curve on a plane, since the deviations of the experimental values from the smooth curve are obviously smaller than from either the Hartree or the Pauling curve.

The curves of Fig. 1 correspond to f values at room temperature for the diamond lattice. From these the values for 0° K. shown in Table 3 are calculated.

The calculations were carried out by means of I.B.M. machines, using a punched-card file which Prof. Schomaker, Pasadena, kindly prepared. I am very much obliged to Mr I. A. Poole for his kind help in wiring the plug-board of the I.B.M. Tabulator and in operating the I.B.M. machines. Furthermore, I wish to thank Miss Hathaway, Mrs Mimi Mark and Mr B. F. Brown for the preparation of the figures.

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X-ray Diffraction Study of Cerous Phosphate and Related Crystals.

I. Hexagonal Modification

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The phosphates of trivalent lanthanum, cerium, and neodymium have been found to be dimorphic. One phase is monoclinic, isomorphous with the mineral monazite; the other is a hexagonal structure of a new type which easily converts to the monoclinic form at moderately high temperatures.

The hexagonal modification crystallizes with the symmetry of D_6^4–$C6_22$. There are three molecules of XPO_4 in the unit hexagonal cell, where X may be La, Ce or Nd. The cell dimensions of the three crystals have been determined, and the complete structure has been deduced. In this structure X is co-ordinated to eight oxygen atoms—four at 2·34 A. and four at 2·66 A.—in such a manner as to leave open, oxygen-lined channels along the hexagonal axis. The presence of zeolitic water in these channels [$XPO_4(0\text{–}0{\cdot}5H_2O)$] is probably necessary to stabilize the structure.

Introduction

This investigation of the crystalline structure of the phosphates of lanthanum, cerium (ous), praseodymium and neodymium was carried out at the Metallurgical Laboratory of the University of Chicago in 1944. A brief résumé of the results has appeared in a letter to the Editor of the *Journal of Chemical Physics* (Mooney, 1948). The compounds were prepared in the form of powder precipitates from aqueous solution by members of a group of the Chemistry Division, Metallurgical Laboratory, under the direction of Dr William Rubinson. The large number of samples made under carefully controlled conditions by this group was indispensible to the successful issue of the X-ray investigation.

The dimorphic forms

The phosphates of lanthanum and the rare earths must be expected to be isomorphous with the mineral monazite, (La, Ce, Di)PO_4, a monoclinic crystal for which the cell size and space group are reported in the literature (Parrish, 1939).

However, X-ray examination of laboratory prepared samples showed that the compounds are dimorphic, and that the two forms often coexist. The more stable form is indeed monoclinic and isomorphous with monazite; the other is a hexagonal structure of a new type. It appears that, at moderate temperatures, the phosphates of cerium and its isomorphs usually crystallize from solution in the hexagonal form; and that they convert rapidly to the monoclinic arrangement at high temperatures. Long digestion periods in the mother liquor also tend to cause conversion to the monoclinic form. However, dried powders of the hexagonal structure type seem to be quite stable at room temperatures, and no evidence of spontaneous conversion to the more stable monoclinic type has been observed. A number of the original samples, re-examined by X-rays after a storage period of four years, were found to have retained the hexagonal structure.

The structure determination of the hexagonal crystal is discussed in the following sections. A report on the monoclinic crystal is in preparation.

X-ray diffraction data

The diffraction photographs were taken from thin cylindrical powder samples, exposed in 9 cm. and in 18 cm. diameter Bradley-type cameras. The radiation used was copper, filtered through nickel foil. Film measurements were made with a steel scale and vernier. The intensities were visually estimated.

Hexagonal-type patterns were obtained from a number of samples of cerous and of lanthanum phosphate, and from one sample of neodymium phosphate. The only sample of praseodymium phosphate which was sufficiently well crystallized to give a recognizable pattern proved to be monoclinic. However, there is no reason to doubt that, under suitable conditions, this compound also exists in the hexagonal phase.

Table 1 gives indexed data for part of the patterns of the three compounds, and shows the close relationship between their structures. Subsequent study and intercomparison of a number of patterns led to the conclusion that well-crystallized samples showed strong preferred orientation such as would occur if the compounds crystallized in fine needles elongated along the *c* axis. Prolonged grinding of the materials produced shifts in relative intensities in agreement with this assumption, as may be seen by comparison of Table 1 with the final data in Tables 3 and 4.

Table 1. *Hexagonal pattern for* XPO$_4$
(Cu $K\alpha$ radiation)

	LaPO$_4$		CePO$_4$		NdPO$_4$	
hkl	$\sin^2\theta$	$I_{\text{obs.}}$	$\sin^2\theta$	$I_{\text{obs.}}$	$\sin^2\theta$	$I_{\text{obs.}}$
100	0·0160	*m*	0·0160	*m*	0·0163	*w*+
101	0·0304	*w*+	0·0306	*w*+	0·0311	*w*
110	0·0477	*m*−	0·0478	*m*	0·0489	*w*+
111 200	0·0641	*s*	0·0641	*s*	0·0653	*s*−
012	0·0730	*w*+	0·0733	*m*−	0·0755	*w*
201	—	—	0·0777	*tr*	—	—
112	0·1045	*w*−	0·1051	*w*	0·1079	*vw*
210	0·1113	*w*−	0·1122	*w*+	0·1145	*vw*
202	—	—	0·1209	*tr*	—	—
211	0·1253	*s*−	0·1260	*m*	0·1294	*m*
003	—	—	0·1287	*w*−	—	—
300 103	—	—	0·1445	*vw*−	—	—
301	0·1567	*w*+	0·1581	*w*+	0·1617	*m*−
212	0·1676	*m*−	0·1690	*m*−	0·1737	*m*
113	—	—	0·1771	*vw*	0·1821	*tr*
220 203	0·1903	*w*	0·1904	*w*+	0·1965	*w*
302	0·1992	*w*	0·1998	*w*	0·2057	*w*−
221	—	—	—	—	—	—
310	0·2058	*m*−	0·2074	*m*−	0·2119	*w*−
311	0·2194	*vw*	0·2231	*w*−	0·2262	*vw*

Cell dimensions and densities

The cell dimensions of the three crystals and the densities calculated therefrom on the basis of three stoichiometric weights per unit cell are given in Table 2. The periodicities were calculated from measurements made on high-angle reflections. The unit hexagonal cell in each case must contain three molecules of XPO$_4$ (where X is Ce, La or Nd), since the directly determined density, to a rough approximation, appeared to be close to 4 g.cm.$^{-3}$. The X-ray densities were calculated for dry crystals. It seems quite certain that under ordinary circumstances these crystals contain some water. This point will be discussed later. It should also be mentioned that there is an unusual difference in the densities of the two modifications of XPO$_4$ crystals, the monoclinic being about 25 % heavier than the hexagonal form.

Table 2. *Cell dimensions and densities*

XPO$_4$	a_1 (A.)	a_3 (A.)	a_3/a_1	ρ (g.cm.$^{-3}$)
LaPO$_4$	7·081 ± 0·005	6·468 ± 0·008	0·9134	4·122
CePO$_4$	7·055 ± 0·003	6·439 ± 0·005	0·9127	4·193
NdPO$_4$	6·98 ± 0·01	6·34 ± 0·02	0·908	4·33

Space-group consideration

The diffraction patterns show only one systematic absence of reflections: that is, planes 00l are absent unless $l = 3n$. This criterion fails to distinguish between several space groups, any one of which provides possible sets of threefold positions for the metal and phosphate ions, and three-, six-, or twelvefold positions consistent with the required tetrahedral grouping of oxygen about phosphorus. These (see *International Tables*) are the following:

$$D_6^4\text{–}C6_22\ (D_6^5\text{–}C6_42)$$
$$C_6^4\text{–}C6_2\quad (C_6^5\text{–}C_6^4)$$
$$D_3^4\text{–}C3_12\ (D_3^6\text{–}C3_221)$$
$$C_3^2\text{–}C3_1\quad (C_3^3\text{–}C3_2)$$

Single-crystal data, by distinguishing between planes hkl, $hk\bar{l}$, $\bar{h}kl$ and $h\bar{k}l$, would at least narrow the possibilities. With only powder data available, the final assignment of the space-group symmetry must follow rather than precede the structure determination.

Atomic positions

A cerous phosphate pattern, obtained from a well-crystallized sample which had been subjected to prolonged grinding, was used for the detailed structure analysis.

Obviously, the high scattering power of cerium, compared with that of phosphorus and oxygen, must predominantly influence the intensities. It follows that evidence of the position of cerium in the structure is not difficult to find. Inspection of the intensities shows that, though all types of general planes are present, no plane having h and k even gives more than a barely observable trace unless $l = 3n$. The cerium atoms, then, must be in positions such that they contribute to planes with h and k even only when $l = 3n$. This condition does not distinguish between the possible space groups, since such positions may be found in any one of them. In $C3_12$ and $C3_1$ they are given by the particular parameter values $\frac{1}{2}, 0, \frac{1}{3}$; $0, \frac{1}{2}, \frac{2}{3}$; $\frac{1}{2}, \frac{1}{2}, 0$; in $C6_22$ and $C6_2$ respectively by the special positions $\frac{1}{2}, 0, 0$; $0, \frac{1}{2}, \frac{2}{3}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{3}$; and by $\frac{1}{2}, \frac{1}{2}, z$; $\frac{1}{2}, 0, \frac{2}{3}+z$; $0, \frac{1}{3}, \frac{1}{3}+z$; if z is 0.

Structure-amplitude calculations based on cerium scattering alone fully confirm this distribution of the metal ions by giving rough agreement between calculated and observed intensities throughout the list of observations. This is demonstrated in Table 3. Fortunately, a number of discrepancies give evidence that the contributions of the light atoms are by no means always negligible, and therefore there is some basis for inquiry into the positions of the phosphate group.

Table 3. *Structure amplitudes observed and those calculated from cerium contributions*

hkl	pF^2		*hkl*	pF^2	
100	*s*	18	311	*w*+	151
101	*s*	131	213	*Nil*	0
110	*m*	15	104	*w*	72
111	*s*+	113	222	*Nil*	0
200			400	*w*	79
102	*s*	109	312	*w*+	139
201	*Trace*	0	401	*Nil*	0
112	*m*−	101	303	*Trace*	17
210	*w*+	12	114	*w*	67
202	*Nil*	0	204	*Nil*	0
211	*s*	192	320	*Trace*	16
003	*w*+	35	402	*Nil*	0
300	*w*−	11	321	*w*	106
103		24	223	*w*	141
301	*m*+	87	410	*w*+	15
212	*s*+	170	313		30
113	*w*−	21	214	*m*+	121
220	*m*	92	411	*w*	119
203		184	322	*m*+	118
302	*m*	196	304	*m*−	57
221	*Nil*	0	105		57
310	*m*	19			

The limitations of the data are such that it is not practical to attempt the location of the phosphorus and of the oxygen atoms from first principles. Rather, it is necessary to consider the phosphate ion as a unit, and to examine critically all reasonable structural arrangements of three such units with relation to the cerium positions in the hexagonal cell. The shape as well as size of the phosphate ion is assumed to be the same as in KH_2PO_4; that is to say, a tetrahedral configuration with phosphorus–oxygen binding distances of 1·56 A. It may easily be seen that possible arrangements are limited to the following. If the space group is $C6_22$, both spatial and symmetry conditions require the centers of the phosphate groups and the cerium ions to be collinear in the z direction, and separated by distances equal to half the c translation. In this case, only one degree of freedom—the rotation of the group about the z axis—requires further definition. If the symmetry is lower than $C6_22$, the cerium and phosphate group center may be either not collinear along z or not exactly half the c translation apart; or neither collinear nor equally spaced. It appears, however, that departures from the highest symmetry arrangement must be small, for otherwise impossible interatomic distances result.

Within the limitations imposed by the symmetry conditions, and with due regard for reasonable atomic separations, a systematic study of the effect of the phosphate group positions on the calculated intensities was made. The criteria useful for testing possible structures were planes whose intensities are observably modified by the light atom contributions, and those whose intensities are due solely to oxygen scattering. The latter are consistently vanishingly small in intensity. The best agreement obtained corresponds to an arrangement consistent with the symmetry of $C6_22$. If the symmetry of the crystal is lower, the deviations from $C6_22$ are too small to be detected by the presently available data.*

The atomic co-ordinates for the proposed structure, following the notation of the *International Tables*, are:

Cerium in (c) $\frac{1}{2},0,0;\ 0,\frac{1}{2},\frac{2}{3};\ \frac{1}{2},\frac{1}{2},\frac{1}{3}$.
Phosphorus in (d) $\frac{1}{2},0,\frac{1}{2};\ 0,\frac{1}{2},\frac{1}{6};\ \frac{1}{2},\frac{1}{2},\frac{5}{6}$.
Oxygen in (k), $x,y,z;\ \bar{y},x-y,\frac{2}{3}+z;\ y-x,\bar{x},\frac{1}{3}+z;$
$y,x,\frac{2}{3}-z;\ \bar{x},y-x,\frac{1}{3}-z;\ x-y,\bar{y},\bar{z};\ \bar{x},\bar{y},z;$
$y,y-x,\frac{2}{3}+z;\ x-y,x,\frac{1}{3}+z;\ \bar{y},\bar{x},\frac{2}{3}-z;$
$x,x-y,\frac{1}{3}-z;\ y-x,y,\bar{z};$

where, in fractions of the unit cell,

$$x=0{\cdot}446,\quad y=0{\cdot}147,\quad z=0{\cdot}360.$$

Table 4 gives the intensities calculated from these parameters by means of the expression,

$$I \propto |F|^2 p\,\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}.$$

The numerical values have been reduced by a convenient factor. Agreement between calculated and observed intensities is generally good. Some discrepancies still remain; in particular, the calculated values for planes 110, 210 and 310 seem low compared with their observed intensities. This may be attributed to some degree of preferred orientation remaining despite the prolonged grinding of the material.

Table 4. *Observed and calculated intensities for* $CePO_4$ *structure*

hkl	$I_{obs.}$	$I_{calc.}$	*hkl*	$I_{obs.}$	$I_{calc.}$
100	*s*	549	400	*w*	109
101	*s*	403	312	*w*+	131
110	*m*	125	401	—	1
111	*s*+	149	303	*Trace*	17
200		455	114	*w*	79
102	*s*	250	204	*Nil*	0
201	*Trace?*	11	320	*Trace*	18
112	*m*−	172	402	—	2
210	*w*+	20	321	*w*	68
202	*Nil*	3	223	*w*	72
211	*s*	162	410	*w*+	18
003	*w*+	64	313		21
300	*w*−	29	214	*m*+	182
103		27	411	*w*	72
301	*m*+	98	322	*m*+	194
212	*s*+	230	304	*m*−	120
113	*w*−	16	105		45
220	*m*	85	403	*vw*	73
203		83	412	*m*−	147
302	*m*	—	500	—	16
221	*Nil*	1	115	*vw*	25
310	*m*	23	501		21
311	*w*+	68	224	—	1
213	*Nil*	10	205	—	0
104	*w*	77	330	*w*	13
222	—	2	323		15

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* The space group was originally reported (Mooney, 1948) as $C3_12$, and the structure built up with two six-fold sets of oxygen atoms. The resulting arrangement has symmetry indistinguishable from $C6_22$.

Discussion of the structure

Fig. 1 shows a projection of the hexagonal cerium phosphate structure on the basal plane. To a close approximation, it can also be taken as representative of the structures of the isomorphous lanthanum, and neodymium phosphates.

The cerium–cerium separation is 4·13 A. The phosphate ion, by preliminary assumption, has been taken to be a tetrahedral grouping of oxygens about phosphorus, with the oxygen–phosphorus distance fixed at 1·56 A. Each cerous ion is coordinated to eight oxygen atoms, four at distances of 2·34 A., and four at 2·66 A. The shorter distances are to the corners of four different tetrahedra, linking atoms which are practically coplanar. The longer distances extend to pairs of oxygens forming the edges of two tetrahedra, one above and one below the plane of the four shorter distances. Conversely, a given phosphate group is coordinated to six cerous ions, each corner by one short bonding distance, and opposite edges by longer bonding distances. The co-ordination distances are comparable with those found in the sesquioxide, Ce_2O_3, where the cerous ion is linked to four oxygens at 2·39 A. and three at 2·66 A. (Zachariasen, 1926, 1929).

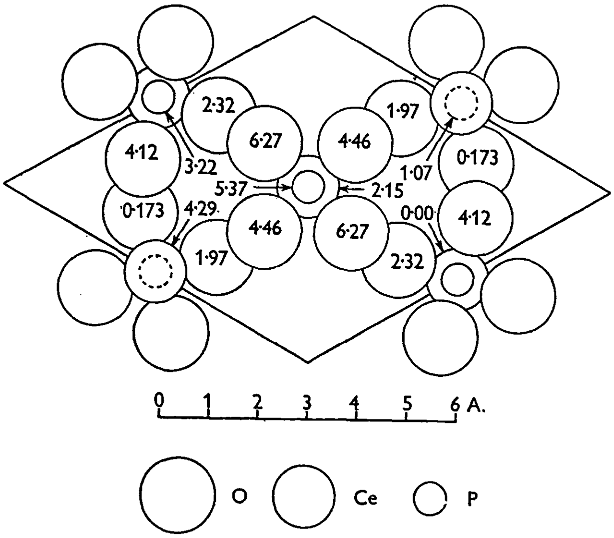

Fig. 1. Projection of $CePO_4$ structure on basal plane. The numbers give the z coordinates of the atoms in Ångström units.

The overall arrangement—which may be described as columns built up of alternate cerous and phosphate ions, extending along the c axis, each column linked to four neighboring columns—is such that open channels run through the structure along the hexagonal axis. Thus the distances from a given oxygen to its nearest oxygen neighbors have an unusual range of values: conventional ones within the network, such as 2·71, 2·88, 3·30 A., and extraordinarily long ones such as 5, 5·26, 5·55 A. to nearest neighbors bordering the open channel.

The existence of such unoccupied spaces explains the comparatively low density of the hexagonal isomorph, which is only 4·19 g.cm.$^{-3}$ in contrast to 5·23 g.cm.$^{-3}$ for the monoclinic type. It also suggests that the crystal structure may be stabilized by the presence of water in the interstices. With this point in mind, it is interesting to examine the configuration of the available spaces. They may be described as cylindrical, oxygen-lined tunnels of diameter 5·3 A. The oxygens are distributed roughly in rings at intervals of one-third of the c axis. The points $0, 0, \frac{1}{2}$; $0, 0, \frac{5}{6}$; $0, 0, \frac{1}{6}$ lie half-way between these rings, and are at distances of 2·85 A. from the eight nearest oxygen atoms. These sites could readily accommodate a neutral molecule of water, or even ions of moderate size if the charges were compensated in some way. However, adjacent sites are only 2·15 A. apart along the hexagonal axis, which precludes the occupancy of every site by water, for instance. At the maximum, only half the sites could be occupied; that is to say, there could be only one and a half molecules of water per unit cell. Therefore, if water is ordinarily present in the crystal there should be no more than half a molecule per cerium atom.

No quantitative experiments have been made to test the degree of hydration of hexagonal $CePO_4$. However, it has been found that air-dried samples do lose weight under protracted vacuum drying at room temperature, and that the structure does not change during the process. On the other hand, drying at moderate temperatures causes slow conversion to the monoclinic form.

It is reasonable to suppose that the crystals ordinarily contain zeolitic water, but there is no real evidence to prove whether or not the presence of water is a necessary condition for the stability of the hexagonal-type structure. The calculated density of the crystal, assuming full hydration—$CePO_4.0{\cdot}5H_2O$—is 4·355 g.cm.$^{-3}$ compared with 4·194 g.cm.$^{-3}$ calculated for dry crystals, a difference of nearly 4 %. Accurate density determinations of air-dried and vacuum-dried samples should thus be of interest. It would also be of interest to learn whether the hexagonal form can be crystallized from other than aqueous solutions.

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