, O. Bonds between the atoms in $CrO_4{}^{3-}$ tetrahedra are represented by broken lines.

It is interesting to note that the atomic position coordinates determined from counter intensity data have standard errors which are approximately one-tenth of the corresponding errors computed for the structure based on film data. Part of the improvement is undoubtedly attributable to the fact that a spherical crystal was used for the counter measurements in place of the needle fragment used for film measurements, and also to the increased number of reflections used in the refinement of counter data. Nevertheless, it is clear that the bulk of the improvement was due to the use of counter measurements, in place of visual estimates.

Estimation of errors

Standard deviations of atomic positions were computed by inversion of the least-squares matrices. Standard deviations of all bond lengths, bond-angles and r.m.s. thermal displacements reported have been computed by the function and error program (ORFFE) of Busing, Martin & Levy (1962*b*).

Discussion

The crystal structures contain discrete CrO_4^{3-} and PO_4^{3-} tetrahedra respectively which in both structures are arranged along the c axis one above another. They appear to be held together primarily by the doubly positive calcium ions. The structure projected along **a** is shown in Fig. 1.

Interatomic distances and interbond angles are listed in Table 8. It is clear that both the phosphate and chromate tetrahedra are significantly distorted from the ideal configuration. The dimensions of the chromate and phosphate tetrahedra are shown in Fig. 2.

Although the same type of distortion is present in both, the chromate tetrahedron shows significantly greater distortion than does the phosphate. This is consistent with the infrared absorption spectra; the Ca_2CrO_4Cl phase show absorption bands which are more widely split than the corresponding bands in the

Table 6. *Atomic thermal parameters in* Ca_2PO_4Cl

Estimated standard deviations are given in parentheses.

A. Anisotropic thermal factors

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca(1)	0·0021$_{(1)}$	0·0019$_{(1)}$	0·0012$_{(1)}$	0·0000	0·0000	0·0003$_{(1)}$
Ca(1)	0·0047$_{(2)}$	0·0019$_{(1)}$	0·0008$_{(1)}$	−0·0007$_{(1)}$	0·0000	0·0000
Cl	0·0069$_{(3)}$	0·0080$_{(2)}$	0·0010$_{(1)}$	0·0043$_{(1)}$	0·0000	0·0000
P	0·0011$_{(2)}$	0·0010$_{(1)}$	0·0008$_{(1)}$	0·0000	0·0000	0·0000
O(1)	0·0036$_{(4)}$	0·0033$_{(3)}$	0·0008$_{(1)}$	0·0007$_{(3)}$	0·0003$_{(2)}$	0·0002$_{(2)}$
O(2)	0·0034$_{(5)}$	0·0021$_{(3)}$	0·0017$_{(2)}$	−0·0012$_{(3)}$	0·0000	0·0004$_{(2)}$

B. R.M.S. displacement along principal axes of thermal ellipsoids (Å)

	1	2	3
Ca(1)	0·064	0·065	0·087
Ca(2)	0·065	0·067	0·098
Cl	0·076	0·081	0·163
P	0·046	0·050	0·067
O(1)	0·064	0·079	0·097
O(2)	0·095	0·098	0·116

Table 7. *Observed and calculated structure factors*: Ca_2PO_4Cl

L	FOBS	FCAL
(H = 0)		
(K = 0)		
2	516	550
12	822	901
14	269	193
(K = 2)		
1	41	26
3	50	45
4	249	242
5	267	254
6	605	652
7	250	247
8	662	730
9	156	153
10	656	720
11	75	74
12	366	344
13	100	95
14	405	388
15	92	91
(K = 4)		
1	640	730
2	166	146
3	297	285
5	545	577
6	72	58
7	375	375
9	518	538
10	231	217
11	150	144
12	685	716
13	390	387
15	256	256
(K = 6)		
3	184	173
4	530	544
5	169	161
6	655	694
7	90	83
8	558	564
9	88	76
10	568	581
11	117	105
12	304	263
13	86	84
(K = 8)		
0	505	491
1	497	506
2	380	373
3	381	375
4	388	375
5	310	297
6	351	341
7	541	563
8	472	454
9	310	304
10	377	372
13	247	245
(K = 10)		
0	429	409
3	257	248
6	366	369
10	344	337
12	281	285
(H = 1)		
(K = 0)		
2	67	51
4	642	706
6	236	216
8	89	87
10	122	118
12	191	180
14	97	87
(K = 1)		
0	147	118
1	536	565
2	107	84
3	278	261
4	116	92
5	554	585
7	175	114
9	418	425
11	95	91
13	290	287
15	110	105
(K = 2)		
0	435	462
1	265	245
3	445	444
5	282	268
6	434	436
7	207	197
8	377	371
9	155	146
10	493	515
11	244	241
12	511	525
13	131	123
14	218	209
15	115	112
(K = 3)		
0	678	778
1	332	317
2	264	231
3	302	282
4	526	547
5	301	290
7	202	191
8	294	290
9	220	216
10	87	82
11	156	150
12	132	122
13	172	166
14	138	131
15	120	114
(K = 4)		
0	239	221
1	73	59
3	155	147
4	274	266
5	129	128
6	130	130
7	100	93
8	99	100
11	92	87
12	115	108
14	115	117
(K = 5)		
0	300	292
1	192	183
2	109	99
3	272	266
4	270	265
5	81	72
6	127	117
7	280	283
8	159	151
10	162	154
11	222	218
12	90	86
15	161	162
(K = 6)		
0	171	161
1	339	331
2	135	121
3	515	541
4	376	380
5	434	443
6	82	67
7	277	269
8	135	127
9	310	302
10	169	161
11	397	399
12	219	209
13	254	255
(K = 7)		
0	247	234
2	224	219
3	123	119
4	229	220
6	198	188
7	146	139
8	232	217
10	144	137
11	137	132
12	198	196
(K = 8)		
0	102	88
1	116	109
3	84	85
6	86	86
7	106	100
(K = 9)		
2	329	311
6	268	254
10	182	184
12	113	118
14	118	118
(K = 10)		
3	312	315
6	117	112
9	202	203
11	249	259
13	165	175
(H = 2)		
(K = 0)		
0	405	381
4	429	393
6	648	716
8	317	315
10	243	224
12	74	68
14	299	295
(K = 1)		
1	529	549
2	617	683
3	547	581
5	384	374
6	557	578
7	455	466
8	672	734
9	267	261
10	422	415
11	329	331
12	582	589
13	218	209
14	362	339
15	249	246
(K = 2)		
1	323	308
2	276	269
3	49	33
4	88	81
5	275	262
6	415	415
8	397	406
9	254	253
10	211	197
13	171	166
14	350	348
(K = 3)		
0	699	793
1	446	446
3	449	451
4	672	750
5	384	383
7	341	338
8	486	492
9	286	281
10	583	610
11	280	277
12	380	363
13	224	219
14	473	457
15	208	209
(K = 4)		
0	438	430
1	286	279
2	184	178
3	194	185
6	284	280
7	390	404
8	227	218
10	132	122
11	177	171
14	243	242
(K = 5)		
1	232	223
2	281	264
3	157	143
4	795	920
5	223	218
6	273	261
7	132	121
8	703	760
9	197	197
10	230	207
11	96	78
12	619	634
(K = 6)		
0	64	58
1	323	325
2	294	294
3	100	93
4	238	245
5	187	180
6	268	261
7	270	268
9	235	227
14	107	102
(K = 7)		
0	274	259
1	143	138
2	705	770
3	124	127
4	288	273
5	173	168
6	665	705
8	236	219
9	152	146
10	573	591
14	486	492
(K = 8)		
1	229	230
5	141	135
7	162	159
9	193	191
15	110	117
(K = 9)		
0	691	734
2	241	229
4	678	708
8	573	602
10	140	129
12	472	491
(K = 10)		
0	90	89
4	120	117
7	244	237
15	153	162
(H = 3)		
(K = 0)		
0	86	62
4	662	743
6	602	661
8	276	259
10	555	599
12	484	487
14	264	260
(K = 1)		
0	408	407
1	324	312
2	187	167
3	424	417
4	215	200
5	164	154
6	53	48
7	383	387
8	177	171
9	106	98
11	287	283
13	100	95
15	205	204
(K = 2)		
0	340	319
4	266	245
5	138	136
6	99	93
7	129	127
8	168	172
9	86	87
10	111	111
(K = 3)		
0	200	158
1	202	187
2	382	361
3	240	220
4	99	90
5	178	165
6	276	262
7	165	156
8	211	205
9	142	122
10	122	109
11	148	142
12	187	194
13	103	98
(K = 4)		
0	198	189
1	304	293
2	426	422
3	515	533
4	511	534
5	336	331
6	300	287
7	316	312
8	183	172
9	212	206
10	373	371
11	388	389
12	293	284
13	190	185
(K = 5)		
0	97	111
1	238	239
2	275	275
3	142	133
5	247	246
6	188	186
7	127	118
9	233	228
10	144	137
(K = 6)		
0	310	304
1	91	90
2	103	92
6	174	178
8	129	135
12	141	133
14	115	121
3	94	77
4	69	66
7	131	122
8	181	178
(K = 7)		
0	297	300
2	153	138
4	252	244
5	101	90
6	158	146
7	100	93
8	246	234
9	102	94
10	125	119
(K = 8)		
1	280	268
3	387	385
5	394	396
7	164	159
11	285	287
13	258	262
(K = 9)		
0	183	171
2	105	101
4	177	168
6	124	119
14	139	149
(K = 10)		
1	142	143
7	108	110
(H = 4)		
(K = 0)		
0	402	397
2	397	394
6	499	513
8	450	433
10	338	313
12	583	585
14	422	414
(K = 1)		
1	57	23
2	258	247
3	139	135
4	75	77
6	225	211
7	144	143
8	64	58
10	255	247
11	125	120
14	166	161
(K = 2)		
0	71	63
1	304	284
3	256	244
4	365	359
5	133	125
7	329	329
9	129	123
10	762	818
11	198	189
12	140	104
13	104	102
14	707	756
15	193	188
(K = 3)		
0	268	279
2	475	493
4	122	118
6	341	343
8	107	103
10	270	258
14	125	120
(K = 4)		
0	585	607
2	510	510
3	180	176
4	762	858
6	504	507
8	487	483
9	76	70
10	315	287
11	170	163
12	519	517
14	326	315
(K = 5)		
1	83	78
2	128	129
5	145	145
6	124	124
8	81	76
9	134	129
10	168	162
14	115	114
(K = 6)		
0	165	145
1	479	488
2	577	593
3	342	331
4	348	332
5	340	331
6	597	608
7	469	466
8	196	180
9	344	341
10	480	478
13	264	272
15	306	314
(K = 7)		
2	182	175
3	135	131
6	162	159
7	116	110
11	135	134
(K = 8)		
0	512	519
2	430	419
3	177	170
4	563	573
5	180	170
6	395	387
9	112	107
12	357	363
14	234	231
(K = 9)		
0	206	201
4	156	157
6	132	132
(K = 10)		
2	267	261
5	268	262
8	355	367
10	194	195
14	170	172
(H = 5)		
(K = 0)		
0	383	362
2	364	365
4	622	685
6	302	293
8	239	228
10	439	438
14	251	257
(K = 1)		
0	174	172
2	290	278
4	58	51
6	259	253
8	167	158
10	151	142
12	87	84
14	168	161
(K = 2)		
3	134	134
7	82	80
9	78	71
11	132	130
(K = 3)		
2	66	60
5	239	232
7	256	254
9	211	204
13	175	171
15	162	167
(K = 4)		
3	281	271
6	276	270
9	298	293
11	168	164
12	208	201
13	243	241
(K = 5)		
0	252	211
2	339	337
8	205	200
10	239	215
12	144	142
14	208	204
(K = 6)		
0	78	77
3	102	97
6	109	100
(K = 7)		
2	95	99
8	160	159
11	150	153
15	127	133
5	159	156
7	88	94
8	133	128
9	163	164
10	94	92
12	146	141
13	135	136
(K = 8)		
0	170	161
2	133	123
3	342	336
5	234	225
7	194	187
8	102	98
9	143	138
11	294	298
13	125	131
(K = 9)		
0	194	197
1	96	90
2	158	165
4	156	155
6	180	179
10	168	168
14	158	174
(K = 10)		
0	138	108
7	187	188
15	144	144
(H = 6)		
(K = 0)		
4	245	243
8	457	460
(K = 1)		
2	652	708
5	371	376
8	421	413
11	150	143
12	265	248
13	270	274
14	313	308
15	126	128
(K = 2)		
0	498	519
2	151	150
5	69	63
8	387	385
12	152	153
(K = 3)		
1	200	195
4	90	63
7	169	164
10	574	591
11	113	113
12	157	141
13	137	132
14	452	459
15	140	122
(K = 4)		
1	204	198
4	206	197
7	230	224
10	120	119
11	90	92
12	154	152
15	140	148
(K = 5)		
2	445	434
5	182	177
8	513	519
9	127	129
10	295	288
11	250	258
12	362	360
13	111	114
15	150	160
(K = 6)		
0	243	223
2	148	149
6	139	113
7	135	136
8	193	196
9	120	98
10	165	163
12	111	93
(K = 7)		
0	204	194
2	641	661
4	135	128
5	90	87
6	570	588
7	112	102
8	141	135
10	503	519
14	367	382
(K = 8)		
2	221	227
7	165	165
10	168	174
(K = 9)		
0	422	430
3	117	100
8	404	418
10	126	119
12	348	373
(K = 10)		
6	129	132
10	116	126
(H = 7)		
(K = 0)		
0	344	308
8	171	162
14	204	182
(K = 1)		
2	220	216
5	134	125
8	140	126
10	143	146
14	172	177
(K = 2)		
0	308	294
3	128	117
6	169	160
9	188	185
12	305	299
14	117	120
(K = 3)		
2	119	115
5	179	168
7	175	172
9	150	159
11	116	116
13	130	134
(K = 4)		
0	100	96
3	80	78
6	165	161
9	126	120
11	110	106
14	125	127
(K = 5)		
0	184	174
2	219	214
4	97	87
6	229	225
8	142	135
10	165	165
14	170	183
(K = 6)		
2	151	147
5	284	278
7	152	150
9	208	210
12	145	138
13	180	184
(K = 7)		
0	113	94
1	145	149
4	143	143
(K = 8)		
1	122	116
6	149	142
7	192	176
15	120	127
(K = 9)		
0	104	78
2	149	154
6	148	154
10	111	120
(K = 10)		
2	129	124
5	125	118
7	146	150
11	231	243
(H = 8)		
(K = 0)		
0	749	795
4	553	571
10	112	97
12	433	449
(K = 1)		
2	131	134
4	440	451
6	139	136
9	100	94
12	266	273
(K = 2)		
0	383	371
2	511	515
4	183	172
6	434	431
8	299	293
10	442	443
12	129	120
14	266	272
(K = 3)		
0	143	143
3	98	93
5	98	94
8	179	184
12	237	246
14	142	145
(K = 4)		
2	199	193
5	176	167
8	526	531
11	127	134
13	133	135
15	165	175
(K = 5)		
0	335	340
2	147	152
4	377	392
6	141	141
9	103	102
12	219	231
(K = 6)		
2	411	413
5	108	109
8	236	220
11	111	106
14	236	249
(K = 7)		
14	115	121
12	141	133
8	129	135
6	174	178
3	140	139
0	170	172
(K = 8)		
2	289	294
5	170	177
8	251	256
10	238	246
13	145	155
(K = 9)		
4	122	135
8	115	125
12	145	154
(K = 10)		
0	225	236
3	148	153
6	229	245
8	198	197
11	120	127
14	151	159
(H = 9)		
(K = 0)		
2	178	177
6	176	174
(K = 1)		
15	127	133
11	150	153
8	160	158
5	148	141
3	184	176
0	219	200
(K = 2)		
2	160	151
4	232	231
7	107	102
10	118	117
12	192	205
(K = 3)		
12	144	145
8	216	217
6	154	160
3	98	90
0	245	231
(K = 4)		
0	101	95
6	104	116
(K = 5)		
10	111	107
7	143	145
5	151	151
2	118	108
(K = 6)		
0	124	121
3	179	180
5	131	131
11	159	165
(K = 7)		
12	129	134
8	197	201
4	172	179
0	241	241
(K = 9)		
10	127	132
6	114	116
2	124	123
(K = 10)		
5	136	136

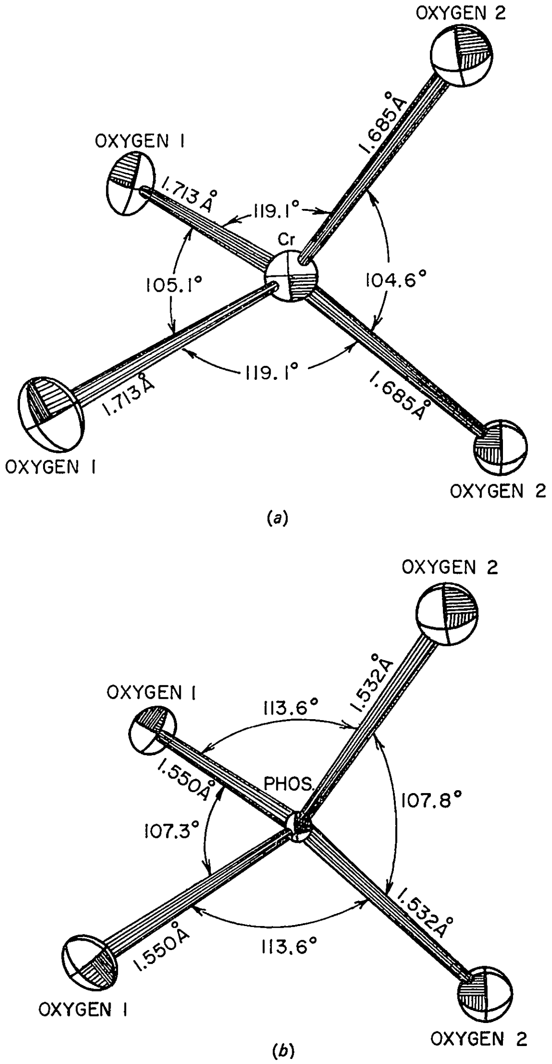

Fig. 2. Dimensions of (*a*) chromate and (*b*) phosphate tetrahedra.

phosphate compound. Both of these compounds show more splitting of the vibrational bands than do the related compounds with apatite structure:

$$Ca_5(CrO_4)_3Cl \quad \text{and} \quad Ca_5(PO_4)_3Cl.$$

The magnetic susceptibility of Ca_2CrO_4Cl has been measured; the magnetic moment per chromium atom is 1·7 Bohr magnetons, compared with 1·73 μ_B expected for Cr^{5+}.

The structure determination confirms that the chromium ions are in the 5+ oxidation state; the four chromium ions in each unit cell are in crystallographically equivalent positions, effectively eliminating the possibility that two Cr^{6+} and two Cr^{4+} ions are present.

Table 8. *Interatomic distances and bond angles*

	X = Cr or P Ca_2CrO_4Cl	Ca_2PO_4Cl
Ca(1)–O(1)	2·512 ± 0·004 Å	2·531 ± 0·002 Å
Ca(1)–O(2)	2·464 ± 0·004	2·491 ± 0·002
Ca(2)–O(1)	2·423 ± 0·004	2·423 ± 0·002
Ca(2)–O(2)	2·595 ± 0·004	2·656 ± 0·002
Cl —Cl	3·572 ± 0·001	3·499 ± 0·002
Cl —O(1)	3·328 ± 0·004	3·262 ± 0·002
Cl —O(2)	3·230 ± 0·004	3·193 ± 0·002
X——O(1)	1·713 ± 0·004	1·550 ± 0·002
X——O(2)	1·685 ± 0·004	1·532 ± 0·002
O(1) -O(2′)	2·694 ± 0·006	2·483 ± 0·003
O(1′)-O(2′)	2·929 ± 0·006	2·579 ± 0·003
O(2) -O(2′)	2·665 ± 0·007	2·477 ± 0·004
O(1) -O(1′)	2·718 ± 0·004	2·496 ± 0·004
O(1)-X-O(2′)	105·0 ± 0·2°	107·3 ± 0·1°
O(1′)-X-O(2)	105·1 ± 0·2	107·3 ± 0·1
O(2)-X-O(2′)	104·6 ± 0·3	107·8 ± 0·2
O(1)-X-O(1′)	105·1 ± 0·3	107·3 ± 0·2
O(1)-X-O(2)	119·1 ± 0·2	113·6 ± 0·1
O(1′)-X-O(2′)	119·1 ± 0·2	113·6 ± 0·1

Furthermore, preliminary electron spin resonance data indicate the presence of Cr^{5+} in solid solutions of these compounds. Apparently there are two magnetically non-equivalent chromiums.

All interatomic distances are reasonable, and compare favorably with corresponding distances reported in the literature. Apparently the distortions cannot be explained simply by considerations of packing alone. Analyses of the spectral properties of these compounds are in progress.

The authors wish to thank Dr J. S. Prener of General Electric Research Laboratory for several large crystals of Ca_2PO_4Cl, and Drs F. Holtzberg and T. A. McGuire of IBM for the magnetic susceptibility measurements.

We thank Leif Singman for helping with the X-ray diffraction measurements on Ca_2PO_4Cl.

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