

AN INVESTIGATION OF THE CRYSTAL
STRUCTURES OF $\text{Cd}_2\text{P}_2\text{O}_7$ AND $\text{Cd}_2\text{V}_2\text{O}_7$

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PETER KWOK-LUN AU, B. Sc.

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AUTHOR: Peter Kwok-lun Au, B. Sc. (University of Hong Kong)

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SCOPE AND CONTENTS:

$\text{Cd}_2\text{P}_2\text{O}_7$ has been found to belong to the space group $P \bar{1}$. The structure has a bent P-O(b)-P bond angle for the anion with the central oxygen O(b) close to sp^2 hybridization. The two PO_4 tetrahedra forming the anion are eclipsed. The cadmium atoms are sixfold co-ordinated to oxygen atoms forming two types of distorted octahedra.

$\text{Cd}_2\text{V}_2\text{O}_7$ belongs to the monoclinic space group $C 2/m$. As with most structures in the thortveitite series that have been determined, the central oxygen in $\text{V}_2\text{O}_7^{4-}$ ion shows enhanced thermal motion. The cadmium atoms are also sixfold co-ordinated to oxygen atoms forming distorted octahedra.

The bonding in $\text{P}_2\text{O}_7^{4-}$ ion is discussed with reference to values predicted by Cruickshank, and those in the $\text{V}_2\text{O}_7^{4-}$ ion compared with values calculated by Barnes and Bachmann.

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CHAPTER I: INTRODUCTION

Many of the pyrocompounds, $X_2O_7^{n-}$, based on tetrahedrally co-ordinated anions are readily prepared in the laboratory, although natural occurring ones include only thortveitite $(Sc,Y)_2Si_2O_7$ (Zachariasen, 1930) and possibly cherveitite $(Pb_2V_2O_7)$, Bariand et al, 1963). Surprisingly, many of these pyrocompounds have structures similar to thortveitite. These include a pyrosilicate, a pyrogermanate, pyroarsenates, pyrophosphates, and the pyrovanadate under investigation. The known compounds and their lattice parameters are shown in Table I-1.

The geometry and bonding of oxygen atoms in tetrahedrally co-ordinated pyro-anions of sulphur, phosphorus, silicon and chlorine has been discussed by Cruickshank (1961). He showed that the XO_4^{n-} ions involving these atoms can support two π -bonding systems in addition to the usual four σ -bonds. One system is formed by the overlap of the $p\pi$ -orbitals of the oxygen atoms with the $3d_{z^2}$ orbital of the central X atoms, and the other by the overlap of $p\pi'$ -orbitals of oxygen atoms with the $3d_{x^2-y^2}$ of X. In terms of the valence-bond designation, each X-O bond has a π -bond order of $\frac{1}{4} + \frac{1}{4} = \frac{1}{2}$, leaving the tetrahedron with a total π -bond order of two. The P-O bond with σ -bond order 1.0 has been calculated from

the Schomaker-Stevenson equation (Schomaker and Stevenson, 1941) to be $1.71 \overset{\circ}{\text{A}}$, and the observed value in isolated PO_4^{-3} groups, where the bond order is $1\frac{1}{2}$, averages $1.54 \overset{\circ}{\text{A}}$.

The role of p-orbital overlap of the oxygen atom with the d-orbitals of the metal ions is modified in the pyrophosphate ion. The central oxygen atom may be in sp , sp^2 , or sp^3 hybridization, or a linear combination of these. In the case of sp hybridization, the oxygen atom is σ -bonded to the two phosphorus atoms, while the two vacant $p\pi$ -orbitals can overlap with the two d-orbitals of the phosphorus atoms so that there are two π -bonding systems running throughout the anion. For the case of sp^2 hybridization of the central oxygen atom, the P-O-P bond angle will be 120° , and the vacant $p\pi$ -orbital which is now perpendicular to the P-O(b)-P plane, can still overlap with a d-orbital on each phosphorus atom. Thus we will have one π -bonding system running throughout the ion with a bond order of two. Because the $p\pi'$ -orbital of the bridging oxygen atom is not available now, the π -system using the $d_{x^2-y^2}$ orbitals remains in two distinct halves, each with a π -bond order of one. The z-direction of phosphorus atoms is taken to be perpendicular to the P-O(b)-P plane. For the π -system running through the ion, if we exclude the structure with the bridging oxygen atom π -bonded to both phosphorus atoms, $4 \times 4 - 1 = 15$ valence bond structures can be written. Of these fifteen structures,

there are three involving π -bonding from one phosphorus atom to the bridging oxygen atom and from the other phosphorus atom to one of its terminal oxygen atoms. There are also nine structures involving π -bonding to each of the terminal oxygen atoms. The π -bond order for the P-O(P) = $3/15 = 0.20$ and P-O = $9/15 = 0.60$. In the orthophosphate case, the π -bond order of 0.5 causes a contraction of $(1.71 \text{ \AA} - 1.54 \text{ \AA}) = 0.17 \text{ \AA}$ from the single bond value of 1.71 \AA . Provided there is a linear relationship between bond order and bond length, the 0.20 and 0.60 π -bond order for the inner P-O(P) and outer P-O in the pyrophosphates should have bond lengths of 1.64 \AA and 1.51 \AA respectively. For the pure sp^3 hybridization, the P-O-P bond angle will be $109^\circ 28'$ and because now there are no available vacant $p\pi$ -orbitals to overlap with the d-orbital of the phosphorus atoms, the two π -systems in the two PO_4 tetrahedra will remain as two separate systems with each outer P-O bond having a π -bond order of $2/3$ and bond length of 1.49 \AA . The P-O(b) bond will be essentially that of a single σ -bond.

The cations, because of their positive charges, may be expected to have an influence on the negatively charged anions, and hence to affect the P-O(b)-P angle. If this affect were mainly electrostatic, we would not expect divalent metal pyrophosphates of different metal ion radii to have profound effects on the anion symmetries, since these

symmetries are largely dependent on the covalency in the anion. However, in Cruickshank's paper no environment effects have been considered.

Similarly considerations of the effect of π -bonding can be extended to the orthovanadates VO_4^{-3} and pyrovanadates $\text{V}_2\text{O}_7^{-4}$ where the vanadium ion is in the +5 oxidation state, and tetrahedrally hybridised using sp^3 and sd^3 orbitals. Two 3d-orbitals on the vanadium atom remain available for π -bonding with oxygen atoms.

As many of the pyrocompounds with tetrahedrally disposed X atoms are isostructural with thortveitite, it is of interest to briefly review this structure. Chemically, thortveitite is $(\text{Sc}, \text{Y})_2\text{Si}_2\text{O}_7$ with appreciable replacement of Sc^{+3} and Y^{+3} by Fe^{+3} and Mn^{+3} . The structure was first proposed by Zachariasen (1930) and was later refined by Cruickshank, Lynton, and Barclay (1962). The crystal is monoclinic with systematic absences of reflections of the type $hk\ell$ when $h + k$ is odd only. Hence, the structure must have one of the possible space groups $C 2$, $C m$, or $C 2/m$. The space group $C 2/m$ was chosen by Zachariasen, while each of the three possible space groups have been refined by Cruickshank and co-workers. The $C m$ space group was rejected because the final refinement gave unreasonable discrepancies among chemically equivalent bonds. The $C 2$ space group was also rejected because O-Si-O angles between chemically equivalent

oxygen atoms at the two ends of the anions differed by considerable amounts. Only the space group C 2/m gave answers reasonable in terms of chemical intuition; thus it was taken to be the correct one. Also the reliability factor R_1 , defined as

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

where F_o and F_c are the observed and calculated structure factors, modified by a statistical factor based upon the number of free independent variables, is lowest for the C 2/m space group. Hamilton (1965) showed that the C m space group could be rejected only at the 25% significance level. The C 2/m space group choice has been confirmed by epr techniques, (Datars and Calvo (private communication)) as have been done with the isostructural β -Mg₂P₂O₇ (Calvo, Leung and Datars 1966) and β -Zn₂P₂O₇ (Chambers, Datars and Calvo, 1965). In the C 2/m space group, the pyroanion is characterized by a linear Si-O-Si bridge, with a crystallographic twofold axis passing through the bridging oxygen. The two tetrahedra of the pyrosilicate ion share a common apex with the mirror plane passing through one of the oxygens which is coplanar with the central oxygen and the silicon atoms. Each of the cations lies on a twofold axis and is octahedrally co-ordinated

to six oxygen atoms, but with considerable distortion.

The divalent pyrophosphates, whose formula may be generalized as $2MO:P_2O_5$ (M=metal ion), can be classified into the "large divalent metal ion" series or the "small divalent metal ion" series, depending on the nature of the metal ion. The luminescence and phases of the "large divalent metal ion" pyrophosphates i.e. of $Ca_2P_2O_7$ and $Ba_2P_2O_7$ have been studied by Ranby, Mash and Henderson (1951), who found three distinct phases in $Ca_2P_2O_7$, two phases in $Sr_2P_2O_7$ and one in $Ba_2P_2O_7$. The low temperature form of $Ca_2P_2O_7$ (δ phase) is stable below $750^\circ C$, the β -form from $750^\circ C$ to $1150^\circ C$ and the high temperature α -form from $1150^\circ C$ to the melting point at $1230^\circ C$. For $Sr_2P_2O_7$, there is just the β and α -form with $750^\circ C$ as the transition temperature, and for $Ba_2P_2O_7$, there is a δ form that appears upon firing at $790^\circ C$.

Crystallographically, the powder photographs of δ - $Ca_2P_2O_7$, β - $Ca_2P_2O_7$ and δ - $Ba_2P_2O_7$ were recorded for identifications by Ranby et al. The lattice parameters of the α -forms of $Ca_2P_2O_7$ and $Sr_2P_2O_7$ were determined from single crystal photographs of the compounds, and appeared to be isostructures, belonging to the orthorhombic system. The β -forms of $Ca_2P_2O_7$ and $Sr_2P_2O_7$ were also shown to be isostructural by Hoffman and Mooney (1960) from powder photographs. Crystallographic data on β - $Ca_2P_2O_7$ have been determined by Corbridge (1957) from rotation photographs and Weissenberg photographs. The space group was shown to be $P4_1$ with eight

molecules per unit cell. Recently Webb (1966) has determined and refined the structure, which has two symmetrically independent pyrophosphate groups, each with two PO_4 tetrahedra joined at a corner. These tetrahedra are in an essentially eclipsed configuration, that is, when looking along the P-P vector, the basal oxygen atoms of one tetrahedron superimposed upon those of the opposite tetrahedron. The cations are co-ordinated to seven, eight and nine oxygen atoms.

The "small divalent metal ion" pyrophosphates studied to date include Mn^{++} , Cu^{++} , Mg^{++} and Zn^{++} . Each of these, with the exception of $\text{Mn}_2\text{P}_2\text{O}_7$, shows a phase transition. The high temperature β -forms, including $\text{Mn}_2\text{P}_2\text{O}_7$, are all isostructural, and belong to the space group $C 2/m$. The space group ambiguities between $C m$, $C 2$ and $C 2/m$ have been resolved in the case of $\beta\text{-Zn}_2\text{P}_2\text{O}_7$ (Calvo 1965b) and $\beta\text{-Mg}_2\text{P}_2\text{O}_7$ (Calvo 1965a) by electron spin resonance. In these experiments, the compounds are doped with Mn^{++} ions. The cations, if the space group is $C 2/m$, lie on crystallographic twofold axes, and are related by the C centering operation and by the mirror plane. The Mn^{++} ions is assumed to occupy such sites and as the magnetic axis of Mn^{++} is invariant except for a change in sign to both these symmetry operations, only one e.s.r. active site should be seen. This analysis agreed with observations confirming the high symmetry space group $C 2/m$ to be the correct one. For the $C 2$ and $C m$ cases, there

would be two sites, but in the latter cases these would be symmetry related. In both these compounds, the central oxygens have non-positive definite anisotropic temperature factors, indicating that this atom cannot be represented by an ellipsoid. The space group of $\text{Mn}_2\text{P}_2\text{O}_7$ could be resolved by anomalous dispersion of Mn^{++} to $\text{CoK}\alpha$ radiation, since for the noncentric space group, Friedel's law would be violated.

The low temperature α -forms of these "small divalent metal ion" pyrophosphates are of lower symmetry than the high temperature β -forms. In each case the structural change from the high to low temperature phases are accompanied by the replacement of the mirror plane by a \underline{c} -glide plane, with the \underline{c} -axis doubled. The \underline{a} -axis is unchanged, doubled and tripled in the α -phases of Cu, Mg and Zn salts respectively (Calvo and Robertson, 1966), leading to the doubling, quadrupling and sextupling of the unit cell volume as compared to their β -phases. The anions have a bent P-O-P angle in these low temperature forms. The cell parameters and space groups of both the α -and β -forms are shown in Table I-2.

The phase equilibrium of $\text{Zn}_2\text{P}_2\text{O}_7$ - $\text{Cd}_2\text{P}_2\text{O}_7$ system and that of CdO - P_2O_5 have been studied by Brown and Hummel (1964). Only one form of $\text{Cd}_2\text{P}_2\text{O}_7$ exists, as is shown by the phase diagram for the $\text{Zn}_2\text{P}_2\text{O}_7$ - $\text{Cd}_2\text{P}_2\text{O}_7$ system in Fig. I-1. $\text{Cd}_2\text{P}_2\text{O}_7$ has been reported by the same authors to show red luminescence at $6190 \overset{\circ}{\text{A}}$ when activated by 1.0 mole % divalent manganese and

heat treated for 48 hours at 850°C.

Further, both the manganese activated and unactivated cadmium pyrophosphate phosphors have been studied for their luminescent properties by Ropp (1962). Both were found to have the same fundamental absorption band, the same response to 2537 Å irradiation with emission peak at 6180 Å, although the activated one showed an enhancement of about a hundred times than that of the unactivated one. Also the characteristic long decay of Mn^{++} emission was observed in $Cd_2P_2O_7:Mn$, indicating the energy transition was the same as that of the Mn^{++} . If we can thus assume that the Mn^{++} is in a cationic site, the generally accepted criterion that a yellow to red emission is indicative of Mn^{++} in an octahedral site and green emission in tetrahedral site suggests that Cd^{++} are octahedrally co-ordinated (Linwood and Weyl, 1942).

The pyrophosphates having the thortveitite structure may be thought of as a derivative of $PbSb_2O_6$ structure (Magneli, 1941). In this structure, there are two hexagonally closed packed layers of oxygen, with the antimony atoms distributed in octahedral sites above an empty site. The ions are then placed between the vacant octahedral sites of the neighboring antimony layers. This bonding is shown in Fig. 236, Wells (1962) and is reproduced in Fig. I-2. In the pyrophosphates having the thortveitite structure, the P-O-P group replaces the Pb ion, causing an elongation in the P-P direction

and hence destroying the original hexagonal symmetry. Also oxygen atoms bonded to neighboring cations in the b-axis direction are separated by an edge of the PO_4 tetrahedron. Thus as the size of the cation increases, these oxygen atoms separate, straining the edge of the PO_4 tetrahedron. This may explain why $Cd_2P_2O_7$ does not crystallize in the $C 2/m$ space group. However, if the size of the anion is increased, the size of cations tolerable in the thortveitite structure may also be increased. This prompted us to investigate the structure of $Cd_2V_2O_7$. Since the only pyrovanadates for which single crystal data have been reported are those of ZrV_2O_7 (Peyronel, 1942) and $Pb_2V_2O_7$ (Bariand et al. 1963) and these have been studied only by powder diffractometry, the solution of the structure of Cadmium pyrovanadate would help characterize the pyrovanadate ion and at the same time provide a basis for an extension of Cruickshank's theory (1961) to the role of 3d orbitals on the bonding of vanadium to oxygen atoms.

TABLE I - 1
 LATTICE PARAMETERS OF $M_2X_2O_7$ COMPOUNDS
 WITH THE THORTVEITITE STRUCTURE

Compound	Radius of X^{+n} ion	$a(\overset{\circ}{\text{A}})$	$b(\overset{\circ}{\text{A}})$	$c(\overset{\circ}{\text{A}})$	$\beta(\overset{\circ}{})$	$d_{001}(\overset{\circ}{\text{A}})$
$Mn_2P_2O_7$ (a)	0.34 $\overset{\circ}{\text{A}}$	6.63	8.58	4.54	102.7	4.43
- $Cu_2P_2O_7$ (b)		6.896	8.11	4.55	109.4	4.29
- $Mg_2P_2O_7$ (c)		6.494	8.28	4.522	103.8	4.37
- $Zn_2P_2O_7$ (d)		6.61	8.29	4.51	105.4	4.36
$Sc_2Si_2O_7$ (e)	0.41 $\overset{\circ}{\text{A}}$	6.542	8.519	4.669	102.5	4.56
$Mg_2As_2O_7$ (f)	0.47 $\overset{\circ}{\text{A}}$	6.584	8.509	4.476	103.9	4.62
$Zn_2As_2O_7$ (g)		6.66	8.36	4.75	104	4.61
$Cd_2V_2O_7$ (h)	0.5 $\overset{\circ}{\text{A}}$	7.088	9.091	4.963	103.3	4.83

(a) K. Lukaszweicz, R. Smajkiewicz, Roczniki Chemii 35,761(1961)

(b) B. E. Robertson, Master's Thesis, McMaster University(1965)

(c) C. Calvo, Can. J. Chem.43, 1139(1965)

(d) C. Calvo, Can. J. Chem.43, 1147(1965)

(e) D. W. J. Cruickshank, R. Lynton, G. A. Barclay, Acta Cryst.
15, 419(1962).

(f) K. Lukaszewicz, Bull. De L'academic Polonaise Des Science
XI, 7, 361(1963).

(g) C. Calvo, private communication.

(h) Present work.

TABLE I - 2

Lattice Parameters and Space Groups
of Small Divalent Metal ion Pyrophosphates

<u>Compound</u>	<u>a(Å)</u>	<u>b(Å)</u>	<u>c(Å)</u>	<u>β(°)</u>	<u>Z</u>	<u>Space Group</u>	<u>Stability Range</u>
-Mg ₂ P ₂ O ₇	12.98	8.28	9.04	103.8	16	B2 ₁ /c	below 68°C
-Mg ₂ P ₂ O ₇	6.494	8.28	4.522	103.8	4	C2/m	above 68°C
-Cu ₂ P ₂ O ₇	6.877	8.113	9.162	109.6	8	C2/c	below 70°C
-Cu ₂ P ₂ O ₇	6.827	8.113	4.567	108.9	4	C2/m	above 70°C
-Zn ₂ P ₂ O ₇	19.83	8.29	9.02	105.4	24	Ic	below 132°C
-Zn ₂ P ₂ O ₇	6.61	8.29	4.51	105.4	4	?	132-155°C
-Zn ₂ P ₂ O ₇	6.61	8.29	4.51	105.4	4	C2/m	above 155°C
Mn ₂ P ₂ O ₇	6.63	8.58	4.54	102.7	4	C2/m	at least to -60°C

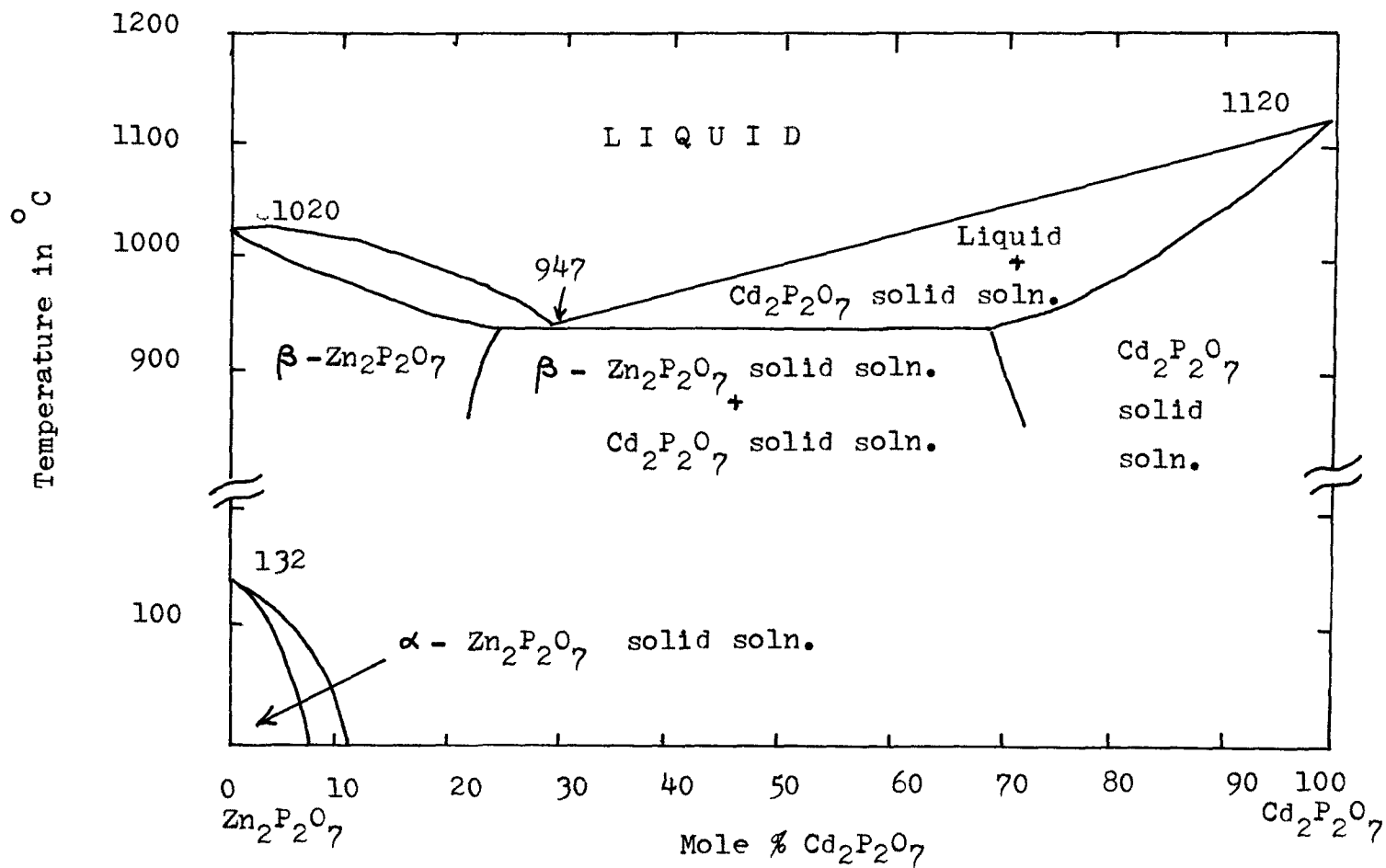


FIG.I - 1: Phase Equilibrium Diagram for the $\text{Cd}_2\text{P}_2\text{O}_7$ - $\text{Zn}_2\text{P}_2\text{O}_7$ System

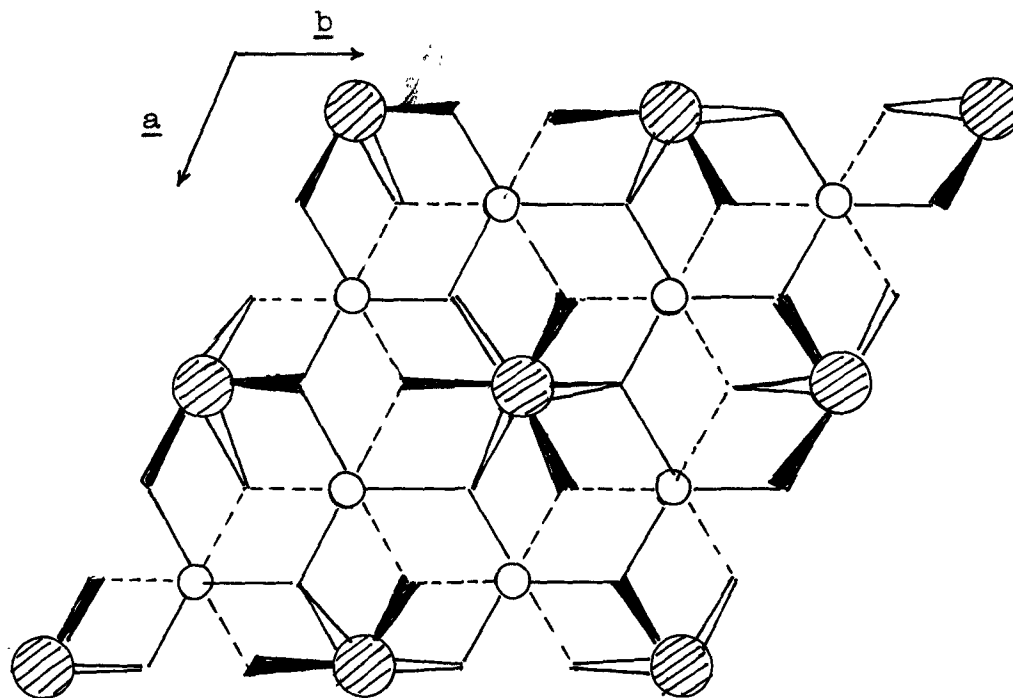


FIG. I - 2: STRUCTURE OF PbSb_2O_6

L E G E N D



Oxygens are at intersections of
co-ordinate sites of metal ions

CHAPTER II: CADMIUM PYROPHOSPHATE

Crystals of $\text{Cd}_2\text{P}_2\text{O}_7$ were prepared by heating stoichiometric amounts of CdCO_3 and $(\text{NH}_4)_2\text{HPO}_4$ until ammonia and carbon-dioxide ceased to evolve. The temperature was then raised to beyond 1120°C , the mixture melted, slowly cooled across the melting point and then quenched to room temperature. The crystals obtained were clear, colourless parallelepipeds.

Accurate parameters were obtained by calibration of the film with reflections from a TiO_2 crystal. The lattice parameters of this tetragonal crystal were taken to be $\underline{a} = 4.5929(5) \text{ \AA}$ and $\underline{c} = 2.9591(5) \text{ \AA}$ (Bauer, 1956). Precession photographs containing the \underline{a}^* and $\underline{a}^* + \underline{c}^*$ axes of TiO_2 were superimposed on films previously exposed to the $(hk0)$ and $(0k\ell)$ type reflections of $\text{Cd}_2\text{P}_2\text{O}_7$ with Zr filtered $\text{MoK}\alpha$ radiation. Calibration curves containing calculated and experimentally measured distances between the TiO_2 spots were made. The corrected distances between reflections arising from $\text{Cd}_2\text{P}_2\text{O}_7$ were then obtained. The accurate parameters of the cadmium salt were $\underline{a} = 6.672(8) \text{ \AA}$, $\underline{b} = 6.623(8) \text{ \AA}$, $\underline{c} = 6.858(7) \text{ \AA}$, $\alpha = 95.80^\circ(5')$, $\beta = 115.38^\circ(5')$, $\gamma = 82.38^\circ(5')$. The estimated standard deviations are in parenthesis.

The density of $\text{Cd}_2\text{P}_2\text{O}_7$ was measured with a Kimax specific gravity bottle of 10 ml. capacity and fitted with a thermometer precise to $\pm 1^\circ\text{C}$. All the available compound was used in the determination, and the trapped air evacuated. The density of the distilled water used was obtained from Handbook of Chemistry and Physics, and measurement gave a density of 4.90 gm. per ml. The calculated density based on two molecules per unit cell was 5.04 gm. per ml.

No symmetry elements were seen in the photographs taken about various axes of the crystal, therefore it must have triclinic symmetry with the space group either $P 1$ or $P \bar{1}$. However, Patterson syntheses using $(hk0)$ and $(0kl)$ data showed the double Cd-Cd peaks characteristic of $P \bar{1}$. This was confirmed using intensity statistics (Howells, Phillips and Rogers, 1949). They showed that the fraction, $N(z)$, of reflexions whose intensities are less or equal to a fraction z of the local average, is given, for a centrosymmetrical crystal, by the relation

$$N(z) = \text{erf} (1/2 z)^{\frac{1}{2}}$$

where erf is the error function. The data from $(hk0)$ zone precession photograph was used in such calculations, limiting reflections to those with $\sin\theta = 0.2$ to 0.6 . These are shown in Table II-1, and the plotted graph of $N(z)$ versus z is shown in Fig II-1, and shows the centrosymmetric behavior. The space group was thus established to be $P \bar{1}$.

Intensity photographs of $(h0l)$ and $(0kl)$ type reflections were obtained with the Weissenberg camera, while those of type $(0kl)$, $(h0l)$ and $(\bar{h}kh)$ were recorded with a precession camera. MoK_α radiation with Zr filter was used throughout. The photographs obtained were with multiple exposure technique and the crystal for the $(h0l)$ type Weissenberg photographs had dimensions $(1.1 \times 1.5 \times 2.2) \text{ mm}^3$. That for the $(h0l)$ precession photograph was of $(1.5 \times 3 \times 7) \text{ mm}^3$.

Two intensity wedges were prepared, one with the Weissenberg camera and the other with the precession camera for use as a standard for the comparison of the intensity of the reflections. For the one taken with Weissenberg camera, a strong reflection was isolated by a screen, exposures were then made with a large oscillation angle comparable to that of a Weissenberg photograph so that more spots may pass through the reflecting sphere and for duration of 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 16, 18, 21, 24, 27, 30, 36, 42, 50, 64, 83, and 128 min. After each exposure, the camera was shifted some 5 mm. to prevent superimposing of spots the photograph. The choice of exposure time being guided by experience, with emphasis on obtaining calibration points near the moderate intensity range. For the wedge prepared with precession camera the photograph was taken as usual, but with the camera shifted upwards by about 5 mm. after each exposure.

The measured intensities corrected for Lorentz-Polarization effects were then used to prepare Patterson synthesis. In general, for a three-dimensional synthesis, the Patterson function $P(u, v, w)$ is defined as

$$P(u, v, w) = V \iiint_{\text{cell}} \rho(x, y, z) \rho(x+u, y+v, z+w) dx dy dz$$

where (x, y, z) is the electron density at x, y, z . $P(u, v, w)$ will have peaks at the ends of vectors between atoms.

The magnitude of these peaks will correspond to the product of the electron density of the atoms giving rise to them.

At $\underline{R} = u\underline{a} + v\underline{b} + w\underline{c}$, we shall have a peak if the vector difference between the atoms A and B, i.e. $\underline{r}_A - \underline{r}_B$ is \underline{R} .

The co-ordinates of this peak, coupled with that of the peak corresponding to the vector $\underline{r}_B - (-\underline{r}_A)$, if the structure is centrosymmetric, enables us to locate atomic co-ordinates of atoms giving rise to the Patterson function. The Patterson function when expressed in terms of structure factors takes on a simpler form which involves only the measure intensity.

That is

$$P(u, v, w) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l}^{\infty} |F(hkl)|^2 \exp 2\pi i (hu + kv + lw)$$

For structures that obey Friedel's Law, this simplifies to

$$P(u, v, w) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l}^{\infty} |F(hkl)|^2 \cos 2\pi(hu + kv + lw)$$

In practice, only the peaks due to interactions with the heaviest atoms can be resolved. For an unit cell of N

atoms with $P\bar{1}$ symmetry, there would be N^2 peaks, N coincide with the origin and $\frac{1}{2}N(N - 1)$ peaks of doubled amplitude.

For $Cd_2P_2O_7$, a double peak Cd-Cd should correspond to 42% of the peak height at the origin, while those corresponding to thru center Cd-Cd vectors, that is single peaks, and Cd-P peaks should correspond to 21% and 13% of the origin peak respectively. The rest of the Patterson function is made up of Cd-O, P-P, P-O, and O-O interactions. The peaks corresponding to the $\underline{r}_{Cd_1} - \underline{r}_{Cd_j}$ interactions were found at $x = 0.40, y = 0.46$, and $x = 0.15, y = 0.82$, and $y = 0.46, z = 0.90$, and $y = 0.82$, and $z = 0.42$ (see Fig II-2). These gave the co-ordinates (0.28, -0.14, 0.34) for Cd_1 and (0.12, -0.34, 0.25) for Cd_2 respectively.

These co-ordinates were then used to calculate structure factors for the 318(Ok ℓ) and 378(h0 ℓ) reflections. The preliminary scale factor K , and temperature factor B defined by

$$KF_o = {}^oF_c \exp \left(\frac{-B \sin^2 \theta}{\lambda^2} \right)$$

were determined for these data. Here F_o is the observed structure factor obtained from the intensities after Lorentz-Polarization correction, and oF_c was the calculated structure factor determined by

$${}^oF_c(hkl) = 2 \sum_{i=1}^N f_i(hkl) \cos 2\pi(hx_i + ky_i + lz_i)$$

The atomic co-ordinates are x_i, y_i, z_i and the scattering factors for the i th species is f_i . These scattering factors

are tabulated in the International Tables. The scattering curve for cadmium was corrected for dispersion effects, using the relation $|f| = f_0 + \Delta f' + \frac{1}{2} \frac{\Delta f''^2}{f_0 + \Delta f'}$, where $\Delta f'$ and $\Delta f''$ were real and imaginary dispersion correction coefficients. The dispersion correction coefficients were obtained from International Tables (vol. III page 216).

These trial co-ordinates gave an overall temperature factor, B, of -0.18 \AA^2 and an unweighted overall reliability factor R_1 of 0.48 where R_1 , also called the unweighted R factor, is defined as

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

with the summation over all the measured reflections.

Refinements were then made with individual isotropic temperature and scale constant variations together with the positional parameters. R_1 went down to 0.35.

Electron density map was then prepared for the (x, z) and (y, z) projections, which readily showed the positions of the phosphorus atoms. Refinement was now carried out for the x, z, co-ordinates of the Cd and P with isotropic temperature factors of the atoms. The 117(hk0) type reflections measured from precession photographs were added. The R_1 value dropped to 0.32 but the temperature factor of Cd_2 became non-positive definite. All the positional parameter and the isotropic temperature factors were then varied, and another two electron density maps based upon the calculated structure factors, were

prepared. Oxygen atoms O_1 and O_2 were located, and their position added to the structure factor calculations. Three cycles of refinement gave non-positive isotropic temperature factors for both cadmium atoms and O_1 . 77 low angle reflections of $(h0l)$ type from Weissenberg photograph were then used for refinement, as these were in good agreement with the calculated structure factors. This gave Cd_2 , P_1 , and O_1 negative B's but R_1 dropped to 0.21. Diadic methods were then used to generate approximate positions of O_3 and O_4 , based on an assumed P-O(b) bond length of 1.6 Å the other P-O bond lengths of 1.5 Å and with P(2)- O_2 as the three fold rotation axis acting on P(2)- O_1 . These positions were used as a guide in locating the corresponding oxygen atoms in the electron density maps which yielded the position of O_5 also. After two cycles, the number of $(h0l)$ type reflections was increased to 237. These were all Weissenberg data that had now been rechecked. R_1 dropped to 0.20 and all B values were positive definite.

O_6 and O_7 were located from electron density maps with the positions of P(1), O_2 and O_5 as a guide. This was done on the assumptions of tetrahedral PO_4 group and P-O bond length assured before. Meanwhile, the Lorentz-Polarization corrected precession data for $(0kl)$, $(\bar{h}kh)$ were then added. All reflections were corrected and those of common reflections averaged. The isotropic temperature factors of the cadmium

atoms were then converted to anisotropic temperature factors by

$$\frac{B \sin^2 \theta}{\lambda^2} = \underline{H} \cdot \underline{B} \cdot \underline{H}.$$

where \underline{B} is the anisotropic temperature dyadic with β_{ij} as the components, and \underline{H} is the reciprocal lattice vector ($h\underline{a}^* + k\underline{b}^* + l\underline{c}^*$). The isotropic temperature factors of the oxygen atoms were then varied, together with the anisotropic temperature factors of cadmium atoms, and isotropic temperature factors of phosphorus atoms. $w = \frac{1}{\sigma^2}$ weights were used, where $\sigma = 0.1 F_0$ if $F_0 > 30$, and $\sigma = 0.3 F_0$ for $F_0 < 30$.

Reflections that were unobserved but with higher values than F_0 were given zero weight. R_1 for all reflections was 0.136 $R_2 = 0.185$, where R_2 , the weighted B factor is defined as

$$R_2 = \left\{ \frac{\sum w^2 (|F_o| - |F_c|)^2}{\sum w^2 |F_o|^2} \right\}^{\frac{1}{2}}$$

The atomic parameters of the atoms are shown in Table II-2, their thermal parameters in Table II-3 and the $540 F_0$ and F_0 in Table II-4.

The geometry of the anions are shown in Table II-5 and Fig II-3, that of the cations in Table II-6 and Fig II-4. All bond lengths are corrected for thermal effects (Busing and Levy, 1964). Here, the mean separation between any two atoms in consideration is calculated first. That component of the vector displacement between the two atoms that is perpendicular to the line of mean separation is then calculated in terms

of the thermal parameters. Using these, two mean interatomic separations were calculated. One, called the 'riding mode', assumes that this separation is independent of one of the atoms. The second assumes the two atoms have no interaction with one another, and is thus a 'non-correlated mode'. The true mean interatomic separation is then taken as the mean of these modes.

TABLE II - 1

$$I = |F_0|^2 \text{ for } \text{Cd}_2\text{P}_2\text{O}_7$$

from Lp corrected data of (hk0) Precession Photograph

Range of $\sin \theta = 0.20$ to 0.60

for application of Intensity Statistics *

h \ k	0	1	2	3	4	5	6	7
$\bar{7}$	310	2,756						
$\bar{6}$	1,743	4,146	8	1,352				
$\bar{5}$	1,475	7	359	1,567	294	381		
$\bar{4}$	260	275	406	7,880	185	485	8	
$\bar{3}$	4	581	3,292	99	2,051	376	1,760	
$\bar{2}$		4,869	2,932	158	692	1,546	3,372	
$\bar{1}$				118	198	1,396	1,890	385
0				995	5,152	142	2,561	8
1				3,314	6	3,054	8	8
2			2,159	2,169	5,529	4	838	514
3		359	2,688	2,201	157	7	160	1,521
4		4,520	1,465	5,107	172	281	1,359	
5		7	1,481	119	284	245	2,870	
6		6,962	343	199	151	4,083		
7		311	412					

* Howells, Philips and Rogers, Research 2, 338, 1949

$N(z)$ in percentages for $hk0$ reflections of $Cd_2P_2O_7$

$$I(z) = I \times (z/10)$$

$$N(z) = (\text{no. of reflections } I(z)) / (\text{no. of reflections in range})$$

z	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$I(z)$	153	307	460	614	767	920	1,074	1,227	1,381	1,534
$N(z)$	17.5	36.0	49.0	54.2	54.7	54.7	55.4	55.4	58.1	64.1

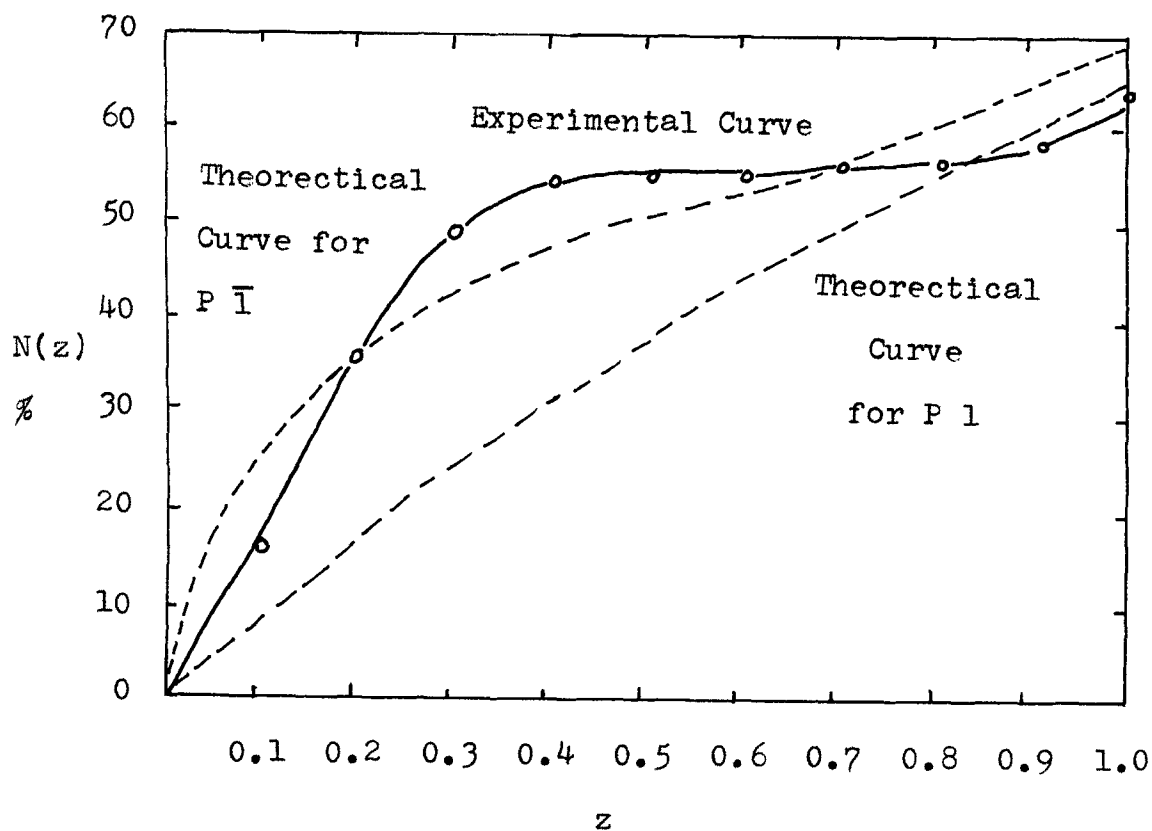


FIG. II- 1

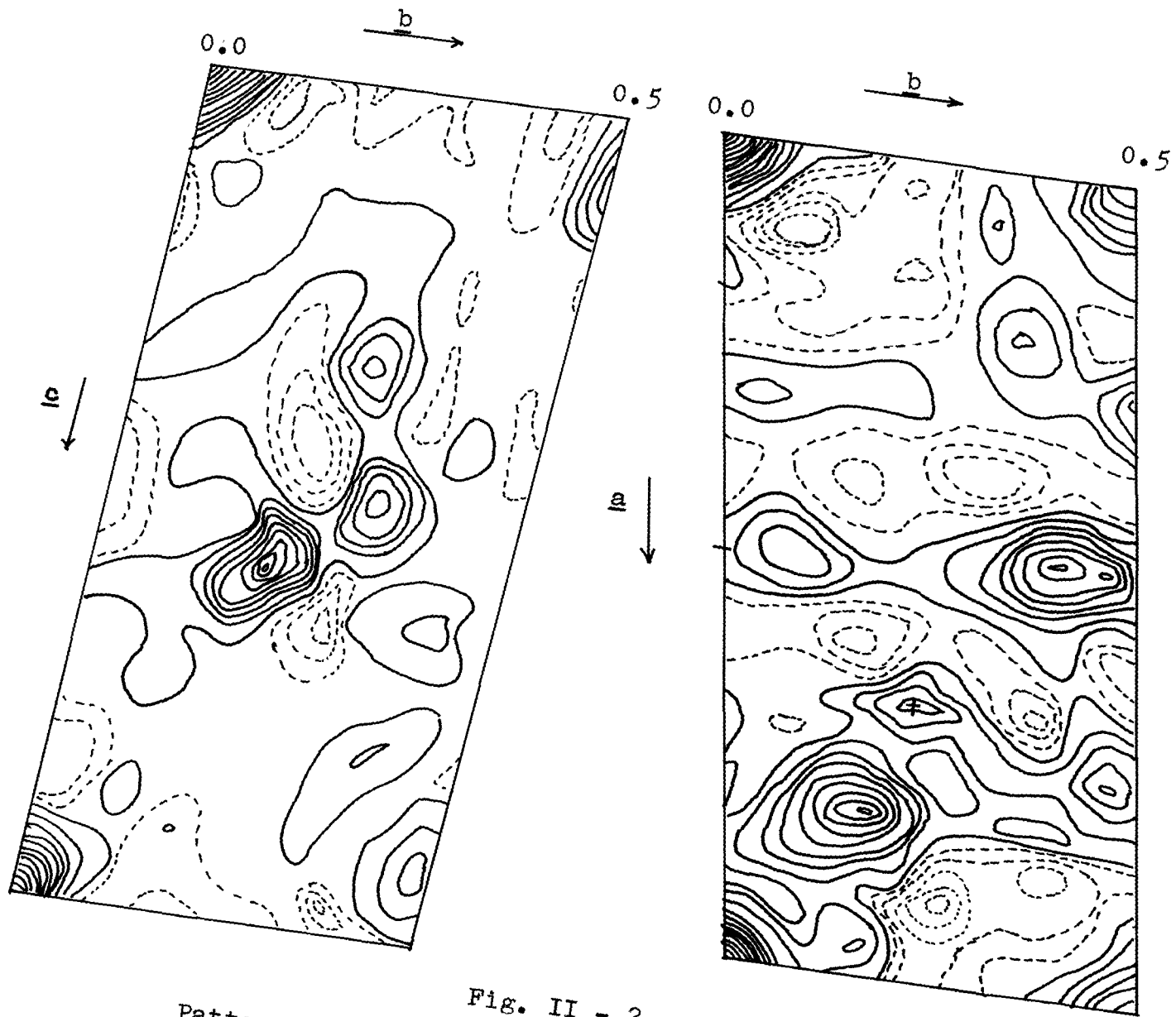


Fig. II - 2
 Patterson Function of $\text{Cd}_2\text{P}_2\text{O}_7$: (hk0) and (0kl) projections

TABLE II - 2

Atomic parameters for $\text{Cd}_2\text{P}_2\text{O}_7$ (e.s.d.'s in parenthesis)

<u>Atom</u>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>
Cd(1)	0.2759 (0.0004)	0.3605 (0.0005)	0.3380 (0.0005)
Cd(2)	0.1168 (0.0004)	0.1604 (0.0004)	0.7475 (0.0004)
P(1)	0.3592 (0.0012)	0.8675 (0.0015)	0.1913 (0.0015)
P(2)	0.2362 (0.0013)	0.6591 (0.0015)	0.7539 (0.0014)
O(1)	0.0690 (0.0048)	0.8244 (0.0047)	0.6269 (0.0048)
O(2)	0.4131 (0.0046)	0.7385 (0.0045)	0.9899 (0.0045)
O(3)	0.9001 (0.0038)	0.4911 (0.0039)	0.2131 (0.0040)
O(4)	0.6135 (0.0047)	0.4340 (0.0046)	0.3500 (0.0047)
O(5)	0.2479 (0.0044)	1.0862 (0.0046)	0.1049 (0.0046)
O(6)	0.5972 (0.0044)	0.8645 (0.0044)	0.3752 (0.0046)
O(7)	0.2051 (0.0050)	0.7668 (0.0048)	0.2213 (0.0052)

TABLE II - 3

Thermal parameters of $\text{Cd}_2\text{P}_2\text{O}_7$ (e.s.d.'s in parenthesis)

a) Mean Square Atomic Displacements in \AA^2 * for Cadmium Atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd(1)	0.0054 (0.0008)	0.0048 (0.0010)	0.0092 (0.0011)	-0.0036 (0.0011)	0.0037 (0.0011)	-0.0050 (0.0014)
Cd(2) [†]	0.0042 (0.0009)	0.0009 (0.0003)	0.0044 (0.0010)	-0.0039 (0.0011)	0.0033 (0.0009)	-0.0009 (0.0010)

b) Isotropic Temperature Factors

Atom	B	e.s.d.
P(1) [†]	-0.08	0.09
P(2)	0.03	0.10
O(1)	0.49	0.39
O(2)	0.57	0.35
O(3)	0.22	0.31
O(4)	0.52	0.36
O(5)	0.56	0.36
O(6)	0.38	0.34
O(7)	1.21	0.45

* Obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where the β_{ij} 's appear as a temperature effect through esp - $(\beta_{11}h^2 + 2\beta_{12}hk\dots)$

† Non-positive definite

TABLE II - 5

Geometry of pyrophosphate anion in $\text{Cd}_2\text{P}_2\text{O}_7$
(e.s.d.'s in parenthesis)

a) Bond lengths in \AA .

$$\text{P}(1) - \text{O}(2) = 1.70(3) \qquad \text{P}(2) - \text{O}(2) = 1.63(3)$$

$$\text{Average inner P - O} = 1.67(3)$$

$$\text{P}(1) - \text{O}(6) = 1.55(3) \qquad \text{P}(2) - \text{O}(\overline{4}) = 1.50(3)$$

$$\text{P}(1) - \text{O}(5) = 1.59(3) \qquad \text{P}(2) - \text{O}(1) = 1.50(3)$$

$$\text{P}(1) - \text{O}(7) = \underline{1.39(3)} \qquad \text{P}(2) - \text{O}(\overline{3}) = \underline{1.52(3)}$$

$$\text{Average } 1.51(3)$$

$$\text{Average } 1.51(3)$$

$$\text{P}(1) - \text{P}(2) = 2.99(1)$$

b) Edges of PO_4 tetrahedrons in \AA .

$$\text{O}(2) - \text{O}(5) = 2.62(4) \qquad \text{O}(2) - \text{O}(1) = 2.61(4)$$

$$\text{O}(2) - \text{O}(6) = 2.50(4) \qquad \text{O}(2) - \text{O}(\overline{3}) = 2.56(4)$$

$$\text{O}(2) - \text{O}(7) = 2.50(4) \qquad \text{O}(2) - \text{O}(4) = 2.44(4)$$

$$\text{O}(5) - \text{O}(6) = 2.64(4) \qquad \text{O}(1) - \text{O}(\overline{3}) = 2.40(4)$$

$$\text{O}(5) - \text{O}(7) = 2.43(4) \qquad \text{O}(1) - \text{O}(4) = 2.50(4)$$

$$\text{O}(6) - \text{O}(7) = 2.51(4) \qquad \text{O}(\overline{3}) - \text{O}(4) = 2.54(4)$$

$$\text{O}(1) - \text{O}(5) = 3.35(4)$$

$$\text{O}(\overline{3}) - \text{O}(7) = 3.13(4)$$

$$\text{O}(\overline{4}) - \text{O}(6) = 3.63(4)$$

c) Bond angles in degrees.

$$\text{O}(2) - \text{P}(1) - \text{O}(5) = 105.8(1.5)$$

$$\text{O}(2) - \text{P}(1) - \text{O}(6) = 100.6(1.5)$$

$$\text{O}(2) - \text{P}(1) - \text{O}(7) = 107.7(1.8)$$

$$\text{O}(5) - \text{P}(1) - \text{O}(6) = 114.8(1.6)$$

$$\text{O}(5) - \text{P}(1) - \text{O}(7) = 109.1(1.7)$$

$$\text{O}(6) - \text{P}(1) - \text{O}(7) = 117.6(1.8)$$

$$\text{O}(2) - \text{P}(2) - \text{O}(1) = 113.6(1.6)$$

$$\text{O}(2) - \text{P}(2) - \text{O}(\overline{4}) = 102.2(1.6)$$

$$\text{O}(2) - \text{P}(2) - \text{O}(\overline{3}) = 108.5(1.5)$$

$$\text{O}(1) - \text{P}(2) - \text{O}(\overline{4}) = 113.0(1.7)$$

$$\text{O}(1) - \text{P}(2) - \text{O}(\overline{3}) = 105.2(1.5)$$

$$\text{O}(4) - \text{P}(2) - \text{O}(\overline{3}) = 114.4(1.6)$$

$$\text{P}(1) - \text{O}(2) - \text{P}(2) = 128.3(1.8)$$

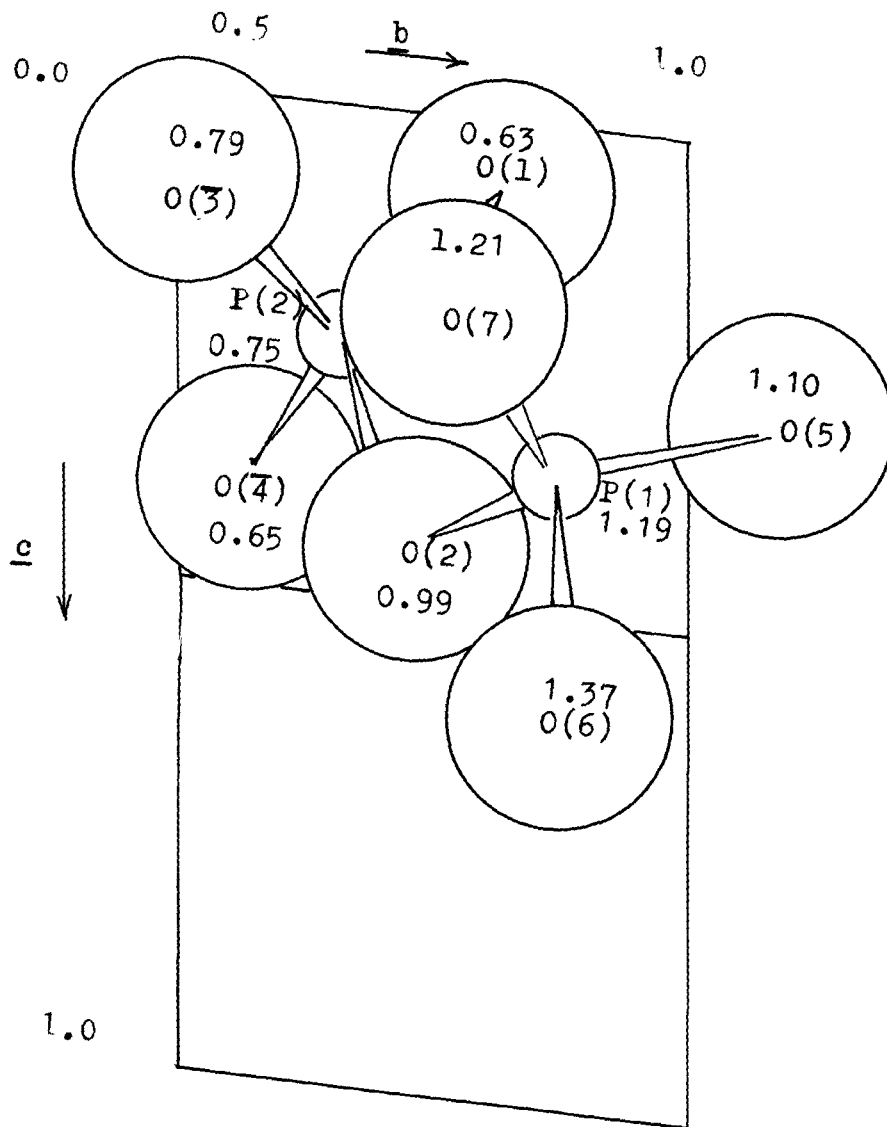


Fig. II - 3
 Geometry of Anion in $\text{Cd}_2\text{P}_2\text{O}_7$

TABLE II - 6

Geometry of Cations in $\text{Cd}_2\text{P}_2\text{O}_7$
(e.s.d.'s in parenthesis)

a) Bond lengths in \AA .

$\text{Cd}(1) - \text{O}(3) = 2.35(2)$	$\text{Cd}(2) - \text{O}(1) = 2.31(3)$
$\text{Cd}(1) - \text{O}(4) = 2.33(3)$	$\text{Cd}(2) - \text{O}(\bar{1}) = 2.33(3)$
$\text{Cd}(1) - \text{O}(\bar{4}) = 2.32(3)$	$\text{Cd}(2) - \text{O}(\bar{3}) = 2.29(2)$
$\text{Cd}(1) - \text{O}(5) = 2.27(3)$	$\text{Cd}(2) - \text{O}(5) = 2.30(3)$
$\text{Cd}(1) - \text{O}(\bar{6}) = 2.37(3)$	$\text{Cd}(2) - \text{O}(\bar{6}) = 2.38(3)$
$\text{Cd}(1) - \text{O}(7) = \underline{2.81(3)}$	$\text{Cd}(2) - \text{O}(\bar{7}) = \underline{2.23(3)}$
Average 2.41(3)	Average 2.31(3)

b) Lengths of edges of CdO_6 octahedrons in \AA .

$\text{O}(3) - \text{O}(\bar{6}) = 3.99(4)$	$\text{O}(\bar{1}) - \text{O}(\bar{6}) = 2.85(4)$
$\text{O}(3) - \text{O}(7) = 2.89(4)$	$\text{O}(\bar{1}) - \text{O}(\bar{7}) = 3.25(4)$
$\text{O}(4) - \text{O}(\bar{6}) = 2.83(4)$	$\text{O}(5) - \text{O}(\bar{6}) = 3.90(4)$
$\text{O}(4) - \text{O}(7) = 3.13(4)$	$\text{O}(5) - \text{O}(\bar{7}) = 2.99(4)$
$\text{O}(\bar{4}) - \text{O}(3) = 3.40(4)$	$\text{O}(1) - \text{O}(\bar{1}) = 2.86(6)$
$\text{O}(\bar{4}) - \text{O}(\bar{6}) = 2.83(4)$	$\text{O}(1) - \text{O}(\bar{6}) = 3.23(4)$
$\text{O}(\bar{4}) - \text{O}(7) = 3.03(4)$	$\text{O}(1) - \text{O}(\bar{7}) = 3.39(4)$
$\text{O}(\bar{4}) - \text{O}(4) = 3.04(6)$	$\text{O}(1) - \text{O}(5) = 3.35(4)$

$$\begin{array}{ll}
 \text{O}(5) - \text{O}(3) = 3.54(4) & \text{O}(\bar{3}) - \text{O}(\bar{1}) = 2.40(4) \\
 \text{O}(5) - \text{O}(\bar{6}) = 3.90(4) & \text{O}(\bar{3}) - \text{O}(\bar{6}) = 3.39(4) \\
 \text{O}(5) - \text{O}(7) = 2.43(4) & \text{O}(\bar{3}) - \text{O}(\bar{7}) = 2.89(4) \\
 \text{O}(5), - \text{O}(4) = 3.36(4) & \text{O}(\bar{3}) - \text{O}(5) = 3.50(4)
 \end{array}$$

c) Bond angles in degrees

$$\text{O}(3) - \text{Cd}(1) - \text{O}(\bar{4}) = 93.9(1.0)$$

$$\text{O}(3) - \text{Cd}(1) - \text{O}(5) = 100.4(1.0)$$

$$\text{O}(4) - \text{Cd}(1) - \text{O}(\bar{4}) = 82.0(1.1)$$

$$\text{O}(4) - \text{Cd}(1) - \text{O}(5) = \underline{93.8(1.0)}$$

$$370.1(1.0)$$

$$\text{O}(3) - \text{Cd}(1) - \text{O}(\bar{6}) = 115.2(0.9)$$

$$\text{O}(3) - \text{Cd}(1) - \text{O}(7) = 67.6(0.9)$$

$$\text{O}(4) - \text{Cd}(1) - \text{O}(\bar{6}) = 74.5(1.0)$$

$$\text{O}(4) - \text{Cd}(1) - \text{O}(7) = \underline{72.0(1.0)}$$

$$329.3(1.0)$$

$$\text{O}(\bar{6}) - \text{Cd}(1) - \text{O}(7) = 146.5(1.0)$$

$$\text{O}(3) - \text{Cd}(1) - \text{O}(4) = 141.0(1.0)$$

$$\text{O}(\bar{4}) - \text{Cd}(1) - \text{O}(5) = 161.7(1.0)$$

$$\text{O}(\bar{1}) - \text{Cd}(2) - \text{O}(\bar{6}) = 74.8(1.0)$$

$$\text{O}(\bar{1}) - \text{Cd}(2) - \text{O}(\bar{7}) = 90.8(1.1)$$

$$o(5) - cd(2) - o(\bar{6}) = 113.1(1.0)$$

$$o(5) - cd(2) - o(\bar{7}) = \frac{82.5(1.1)}{361.2(1.1)}$$

$$o(1) - cd(2) - o(\bar{1}) = 76.1(1.1)$$

$$o(1) - cd(2) - o(5) = 93.2(1.0)$$

$$o(\bar{3}) - cd(2) - o(\bar{1}) = 90.8(1.0)$$

$$o(\bar{3}) - cd(2) - o(5) = \frac{99.2(1.0)}{359.3(1.0)}$$

$$o(1) - cd(2) - o(\bar{3}) = 166.3(1.0)$$

$$o(\bar{3}) - cd(2) - o(\bar{7}) = 79.4(1.0)$$

$$o(\bar{6}) - cd(2) - o(\bar{7}) = 163.8(1.1)$$

33a

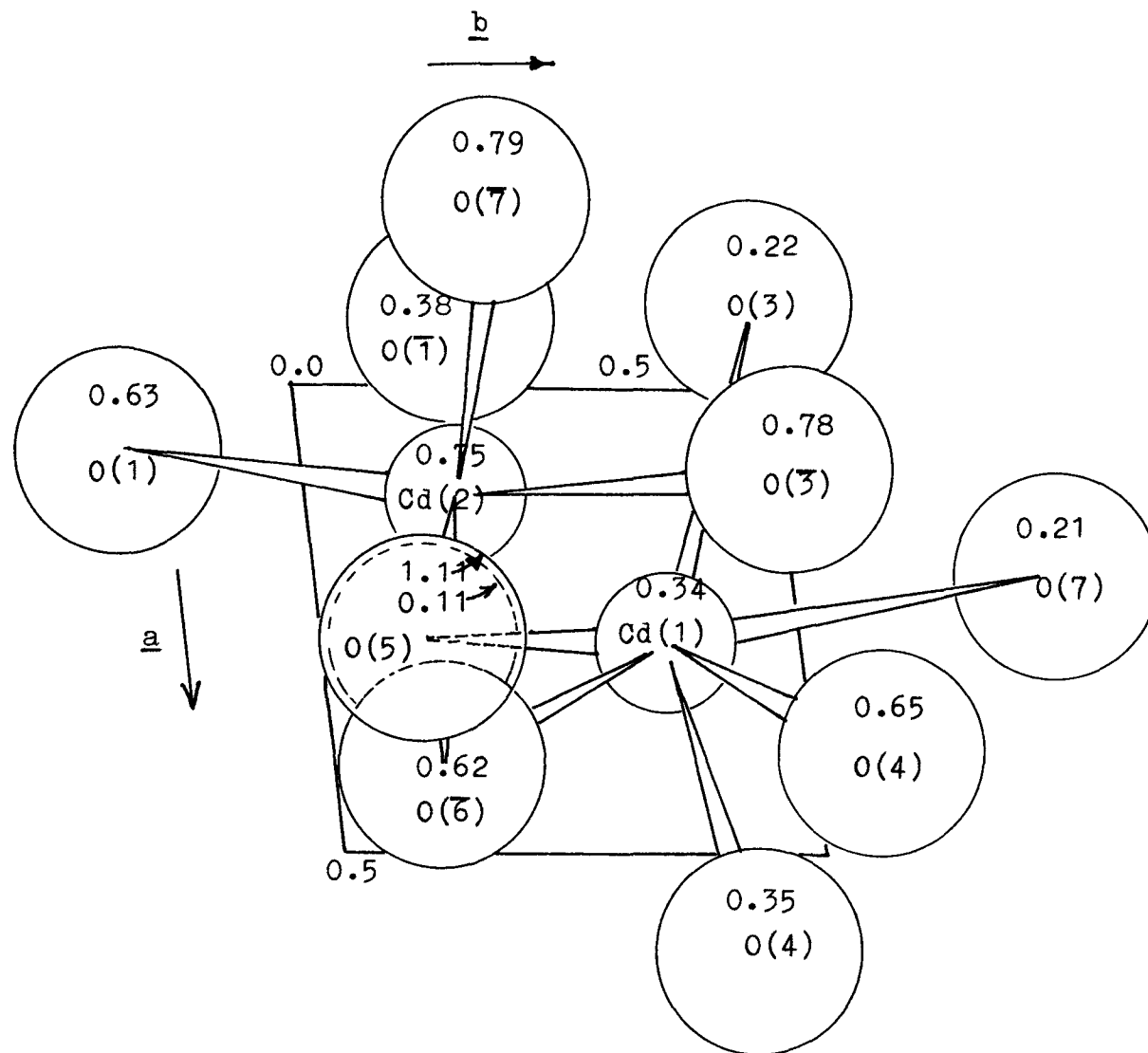


Fig. II - 4

Geometry of Cations in $\text{Cd}_2\text{P}_2\text{O}_7$ (Space Group $P\bar{1}$)

CHAPTER III : CADMIUM PYROVANADATE

Crystals of cadmium pyrovanadate were prepared by gently heating stoichiometric amounts of CdCO_3 and NH_4VO_3 in a small vycor vessel until ammonia and carbon dioxide ceased to evolve, and then raising the temperature of the mix beyond its melting point, about 900°C , and slowly cooling to room temperature. The crystals were yellowish-green in colour.

Accurate parameters were obtained from films calibrated with reflections from a TiO_2 crystal. The method used was similar to that described for $\text{Cd}_2\text{P}_2\text{O}_7$. The parameter values are: $a = 7.088(5) \text{ \AA}$, $b = 9.091(5) \text{ \AA}$, $c = 4.963(5) \text{ \AA}$ and $\beta = 103^\circ 21'(5')$. here the e.s.d.'s are in parenthesis.

There are two molecules per unit cell, as has been found for the other members of this family, although an accurate density could not be obtained. This may have been because the limited amount of crystals prepared had reacted with vycor at the surface of the container.

Intensity photographs of the zeroth, first, and second layer lines of the (100) zone and the zeroth and first layer line of the (010) zone were taken with an integrating precession camera using MoK_α radiation. The crystal was of

dimensions $0.1 \times 0.15 \times 0.20 \text{ cm}^3$. A smaller crystal, about half of the linear dimensions of the former was used to record $(hk0)$ and $(hk1)$ reflections. Three exposures were taken for time intervals differing by a factor of three. Reflections indexed as hkl were found to be systematically absent when $h + k$ was odd. No other extinctions were found. The space group thus belongs to one among Cm , $C2$ and $C2/m$. Attempts to prepare larger crystals doped with Mn^{+2} for esr experiments to resolve the space group ambiguity were unsuccessful⁺. It was then decided to use the anomalous scattering by Cd or V with MoK_{α} and CuK_{α} radiations. The presence of accentricity in the crystal x-rayed under conditions yielding anomalous dispersion could give different intensities for reflections from Friedel equivalent faces. Both Cm and $C2$ space groups are accentric except the $h0$ projection of $C2$ which is centric. The $C2/m$ space group is centric and thus could be distinguished by this experiment.

The effect of anomalous dispersion can be easily treated. Anomalous scattering can occur when the K absorption edge of a constituent of the scattering material is on the

⁺ Recently C. Calvo and C. V. Stager have looked at Mn^{+2} doped $Cd_2V_2O_7$ and the space group appears to be $C2/m$. (Private communication, C. Calvo).

the long wavelength side of the radiation used. Such a phenomenon is accompanied by an anomalous phase shift, and the resultant wave can be expressed in terms of the normal wave, f_0 , with a complex correction term f' and if'' , i.e.

$$f = f_0 + f' + if''$$

Because of the factor i in f'' , f'' is always $\pi/2$ in advance of the phase of f' . Now for an asymmetric system

$$F_{\underline{H}} = \sum_j f_j \exp(2\pi i \underline{H} \cdot \underline{r}_j)$$

$$F_{\overline{H}} = \sum_j f_j \exp(-2\pi i \underline{H} \cdot \underline{r}_j)$$

If an asymmetric crystal contains an atom with anomalous scattering effect, we could represent the structure factor F as a sum of the structure factor due to that atom A_F and that of the remaining normal atoms R_F , i.e.

$$F = A_F + R_F = A_{F'} + A_{F''} + R_F$$

where $A_{F'}$ is the real component and $A_{F''}$ the imaginary one. And as shown before, $A_{F''_{\underline{H}}}$ and $A_{F'_{\overline{H}}}$ are equal in magnitude but opposite in sign. This would give rise to different $F_{\underline{H}}$ and $F_{\overline{H}}$ unless the resultant of R_F and $A_{F'}$ is perpendicular to $A_{F''}$. For centric systems, because (hkl) and $(\overline{h}\overline{k}\overline{l})$ would be equivalent by symmetry, the structure factors will have the same phase of either zero or π , and reflections

from (hkl) and $(\bar{h}\bar{k}\bar{l})$ would therefore be indistinguishable even though anomalous scattering occurs.

For $Cd_2V_2O_7$, the K absorption edge of vanadium is at 2.269 \AA , longer than the wavelengths of CoK_α (1.793 \AA), CuK_α (1.542 \AA) and MoK_α (0.7107 \AA). However, for MoK_α , the value f'' for vanadium is around 0.7 (International Tables for X-ray Crystallography, Vol. III, p. 213), and so even if anomalous scattering occurs, it would not be easily discernable. For CuK_α , and CoK_α , the situation is different, f'' has a fairly high value of 2.3 for copper and 2.56 for cobalt (James, W. R., p. 608), even for fairly high angles. Also since f'' values is fairly independent of $(\sin \theta)/\lambda$ values compared with the rapid decrease of f_0 with increase in $\frac{\sin \theta}{\lambda}$, we would therefore expect a difference in intensity between reflections (hkl) and $(\bar{h}\bar{k}\bar{l})$ with accentric space groups, especially for those at high angles. However, no systematic difference between reflections (hkl) and $(\bar{h}\bar{k}\bar{l})$ was detected. The crystal is therefore symmetric and belong to the $C 2/m$ space group. Since all the small divalent metal ion pyrophosphorus belong to the $C2/m$ group, one would expect that $Cd_2V_2O_7$ would also.

The intensity of the $nk\bar{l}$, and $kn\bar{l}$ ($n = 0, 1, 2,$) $(hk0)$ and (hkl) reflections were measured with a Leeds-Northrup No. 6700P-1 type G micrphotometer. The estimated precision obtained was 5%.

The reflections were corrected for Lorentz-Polarization effects. Since $\text{Cd}_2\text{V}_2\text{O}_7$ is isostructural with $\beta\text{-Zn}_2\text{P}_2\text{O}_7$ (Calvo, 1965b), the positional parameters of this compound were used for the trial structure. These were put into a least-square program with 108 ($0kl$) and 114 ($2kl$) reflections. The unobserved reflections were taken as half that of the minimum observed value. The scattering curves for cadmium and vanadium were corrected for dispersion effects for $\text{MoK}\alpha$ radiation. In $\beta\text{-Zn}_2\text{P}_2\text{O}_7$, the cations lie on the crystallographic twofold axis, phosphorus and O_{II} lie on mirror planes and O_{I} at a centre of inversion. Both the positional parameters not fixed by symmetry, and the individual isotropic temperature factors together with the scale constants were varied using unit weights. The overall R_1 factor obtained was 0.205. The ($h0l$), ($h1l$), and ($1kl$) reflections were scaled and the common reflections averaged. These were then refined for another cycle with the ($0kl$) and ($2kl$) reflections. The R_1 value dropped down to 0.112. The ($hk0$) and (hkl) data were then added, and refined with isotropic temperature factors converted into anisotropic ones. Further anisotropic refinements yielded non-positive definite values for the temperature factor of O_{II} . The weighted R factor for all reflections at this stage was 0.13.

The refinement was then carried out allowing the cadmium and vanadium ions to have anisotropic temperature

factors, but with isotropic temperature factors for the oxygen atoms. R_2 changed from 0.128 to 0.126, and R_1 , for observed reflections, from 0.073 to 0.071 after two cycle. Little variations in the positional parameters were noted and all temperature factors were positive definite.

Absorption corrections were then made on an idealized spherical crystal taken to have radius $r = 0.09$ mm.. The linear absorption coefficient $\mu = 115 \text{ cm.}^{-1}$ for $\text{Cd}_2\text{V}_2\text{O}_7$. For MoK_α radiation the value of r was obtained by assuming the spherical crystal to have the same volume as the crystal used. In one further cycle of refinement, the overall R_1 value was 0.067, and R_2 0.098. However, O_I and O_{II} when refined with anisotropic temperature factors have non-positive temperature factors.

These were converted back to isotropic temperature factors, using the values of the last isotropic refinement for the oxygen atoms. Weights were changed from unity to $1/\sigma^2$, where $\sigma = 0.1F_0$ for $F_0 > 30$ and $\sigma = 0.3F_0$ for $F_0 < 30$. Unobserved reflections with values greater than the calculated values were given zero weight. The R_1 value for the observed reflections was 0.073 and for the unobserved reflections was 0.076. The corresponding R_2 values were 0.107 and 0.120 respectively. All temperature factors were now positive definite.

The positional and thermal parameters of the atoms are shown in Table III-1 and Table III-2. The 421 unique F_0

and F_c are collected in Table III-3. The geometry of the cation and anion are shown in Fig. III-1. The bond lengths and angles are shown in Table III-4 for the anion and in Table III-5 for the cations. All bond lengths are corrected for thermal motions of the atoms in Chapter II.

TABLE III - 1

Atomic parameters for $\text{Cd}_2\text{V}_2\text{O}_7$ (e.s.d.'s in parenthesis)

<u>Atom</u>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>	<u>Point Symmetry</u>
Cd	0.0000	0.3053 (0.0001)	0.5000	2
V	0.2263 (0.0005)	0.0000	0.9089 (0.0007)	m
O _I	0.0000	0.0000	0.0000	$\bar{1}$
O _{II}	0.3863 (0.0018)	0.0000	0.2098 (0.0029)	m
O _{III}	0.2380 (0.0013)	0.1570 (0.0010)	0.7198 (0.0019)	1

TABLE III - 2

Thermal parameters of $\text{Cd}_2\text{V}_2\text{O}_7$ (e.s.d.'s in parenthesis)(a) Mean Square Atomic Displacements in \AA^2 for Cd and V ($\times 10^{-4}$)

<u>Atom</u>	<u>U₁₁</u>	<u>U₂₂</u>	<u>U₃₃</u>	<u>U₁₂</u>	<u>U₁₃</u>	<u>U₂₃</u>
Cd	9.2 (0.6)	9.1 (0.5)	9.7 (0.7)	0	1.1 (0.5)	0
V	9.4 (1.2)	10.5 (2.1)	5.4 (1.3)	0	-0.4 (1.3)	0

(b) Isotropic Temperature Factors.

<u>Atom</u>	<u>B</u>	<u>e.s.d.</u>
O _I	0.2	0.2
O _{II}	0.3	0.2
O _{III}	0.5	0.1

TABLE III-3

H	K	L	F(θ)	F(C)	H	K	L	F(θ)	F(C)	H	K	L	F(θ)	F(C)	H	K	L	F(θ)	F(C)	H	K	L	F(θ)	F(C)			
0	0	0	19.9	-12.6	-8	0	0	47.5	50.2	-3	3	3	32.6	32.4	1	1	1	1	1	1	1	1	1	39.3	46.7		
0	0	0	92.6	-104.3	-8	0	0	36.6	-38.9	-3	3	3	13.5	-0.5	1	1	1	1	1	1	1	1	3	3	3	33.9	33.3
0	0	0	41.4	-35.4	-8	0	0	16.4	-16.6	-3	3	3	51.1	53.8	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	38.1	-35.7	-8	0	0	36.4	-35.7	-3	3	3	17.0	-13.7	1	1	1	1	1	1	1	1	6	6	6	33.9	33.3
0	0	0	46.8	-47.2	-8	0	0	22.2	22.2	-3	3	3	12.4	-4.3	1	1	1	1	1	1	1	1	4	4	4	33.9	33.3
0	0	0	18.3	21.5	-8	0	0	57.7	-64.6	-3	3	3	17.0	6.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	30.0	-34.6	-8	0	0	61.1	-58.9	-3	3	3	36.5	32.6	1	1	1	1	1	1	1	1	4	4	4	33.9	33.3
0	0	0	49.3	46.1	-8	0	0	40.3	35.7	-3	3	3	19.6	-26.6	1	1	1	1	1	1	1	1	3	3	3	33.9	33.3
0	0	0	23.5	23.5	-8	0	0	17.1	-17.4	-3	3	3	27.6	26.2	1	1	1	1	1	1	1	1	4	4	4	33.9	33.3
0	0	0	30.7	-29.0	-8	0	0	8.4	0.2	-5	5	5	17.0	-29.1	1	1	1	1	1	1	1	1	4	4	4	33.9	33.3
0	0	0	44.4	44.4	-8	0	0	22.3	-19.5	-5	5	5	25.3	-29.1	1	1	1	1	1	1	1	1	4	4	4	33.9	33.3
0	0	0	66.6	-18.2	-8	0	0	28.4	-26.8	-5	5	5	18.7	17.7	1	1	1	1	1	1	1	1	4	4	4	33.9	33.3
0	0	0	76.4	-76.9	-8	0	0	15.1	15.1	-5	5	5	17.9	-1.0	1	1	1	1	1	1	1	1	4	4	4	33.9	33.3
0	0	0	6.3	-3.9	-8	0	0	77.5	-73.3	-5	5	5	19.2	19.4	1	1	1	1	1	1	1	1	4	4	4	33.9	33.3
0	0	0	23.3	-21.0	-8	0	0	7.3	-1.9	-7	7	7	23.4	24.6	1	1	1	1	1	1	1	1	4	4	4	33.9	33.3
0	0	0	17.9	-17.9	-8	0	0	13.9	-11.7	-7	7	7	19.6	6.6	1	1	1	1	1	1	1	1	4	4	4	33.9	33.3
0	0	0	32.8	-17.4	-8	0	0	57.1	-54.8	-7	7	7	25.8	23.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	11.7	-28.9	-8	0	0	24.3	-29.1	-7	7	7	18.6	-9.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	34.3	-17.3	-8	0	0	28.8	-27.7	-7	7	7	19.8	8.6	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	29.1	33.2	-8	0	0	14.9	-11.8	-9	9	9	10.4	-0.2	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	36.7	-36.3	-8	0	0	20.2	-18.8	-9	9	9	18.6	-16.1	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	17.9	-18.4	-8	0	0	31.0	-28.9	-9	9	9	11.1	22.7	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	39.6	-42.2	-8	0	0	8.8	-8.8	-9	9	9	31.5	-31.8	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	10.0	-10.0	-8	0	0	52.8	-58.3	-9	9	9	13.0	13.0	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	17.9	-18.4	-8	0	0	23.5	-25.5	-9	9	9	47.8	-50.0	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	10.0	-10.0	-8	0	0	20.5	-21.7	-9	9	9	73.9	-78.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	12.4	-12.4	-8	0	0	16.8	-17.1	-9	9	9	4.1	-4.1	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.3	-13.3	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	14.4	-14.4	-8	0	0	26.4	-25.9	-9	9	9	14.1	-15.9	1	1	1	1	1	1	1	1	5	5	5	33.9	33.3
0	0	0	13.7	-13.7	-8	0	0	43.2	-44.8	-9	9	9	47.2	-48.4	1	1											

TABLE III - 4

Geometry of Pyrovanadate Anion in $\text{Cd}_2\text{V}_2\text{O}_7$
(Space Group C 2/m)

e.s.d.'s in parenthesis

a) Bond lengths of anions in Å.

$$\text{V} - \text{O}_I = 1.767(3)$$

$$\text{V} - \text{O}_{II} = 1.658(14)$$

$$\text{V} - \text{O}_{III} = 1.718(9)$$

b) Distances between oxygen atoms in Å.

$$\text{O}_I - \text{O}_{II} = 2.705(13)$$

$$\text{O}_I - \text{O}_{III} = 2.808(9)$$

$$\text{O}_{II} - \text{O}_{III} = 2.807(15)$$

c) Bond angles in degrees.

$$\text{O}_I - \text{V} - \text{O}_{II} = 104.3(0.5)$$

$$\text{O}_I - \text{V} - \text{O}_{III} = 107.4(0.3)$$

$$\text{O}_{II} - \text{V} - \text{O}_{III} = 112.5(0.4)$$

$$\text{O}_{III} - \text{V} - \text{O}_{III} = 112.3(0.6)$$

TABLE III - 5

Geometry of Cation Octahedron in $\text{Cd}_2\text{V}_2\text{O}_7$
(Space Group C 2/m)

e.s.d.'s in parenthesis

a) Bond lengths in \AA .

$$\text{Cd} - \text{O}(1) = \text{Cd} - \text{O}(12) = 2.303(9)$$

$$\text{Cd} - \text{O}(2) = \text{Cd} - \text{O}(22) = 2.240(9)$$

$$\text{Cd} - \text{O}_{\text{III}} = \text{Cd} - \text{O}_{\text{III}_2} = 2.240(9)$$

b) Length of edges in \AA .

$$\text{O}(1) - \text{O}(12) = 2.948(27)$$

$$\text{O}(1) - \text{O}_{\text{III}} = \text{O}(12) - \text{O}_{\text{III}_2} = 3.284(10)$$

$$\text{O}_{\text{III}} - \text{O}_{\text{III}_2} = 3.575(18)$$

$$\text{O}(2) - \text{O}(1) = \text{O}(22) - \text{O}(12) = 3.206(15)$$

$$\text{O}(2) - \text{O}_{\text{III}} = \text{O}(22) - \text{O}_{\text{III}_2} = 2.768(13)$$

$$\text{O}(2) - \text{O}(12) = \text{O}(22) - \text{O}(1) = 2.816(14)$$

$$\text{O}(2) - \text{O}_{\text{III}_2} = \text{O}(22) - \text{O}_{\text{III}} = 3.776(13)$$

c) Bond angles in degrees.

$$\text{O}(1) - \text{Cd} - \text{O}(12) = 79.6(5)$$

$$\text{O}(1) - \text{Cd} - \text{O}_{\text{III}} = 92.6(4)$$

$$\text{O}(12) - \text{Cd} - \text{O}_{\text{III}_2} = 92.6(4)$$

$$\text{O}_{\text{III}} - \text{Cd} - \text{O}_{\text{III}_2} = 105.9(5)$$

$$O(2) - Cd - O(1) = O(22) - Cd - O(12) = 89.8(4)$$

$$O(2) - Cd - O_{III} = O(22) - Cd - O_{III_2} = 76.3(3)$$

$$O(2) - Cd - O(12) = O(22) - Cd - O(1) = 76.6(4)$$

$$O(2) - Cd - O_{III_2} = O(22) - Cd - O_{III} = 130.5(3)$$

\xrightarrow{c}

46

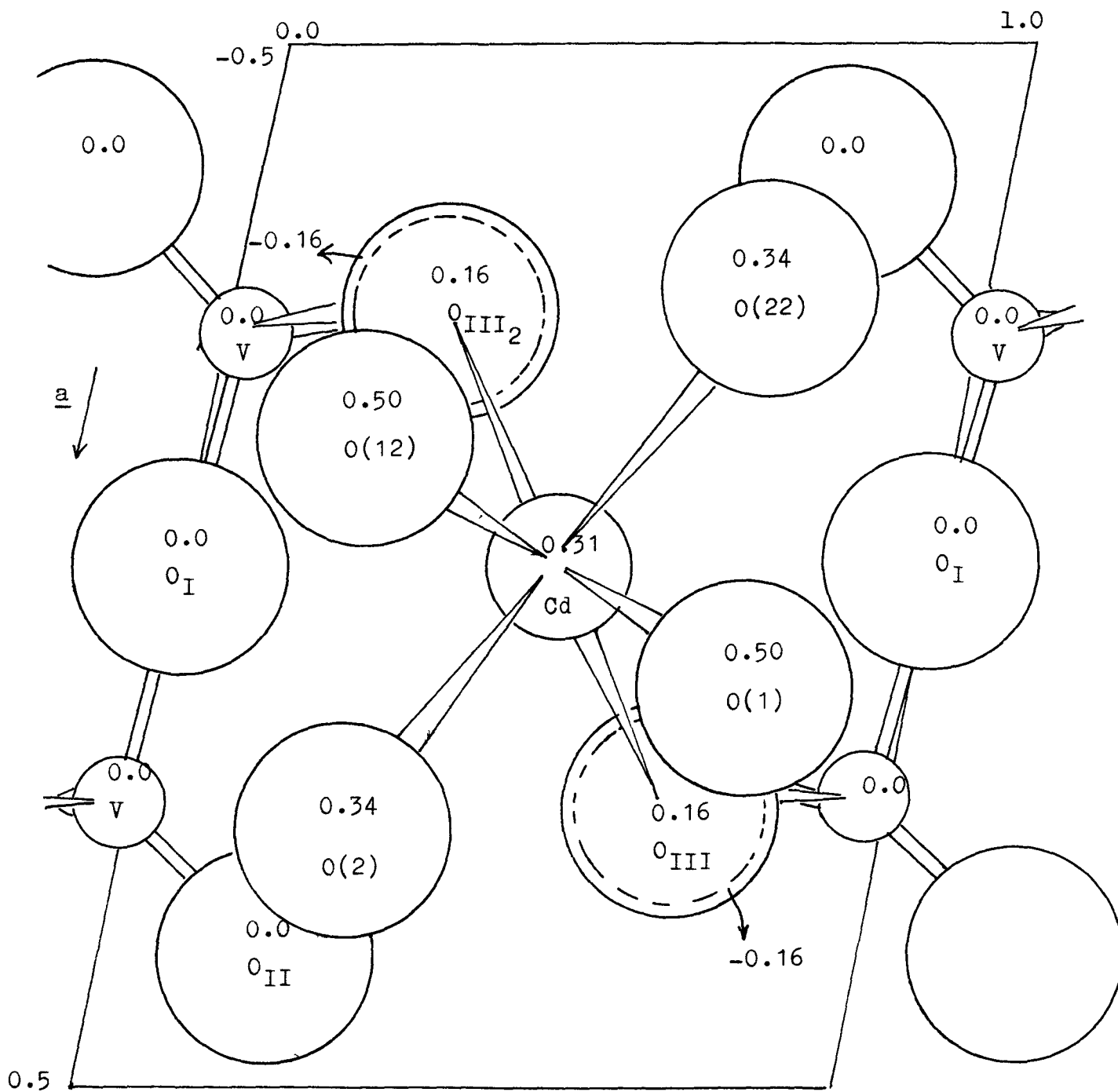


Fig. III - 1

Geometry of Cation and Anion in $\text{Cd}_2\text{P}_2\text{O}_7$ (Space Group $C2/m$)

CHAPTER IV: DISCUSSION

(a) Cadmium Pyrophosphate.

Cadmium pyrophosphate has been found to belong to the space group $P\bar{1}$. There are two kinds of distorted cadmium-oxygen octahedrons in the structure. The pyrophosphate anion is bent at the bridging central oxygen atom, and the two PO_4 tetrahedra in the anion are essentially eclipsed as viewed along the P-P vector. The two cadmium-oxygen octahedrons are shown around the $P_2O_7^{4-}$ unit in Fig. IV - 1. This Fig. is a projection on the a - b plane.

The geometry of the pyrophosphate anion is shown in Fig. II-2, and the bond lengths and bond angles are shown in Table II-5. The P(1)-O(2)-P(2) bond angle is $128.3(1.8)^\circ$, so that the bridging oxygen O(2) can be regarded to be largely sp^2 hybridised. There is thus one $p\pi$ -orbital left for overlapping with the d-orbitals of the phosphorus atoms, and hence only one π -bonding system extends throughout the whole pyrophosphate anion. The bond lengths of phosphorus atoms to this central oxygen are $1.70(3) \text{ \AA}$ and $1.63(3) \text{ \AA}$ for P(1)-O(2) and P(2)-O(2) respectively. These distances have been corrected for the effects of thermal motions as shown

in Chapter II. For a bond angle of 120° , Cruickshank has calculated the bond distance of phosphorus atom to central oxygen to be 1.64 \AA , because of a π -bond order of 0.2. This assumes linear relationship of bond length to bond order. This agrees with our average inner P-O bond length of $1.67(3) \text{ \AA}$.

The terminal oxygen-phosphorus bond lengths of the PO_4 tetrahedron on P(1) are $1.55(3) \text{ \AA}$, $1.59(3) \text{ \AA}$ and $1.39(4) \text{ \AA}$ for P(1) to O(6), O(5) and O(7) respectively, corrections have been made for effects of thermal motion. This gives an average bond length of $1.51(3) \text{ \AA}$ for the terminal oxygens to P(1). Cruickshank's calculated value for this outer P-O bond for sp hybridised central oxygen is 1.51 \AA based upon a π -bond order of 0.60. The bond angles about the PO_4 group are nearly those of a regular tetrahedron as seen in Table II-4. The average value is $110.6(1.6)$ degrees.

For the PO_4 tetrahedron around P(2), the terminal oxygen-phosphorus bond lengths are $1.50(3) \text{ \AA}$, $1.50(3) \text{ \AA}$ and $1.52(3) \text{ \AA}$ for P(2) bonded to O(4), O(1), and O(3) respectively. This also gives an average bond length of $1.51(3) \text{ \AA}$. The bond angles are again close to those in a regular tetrahedron with an average of $109.3(1.6)$ degrees.

There is thus a small difference in the two PO_4 tetrahedra in the pyrophosphate anion. However, the average value of bond lengths agrees with that calculated by Cruickshank. The average bond angles around P(2) are closer to the tetrahedron

angles than those in the P(1) unit. However, when the individual outer P-O bond lengths are compared, those around P(1) are longer than those around P(2), except for P(1)-O(7) which seems to be abnormally short. It will be seen later that O(7) yields extra long Cd-O bond in the cadmium-oxygen octahedron around Cd(1).

The two PO_4 tetrahedra in the pyrophosphate anion are essentially eclipsed. When viewed down the P-P vector, O(5), O(7) and O(6) of the PO_4 unit around P(2) nearly project upon O(1), O(3) and O(4) respectively of the tetrahedron around P(1). Also the two tetrahedra are 'bent' towards Cd(2) which uses O(1) and O(5) as an edge in its octahedron formed with oxygen atoms. This is shown by the contraction in length in O(1)-O(5) which is $3.35(4) \overset{\circ}{\text{A}}$, as compared with the distance between O(4)-O(6) of $3.63(4) \overset{\circ}{\text{A}}$. The slight distortion from the regular tetrahedron of the two PO_4 groups around P(1) and P(2) is shown in Table II-5 b). There, the corresponding edges are compared.

Both Cd(1) and Cd(2) are sixfold co-ordinated as shown in Fig. II-3. The cation polyhedrons are fairly irregular. Cd(1) forms its distorted octahedron with oxygens O(3), O(4), O(4), O(5), O(6) and O(7) at the vertices. The oxygen atoms O(3), O(4), O(6) and O(7) are almost co-planar with the cadmium. However, these oxygen ligands do not subtend right angles at the central cadmium atom, but are very much distorted

from the arrangements of equatorial ligands of a regular octahedron. The bond angle of $O(\bar{6})-Cd(1)-O(7)$ is $146.5(1.0)$ degrees and that of $O(3)-Cd(1)-O(4)$ is only $141.0(1.0)$ degrees, while in the case of a regular octahedron, these would be 180° . The oxygen atoms $O(3)$ and $O(4)$ are bent away from $O(\bar{6})$ toward $O(7)$. The bond lengths corresponding to $Cd(1)-O(3)$, $Cd(1)-O(4)$, $Cd(1)-O(\bar{6})$ and $Cd(1)-O(7)$ are $2.35(2) \text{ \AA}$, $2.33(3) \text{ \AA}$, $2.37(3) \text{ \AA}$, and $2.81(3) \text{ \AA}$ respectively. The axial oxygen atoms $O(\bar{4})$ and $O(5)$ are also distorted. $O(5)$ is slightly bent away from $O(3)$, otherwise it is almost perpendicular to the equatorial plane. $O(\bar{4})$ is bent towards $O(4)$ and $O(7)$. The bond lengths of $Cd(1)-O(\bar{4})$ and $Cd(1)-O(5)$ are $2.32(3) \text{ \AA}$ and $2.27(3) \text{ \AA}$ respectively, and bond angle of $O(\bar{4})-Cd(1)-O(5)$ is $161.7(1.0)^\circ$.

The octahedron around $Cd(1)$ shares corners with that of $Cd(2)$ at $O(5)$ and $O(\bar{7})$, and edge across a centre of symmetry with $Cd(\bar{1})$, and an edge including $O(3)$ and $O(7)$ with $Cd(2)$. It also shares a corner with $O(4)$ of the pyrophosphate ion, and corners at $O(5)$ and $O(7)$ of the anion one unit cell down along the c -axis. Thus there is one corner sharing with an oxygen atom of the PO_4 tetrahedron around $P(1)$ and with two oxygen atoms in the PO_4 around $P(\bar{1})$. The edge along $O(4)$ and $O(\bar{4})$ is shared with the tetrahedron around $Cd(\bar{1})$. The $Cd(1)-O_6$ octahedron thus joins the pyrophosphate anion in neighboring units.

The oxygen atoms around Cd(2) are less irregular than those of Cd(1). These Cd-O bond lengths range from about 2.23 Å to 2.38 Å. This octahedron is still distorted, but not so much as that around Cd(1). The equatorial oxygen atoms are O($\bar{1}$), O($\bar{7}$), O(5) and O($\bar{6}$), and these are almost planar with Cd(2). The bond angle O($\bar{6}$)-Cd(2)-O($\bar{7}$) is $163.8(1.1)^\circ$, but O(5) is bent towards O($\bar{7}$), and O($\bar{1}$) is bent towards O($\bar{7}$). The bond angle O($\bar{3}$)-Cd(2)-O($\bar{7}$) is $79.4(1.0)^\circ$. The other axial oxygen atom O(1) is, however, more distorted than O($\bar{7}$). The bond angle O(1)-Cd(2)-O($\bar{3}$) is $166.3(0.9)^\circ$. O(1) is bent towards the side formed by O($\bar{1}$)-O($\bar{7}$) of the equatorial plane. The two kinds of cadmium-oxygen octahedrons have therefore the similar feature of one bent axial oxygen atom towards the equatorial plane, with their axial oxygen atoms subtending bond angles of similar magnitudes around 160° .

Each of the terminal oxygen atoms in the pyrophosphate anion is bonded to two cadmium atoms and one phosphorus atom. Also the sum of bond angles subtended by these metal atoms at the different terminal oxygen atoms is close to 360° , showing that the metal atoms are approximately co-planar with the oxygens. These, together with the Cd-O and P-O bond lengths, are shown in Table IV-1. For most cases, the Cd-O-Cd and Cd-O-P bond angles are close to 120° , indicating that these terminal oxygen atoms may be mostly sp^2 hybridised. The remaining p- π orbital then overlap with both the two

cadmium atoms and the phosphorus atom, delocalizing the π -bonding orbital of the pyrophosphate anion to the metal atoms as well. The Cd-O bonds should thus have some π -bond characters. Since the radii of O^{2-} and Cd^{2+} are 1.45 Å and 0.92 Å respectively (Ketelaar), the Cd-O bond length of 2.37 Å is predicted. This when compared with the average of 2.30 Å found here, gives support for some degree of π -bonding in the Cd-O bonds.

Both Cd(2) and P(1) have non-positive definite temperature factors. The cadmium atoms have been refined anisotropically and the phosphorus atom isotropically. These negative values for the temperature factors imply that Cd(2) cannot be represented by an ellipsoid and P(1) by a sphere. The seemingly short P(1)-O(7) distance, resulting in an abnormally large bond length in Cd(1)-O(7) suggests that further refinements in the structure is desirable. In the last refinement, the positional co-ordinates of O(7) have the highest e.s.d. and also the highest isotropic temperature factor among the oxygen atoms. Also refinements have been carried out without the oxygen atoms O(6) and O(7), but only little change in the value of R results. This shows that the structure with the present data is not very sensitive to these oxygen atoms. The present data used are only two-dimensional, and for further refinement three-dimensional data seems to be necessary.

b) Cadmium Pyrovanadate.

Cadmium pyrovanadate has been shown to belong to the monoclinic space group $C 2/m$. The geometrical features of both the pyrovanadate anion and the cadmium-oxygen polyhedrons as seen in the a-c projection is shown in Fig. III-1, Tables III-4, and III-5.

For the pyrovanadate anion, the two vanadium atoms, the central oxygen O_I and one terminal oxygen atom, O_{II} , of each of the VO_4 tetrahedral are in the mirror plane. The $V_2O_7^{-4}$ unit is composed of two VO_4 tetrahedra sharing an apex. O_I forms this shared apex, and a crystallographic twofold axis passes through it. The two VO_4 tetrahedra are thus symmetrically related. Also the two vanadium atoms are related by this twofold axis, the bond angle $V-O_I-V$ is thus linear. Each of the remaining two pairs of oxygen atoms $O_{III'}$ and $O_{III''}$ are related by the mirror plane. The two VO_4 tetrahedrons are staggered when viewed down the V-V vector.

, Each of the terminal oxygen atoms are bonded to three atoms: the vanadium atom and two cadmium atoms. The vanadium atom is tetrahedrally co-ordinated to the central oxygen and the terminal oxygen atoms in the anion. The bond angles of O_I-V-O_{II} , O_I-V-O_{III} , $O_{II}-V-O_{III}$ and $O_{III}-V-O_{III'}$, are $104.3(0.5)^\circ$, $107.4(0.3)^\circ$, $112.5(0.4)^\circ$ and $112.3(0.6)^\circ$ respectively. These are close to the tetrahedral angle of $109^\circ 28'$. For the bond lengths of $V-O_I$, $V-O_{II}$, and $V-O_{III}$, the values are

1.767(3) Å, 1.658(14) Å, and 1.718(9) Å respectively with the e.s.d.'s in parenthesis. These values have been corrected for thermal effects.

Each of the cadmium atom is co-ordinated to six oxygen atoms in a distorted octahedron. The twofold axis passes through the cadmium, and thus three of the oxygen atoms would generate all the oxygen atoms of the octahedron. The unique cadmium-oxygen bond distances are one with value of 2.303(9) Å and two of 2.240(9) Å. Each of the cadmium-oxygen octahedron shares three edges with neighboring cadmium atoms. Of the edges that are shared with other cadmium atoms, two are related by the twofold axis, and are the shortest length of 2.768(13) Å, and the remaining one in the mirror plane and is of length of 2.948(27) Å. This is shown in Fig. IV-1, which also shows the environment of the pyrovanadate anion in the a - b plane projection. The cadmium atoms forms sheets of distorted hexagonal network with two cadmium-cadmium separated by 3.539(3) Å, and four by 3.684(2) Å. The distorted hexagonal bond angles between cadmium atoms have values of 105.85(3)° and 148.30(6)°. The anions lie on the centres of these distorted cadmium hexagons, with the central oxygen atom midway between cadmium sheets. The anions thus form a link between these sheets through the terminal oxygens of the $V_2O_7^{-4}$ group. This structure is thus similar to other members of the thortveitite series.

The determined bond lengths of the structure give us some means of studying the bonding in the pyrovanadate anion. The linear $V-O_I-V$ bond angle implies that O_I is mainly sp^2 hybridised. The two remaining $p-\pi$ orbitals of this central oxygen atom will therefore be available for π -bonding with the d -orbital of the vanadium atoms, and so O_I may join fully in both π -systems. Because all the available orbitals are used, O_I will not be bonded to another atoms except the already π -bonded vanadium. On the simple picture that Cruickshank used, this will give a π -bond order of $2/5$ for the inner $V-O$ bond and a π -bond order of $8/15$ for the outer bonds. Assuming the ionic radii for V^{5+} and O^{2-} to be 0.59 and 1.40 \AA respectively, Barnes and Bachmann (1961) calculated the co-valent single and double bond radii of tetrahedrally co-ordinated vanadium to be 1.20 and 1.10 \AA respectively, and obtained 1.79 and 1.57 \AA as bond lengths for the single and double bond. These values have been corrected for electronegativity differences. Based on these values, the inner and outer $V-O$ bond lengths would be 1.702 \AA and 1.674 \AA respectively. Our values for the inner $V-O$ bond length is $1.767(3) \text{ \AA}$, and for the outer bonds, and average of $1.698(12) \text{ \AA}$. These values do not agree too well with the calculated ones, but are in agreement for the longer and shorter aspects of the outer and inner bonds.

The $V-O_{II}$ bond length is shorter than the for $V-O_{III}$

although this difference is not significant because of the larger e.s.d. for the V-O_{II} bond. The two cadmium atoms bonded to O_{III} are at two different distances of 2.240 Å and 2.303 Å. The closeness of O_{III} to one of the Cd⁺⁺ may be one of the reasons why its V-O_{III} bond length is longer than that of O_{II} because the attraction Cd⁺⁺ has over on the oxygen. Also the isotropic temperature factor of O_{III} is about 2/5 larger than that of O_{II}, and this larger thermal motion may have exhanced the bond difference.

Each of the terminal oxygen atoms is essentially in the sp² hybridization, as shown by the closeness of the sum of angles subtended by the bonded cadmium and vanadium atoms to the 360° value in Table IV-2. There will thus be a p-π orbital available for bonding, and this may overlap with the d-π orbitals of the cadmium atoms. The π-electrons in the pyrovanadate anion will thus be delocalized over the hexagonal network of the cadmium atoms. This same feature has been observed in Cd₂P₂O₇ and other pyrophosphates.

Both the vanadium and cadmium atoms have components of anisotropic temperature factors of about the same value, with the exception that the mean square atomic displacement u_{33} of vanadium is about twice of cadmium. The only non-zero component of the u_{ij} is u_{13} , and this is of about one order below those of the u_{ii} form. The cadmium and vanadium atoms can thus be represented as ellipsoids with about the same

mean-square amplitude of displacement for the cadmium atom, and with the major principal axis along \underline{b} for vanadium.

The average Cd-O bond length in $\text{Cd}_2\text{V}_2\text{O}_7$ is $2.261(9)$ Å compared with the value of $2.314(29)$ for $\text{Cd}_2\text{P}_2\text{O}_7$. This again shows that there is some degree of π -bonding in the Cd-O bonds.

In summary, more structural work should be done to characterize the bond length of single and double bonded V-O distances in the pyrovanadate ion, as the values found experimentally do not agree too well with the calculated ones. It is difficult to comment on the applicability of the linear relationship between bond order and bond length, as assumed by Cruickshank. This is due to the fact that we do not yet know for sure what the really correct single and double bond for the vanadium-oxygen bond would be. However, the longer bond length for the inner V-O bond than the outer V-O thus indicate the features of a higher bond order of the outer V-O bonds than the inner ones.

In conclusion, we see that although the bulkiness of the cadmium atoms has caused the crystals of $\text{Cd}_2\text{P}_2\text{O}_7$ to forsake the thortveitite structure and crystallize in the $P\bar{1}$ space group, by increasing the size of anion, we have increase the tolerable size of the cation so that the thortveitite structure is again restored in the case of $\text{Cd}_2\text{V}_2\text{O}_7$.

TABLE IV - 1

Environment of Ligands around Terminal Oxygen
Atoms of Pyrophosphate Anion in $\text{Cd}_2\text{P}_2\text{O}_7$

a) Bond lengths in Å

$$\text{O}(1) - \text{Cd}(2) = 2.31(3) \quad \text{O}(5) - \text{Cd}(1) = 2.27(3)$$

$$\text{O}(1) - \text{Cd}(\bar{2}) = 2.33(3) \quad - \text{Cd}(2) = 2.30(3)$$

$$\text{O}(1) - \text{P}(2) = 1.50(3) \quad - \text{P}(1) = 1.59(3)$$

$$\text{O}(\bar{3}) - \text{Cd}(\bar{1}) = 2.35(2) \quad \text{O}(6) - \text{Cd}(\bar{1}) = 2.37(3)$$

$$\text{O}(\bar{3}) - \text{Cd}(2) = 2.29(3) \quad - \text{Cd}(\bar{2}) = 2.38(3)$$

$$\text{O}(\bar{3}) - \text{P}(2) = 1.52(3) \quad - \text{P}(1) = 1.55(3)$$

$$\text{O}(4) - \text{Cd}(1) = 2.33(3) \quad \text{O}(7) - \text{Cd}(1) = 2.81(3)$$

$$\text{O}(4) - \text{Cd}(1) = 2.30(3) \quad - \text{Cd}(\bar{2}) = 2.23(3)$$

$$\text{O}(4) - \text{P}(2) = \underline{1.50(3)} \quad - \text{P}(1) = \underline{1.39(3)}$$

$$\text{Average of Cd-O} = 2.32(3) \quad \text{Average of CdO} = 2.39(3)$$

$$\text{Overall Average Cd-O, excluding } (\text{O}_7) = 2.31(3)$$

b) Bond angles in degrees

$$\text{Cd}(1) - \text{O}(5) - \text{Cd}(2) = 115.2(1.3)$$

$$\text{Cd}(1) - \text{O}(5) - \text{P}(1) = 120.7(1.6)$$

$$\text{P}(1) - \text{O}(5) - \text{Cd}(2) = \underline{122.9(1.6)}$$

$$358.8(1.5)$$

$$\text{Cd}(\bar{1}) - \text{O}(6) - \text{Cd}(\bar{2}) = 106.3(1.1)$$

$$\text{Cd}(\bar{1}) - \text{O}(6) - \text{P}(1) = 121.8(1.5)$$

$$\text{P}(1) - \text{O}(6) - \text{Cd}(\bar{2}) = \underline{114.0(1.4)}$$

$$342.1(1.3)$$

$$\text{Cd}(1) - \text{O}(7) - \text{Cd}(\bar{2}) = 95.8(1.1)$$

$$\text{Cd}(1) - \text{O}(7) - \text{P}(1) = 124.6(1.7)$$

$$\text{P}(1) - \text{O}(7) - \text{Cd}(\bar{2}) = \underline{138.9(2.0)}$$

$$359.3(1.6)$$

$$\text{Cd}(2) - \text{O}(1) - \text{Cd}(\bar{2}) = 104.0(1.1)$$

$$\text{Cd}(2) - \text{O}(1) - \text{P}(2) = 119.4(1.6)$$

$$\text{P}(2) - \text{O}(1) - \text{Cd}(\bar{2}) = \underline{127.8(1.7)}$$

$$351.2(1.5)$$

$$\text{Cd}(1) - \text{O}(\bar{4}) - \text{Cd}(\bar{1}) = 98.0(1.1)$$

$$\text{Cd}(1) - \text{O}(\bar{4}) - \text{P}(2) = 135.0(1.8)$$

$$\text{P}(2) - \text{O}(\bar{4}) - \text{Cd}(\bar{1}) = \underline{124.7(1.6)}$$

$$357.7(1.5)$$

$$\text{Cd}(\bar{1}) - \text{O}(\bar{3}) - \text{Cd}(2) = 108.4(1.0)$$

$$\text{Cd}(\bar{1}) - \text{O}(\bar{3}) - \text{P}(2) = 110.6(1.3)$$

$$\text{P}(2) - \text{O}(\bar{3}) - \text{Cd}(2) = \underline{131.4(1.4)}$$

$$350.4(1.2)$$

TABLE IV - 2

Environment of Ligands around Terminal Oxygen Atoms
of pyrovanadate anion in $\text{Cd}_2\text{V}_2\text{O}_7$

a) Bond lengths of Cd-O in Å

$$\text{Cd}(2_1) - \text{O}_{\text{II}} = \text{Cd}(2_1') - \text{O}_{\text{II}} = 2.303(9)$$

$$\text{Cd}' - \text{O}_{\text{III}} = 2.240(9)$$

$$\text{Cd}(2_1) - \text{O}_{\text{IV}} = \underline{2.240(9)}$$

$$\text{Average } 2.261(9)$$

b) Bond angles in degrees

$$\text{Cd}(2_1) - \text{O}_{\text{II}} - \text{Cd}(2_1') = 100.42(0.52)$$

$$\text{Cd}(2_1) - \text{O}_{\text{II}} - \text{V} = 129.03(0.27)$$

$$\text{V} - \text{O}_{\text{II}} - \text{Cd}(2_1') = \underline{129.03(0.27)}$$

$$358.48(0.35)$$

$$\text{Cd}' - \text{O}_{\text{III}} - \text{Cd}(2_1) = 105.49(0.36)$$

$$\text{Cd}' - \text{O}_{\text{III}} - \text{V} = 120.55(0.45)$$

$$\text{V} - \text{O}_{\text{III}} - \text{Cd}(2_1) = \underline{129.93(0.48)}$$

$$355.97(0.43)$$

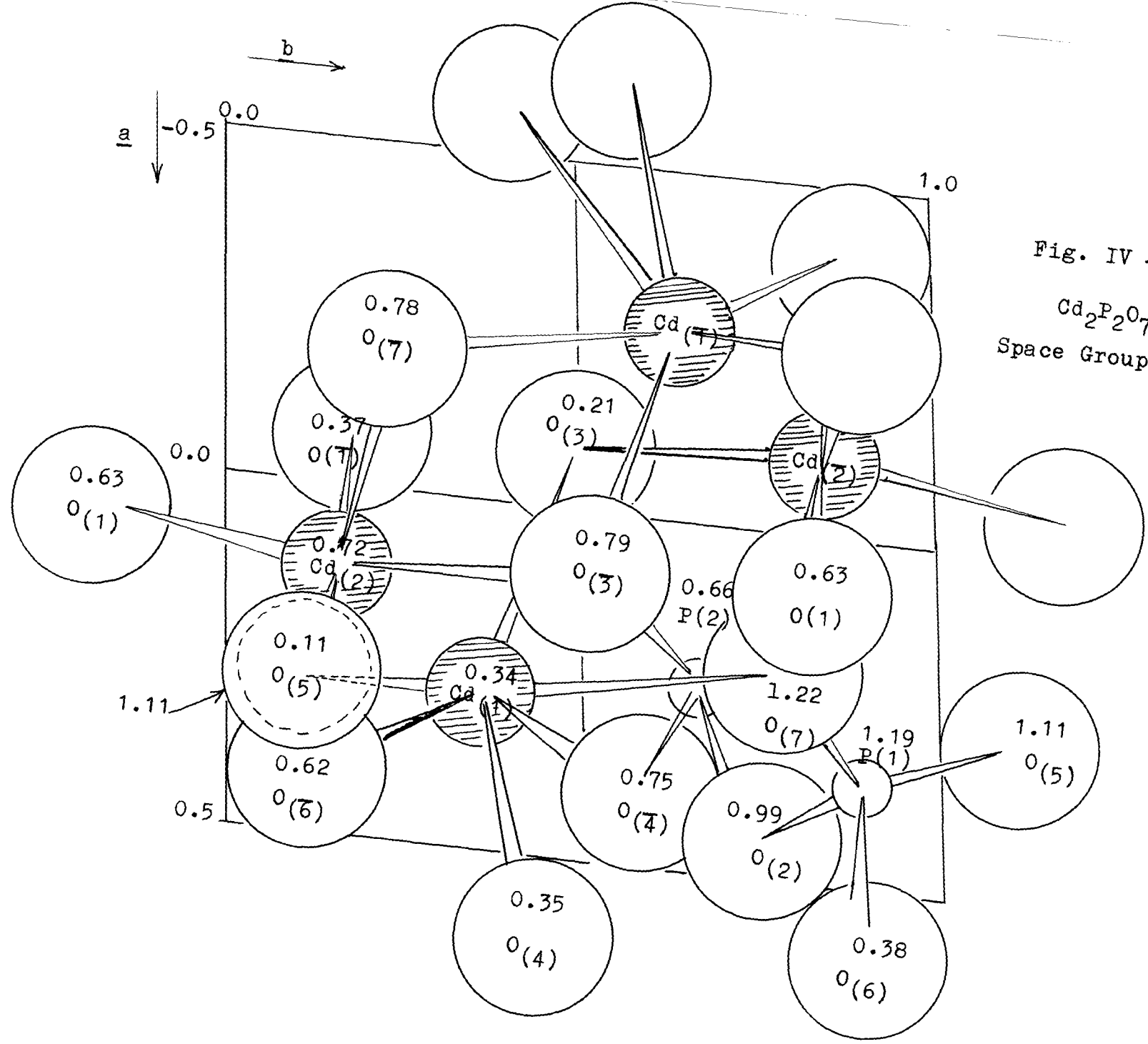


Fig. IV - 1
 $\text{Cd}_2\text{P}_2\text{O}_7$
 Space Group $P\bar{1}$

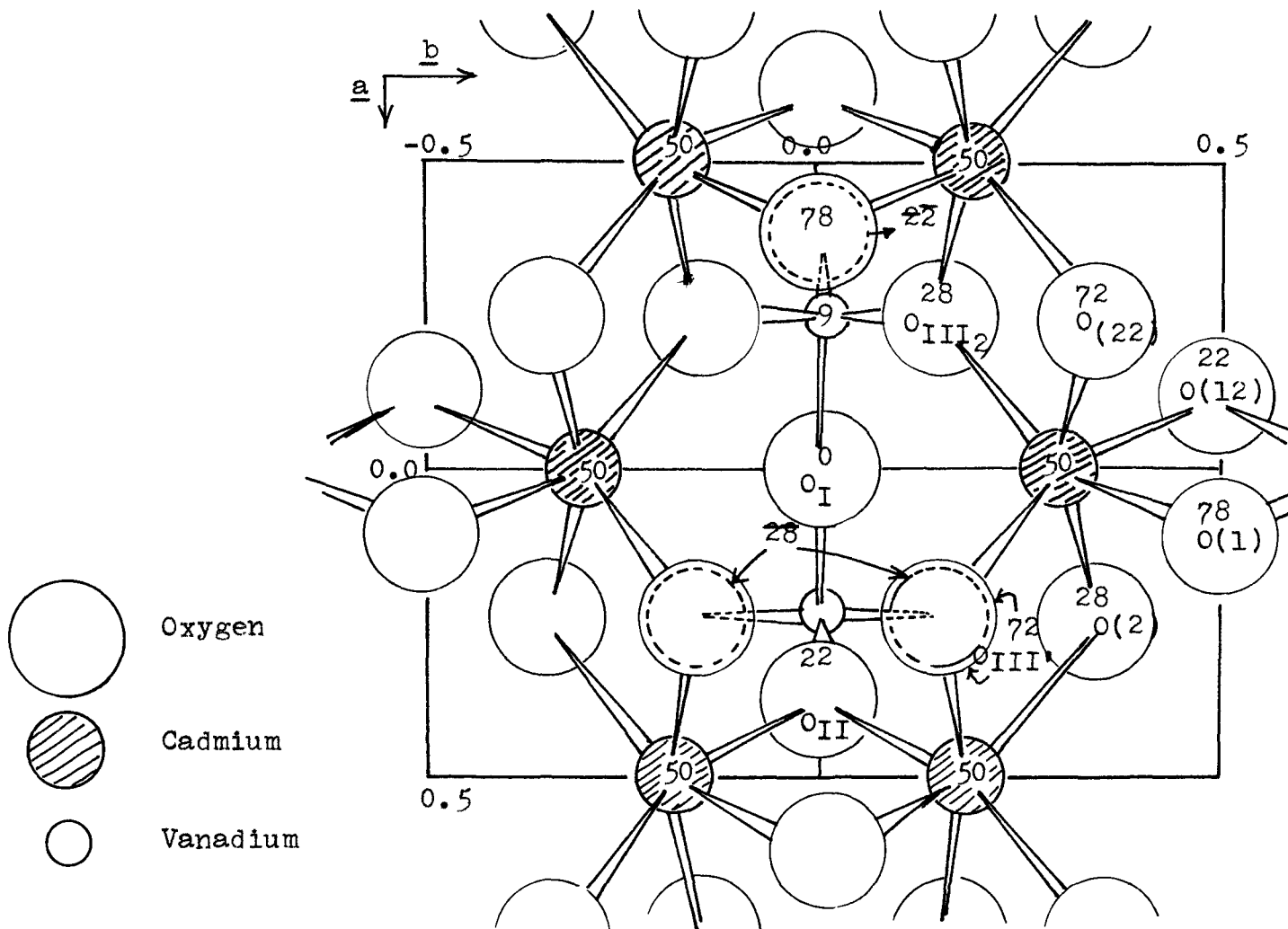


Fig. IV - 2
 Hexagonal Arrangement of Cd^{+2} layer
 in $\text{Cd}_2\text{V}_2\text{O}_7$ (Space Group $C 2/m$)
 z co-ordinates in $\times 10^2$ units

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