Investigation of Epitaxy Relationships Between Ca$_5$(PO$_4$)$_3$OH and Other Calcium Ortho-Phosphates*

B. Dickens$^+$ and L. W. Schroeder**

National Bureau of Standards, Washington, D.C. 20234

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A procedure for generating and quantitatively comparing possible cases of epitaxy and twinning has been devised and applied to the study of epitaxy between Ca$_5$(PO$_4$)$_3$OH and other calcium orthophosphates. For any two given lattices, pairs of nets which match dimensionally within prescribed limits are found and sorted in order of increasing mismatch. The crystal structural parameters are used to generate and match atomic patterns corresponding to each pair of nets. Pattern matching is done by comparing magnitudes of vectors describing the immediate environment of each atom in turn, and does not require orienting the two patterns relative to one another. Atomic charges related by each vector are also considered. Use of the vector sets introduces the limitation that twinning involving reorientation in a contact plane cannot be distinguished from no reorientation (identity match). An additional method which uses these results to match complete patterns is suggested. The procedure is general in nature and has been applied here to the study of possible epitaxies between Ca$_5$(PO$_4$)$_3$OH and Ca$_8$H$_2$(PO$_4$)$_6$·5H$_2$O, Ca$_4$O(PO$_4$)$_2$, CaHPO$_4$, CaHPO$_4$·2H$_2$O, Ca(H$_2$PO$_4$)$_2$·H$_2$O, β-Ca$_3$(PO$_4$)$_2$ and Ca$_5$(PO$_4$)$_2$SiO$_4$. Of these cases, only the epitaxies Ca$_5$(PO$_4$)$_3$OH/Ca$_8$H$_2$(PO$_4$)$_6$·5H$_2$O and Ca$_5$(PO$_4$)$_3$OH/Ca$_4$O(PO$_4$)$_2$ appear to have sufficient structural similarity to occur in practice.

Key words: Computer assessment; crystal structures; epitaxy; inter-layerings; nonstoichiometry; structural considerations; twinning.

1. Introduction

The purpose of this investigation was to examine possible epitaxies between Ca$_5$(PO$_4$)$_3$OH (hydroxyapatite) and other calcium ortho-phosphates. These epitactical relationships are of interest for the following reasons: (i) Ca$_5$(PO$_4$)$_3$OH may be considered as an idealization of the major inorganic phase in the human body and its crystal chemistry obviously influences the properties of hard tissues, and (ii) epitactical relationships have been suggested to be important in explaining the apparent nonstoichiometry of Ca$_5$(PO$_4$)$_3$OH [1][1] and in the growth of biomineral material *in vivo* [2].

Similarity in chemical content and periodicity of the chemical pattern between two planes in the component structures is an important requirement [3] for epitaxy to occur under mildly forcing conditions such as low degrees of supersaturation. From the purely metric point of view, we may treat periodicity in terms of matching nets, one in each of the two components. In general, the metric fit of such nets will not be perfect, and the resultant misfit will be accommodated by lattice strain near the epitactical layer and/or by dislocations.

For the chemical aspects of epitaxy, we obviously should consider major structural features such as layers, corrugated sheets etc., as prime candidates for the interfaces. Many structures contain layers in which the intra-layer bonds are strong and the interlayer bonds are weak. Especially in the case of inorganic salts, the atomic configurations in such layers will be relatively stable and hence can be expected to be found in more than one structure. They should be good candidates for epitaxy contact planes. However, the chemical pattern itself should not have a large motif, because this would provide many structural features to match, and the probability of finding a similar motif in another compound would necessarily be low. From the above considerations, it follows that the most likely candidates for contact layers in possible epitaxies will be planes of low Miller indices, i.e., forms such as {100}, {110}, or {210} etc.

[1] Figures in brackets indicate literature references at the end of this paper.

The first part of this paper describes a procedure to quantify the above considerations. In the second part, the procedure is used to assess the likelihood of epitaxy between $Ca_5(PO_4)_3OH$ and several other calcium ortho-phosphates.

2. Method

Vectors in each of the candidate crystal lattices are used to define nets which are compared with each other, using metric criteria, to provide possible candidates for epitactical interfaces. "Most likely" pairs of nets, having passed a comparison of periodicities (see below), are used to generate planes of atoms in both crystal structures. The local atomic environments of atoms in these planes are compared to provide an estimate of the structural similarity of the planes. This estimate is taken as a measure of the likelihood of epitaxy between the two compounds. The method was developed for ionic salts.

The two cornerstones of our approach are therefore:
(i) Generate and examine in a *systematic*, quick manner all possible cases of epitaxy and twinning that may occur.
(ii) Establish a relative probability of occurrence among the possible cases to delineate those requiring further study.

Our approach is completely general in that it can be applied to any substance that forms a crystalline phase. Generation of possible cases of epitaxy or twinning which are specified in terms of contact planes requires only unit cell dimensions. Further evaluation of these cases in terms of atomic correspondences requires atomic positions. These procedures have been implemented in two Fortran IV programs, MATCH1 and MATCH2, the rationales and algorithms of which are described in detail in [4].

3. Metric Fits

MATCH1 generates two-dimensional nets whose meshes contain vectors with components on the crystallographic axes. The vectors have a maximum of 5 times any one unit cell axis as a component (i.e., are of maximum index $\leqslant 5$), and have moduli (lengths) $L \leqslant 20$ Å. These are generous limits. All nets in one crystalline component are compared with all nets in the other. Vectors are paired if the misfits of the component lengths L_{Ai} and L_{Bj} are < 15 percent (the two crystalline components are labelled A and B). The vectors belonging to component A are taken in pairs to define nets in component A. A net in component B is defined by taking the vectors in B which have been tagged as matches with the vectors in A. The angle between the vectors in A is calculated and compared with the angle

calculated for B. If the difference in angles is less than some user-chosen limit, typically $10°$, the net in A is paired with the net in B. Paired nets are then ordered using a sort key calculated with the following criteria in mind:

(1) Corresponding mesh points for the two nets should be as close as possible (i.e., the nets should approach coincidence) to reduce the amount of lattice strain or number of lattice dislocations required to accommodate mismatch between the two structures.

(2) The atomic pattern of the planes should be simple because the simpler the pattern the higher the probability of its being matched by a similar layer in some other compound. That is, it is easier to match a pattern with few details than one with many details.

To quantify the criteria in (1) and (2), and to control their contributions to the sort key, the following quantities are currently used:

(i) $2RL/$(Sum of long diagonals of the nets A and B) where RL is the distance between the corresponding lattice points for net A and net B.

(ii) $2RS/$(Sum of short diagonals of the nets A and B) where RS is similar to RL. The theoretical range of quantities (i) and (ii) is 0 to 2. These indices yield a measure of how well criterion (1) is being fulfilled.

(iii) $K[|(\text{area A-30})/30| + |(\text{area B-30})/30|]$, where we assign (for this investigation) a unit area of 30 $Å^2$ as that occupied by a basic structural unit, e.g., one cation and one anion, and area A and area B are the areas of the cells in net A and net B respectively. The range of the index is restricted to 0 to 2 by choosing K, the scale factor. The maximum area allowed is governed by the maximum length allowed for a net vector and is typically about 400 $Å^2$.

The sum of the three quantities (i), (ii) and (iii), is used as the composite sort parameter. Nets with low values of this parameter are considered the most probable candidates for structural matches. Our preliminary results have shown, in confirmation, that the most important structural matches (as determined using MATCH2) in lists of nets which have been sorted using these combined criteria do usually occur in the first three or five members of the list.

4. Structural Fits

MATCH2 produces a quantitative estimate of the likelihood of forming aggregates composed of phases for which the detailed crystal structures are known. The program needs as input (i) the unit cells, symmetry

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operations and atomic coordinates for the structures under consideration, and (ii) two vector pairs, each pair defining a plane through one of the two crystal structures, or two planes, defined via their Miller indices. The planes so defined may be the result of visual inspection of the crystal structures or may be obtained in a more objective manner as output of the net-match generating program MATCH1.

A slice of predetermined thickness, typically from 1.5 Å to 2.0 Å and parallel to the defining net, is then taken through each crystal structure. These slices are used as possible contact planes in epitaxy or twinning. The set of vectors between atoms in the slice is used to compare atomic arrangements in slices. Figures of merit which represent the degree of similarity between slices are derived. High interslice figures of merit suggest possible epitaxy of the two compounds with the slices under consideration as the contact planes.

In our studies of calcium phosphates, we have found it satisfactory to use only the Ca and P atoms to populate the slices. This reduces the number of slices considered. Slices through the crystal structure and parallel to the defining net are calculated by allowing each atom in the unit cell of the "simplified" structure to define its own slice. Options exist for (i) proceeding with all slices, (ii) removing redundancies based on equal numbers of identically labeled atoms (e.g., Ca1) or (iii) removing redundancies and subsets. Typically, we choose the third option.

All atoms within p Å of the plane under consideration are used to make up the slice through the structure. The variable p must be selected with care. Too large a value will give a slice which is too thick to be considered a contact plane, and which effectively includes some atoms which would have to be in the body of the crystal if the actual surface were defined by other atoms in the slice. Too small a value for p may result in some atoms being wrongly excluded from the slice. We have found that an appropriate value is 1.0 Å, which, being the distance from the defining plane to the edge of the slice, gives a slice thickness of 2.0 Å, i.e., roughly an atomic diameter. The slice is considered to contain all those atoms whose *centers* lie within the slice. Only those slices with more than two atoms in them are saved for later use. Examples of such slices in $Ca_5(PO_4)_3OH$ are given in figure 1.

The next step is to delineate the atomic environments. One possibility is to take the vector set for all atoms which make up the repeat pattern of the slice. This system works very well for comparing two repeat patterns which are approximately the same size and extend through the same number of unit cells, but does not work where one net is a subset of the other. The second method, which is the one used here, involves assembling an atom motif from those atoms which lie within some preconceived distance of the motif-defining atom. Typically this distance has been 6.0

Å, which allows for first and second nearest neighbors. Specifically, the distance was chosen to allow the program to pick out P atoms in both neighboring PO_4 groups in $PO_4...Ca...PO_4$ chains when the Ca motif is being constructed and yet not include atoms beyond the first layer of the environment (see fig. 2). This method is obviously independent of the area of the plane.
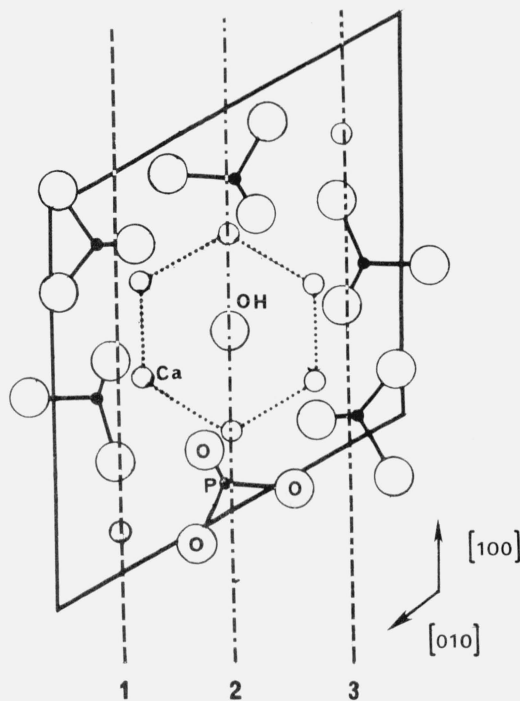

FIGURE 1. *Three possible contact planes in* $Ca_5(PO_4)_3OH$ *according to the concept of a 2 Å slice of* Ca *and/or* P *atoms.*
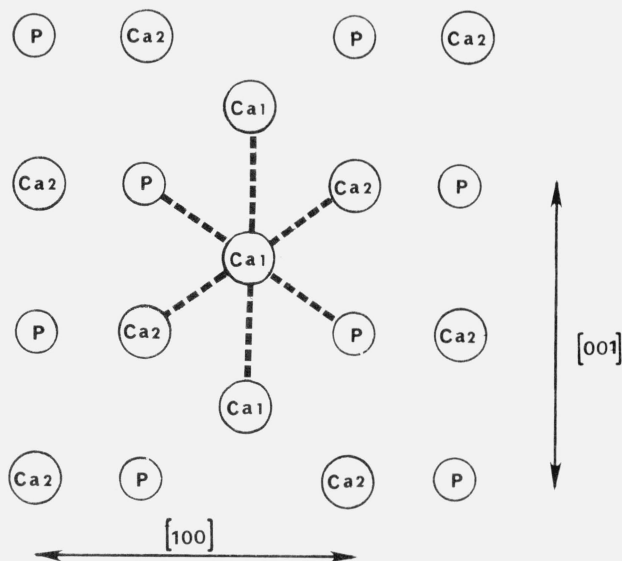Slices 1 and 3 are identical and both need not be considered.

FIGURE 2. *The* Ca(1) *motif in* $Ca_5(PO_4)_3OH$, *defined as described in the text.*

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Up to four neighboring unit cells are searched to find those atoms which lie on the plane and which are nearest to the central atom of the motif, i.e., the motif definer. Provision is made for including all atoms with a given alphanumeric label whose distances to the motif definer are less than 1.25 times the shortest distance from this type of atom to the motif definer.

When the motif has been assembled by considering all the atoms in the slice, the moduli of the vectors between all atoms within the motif are calculated to provide a quantitative description of the motif. It should be noted that the vector set does not contain any information on the relative orientation of the two patterns to be matched. This is a serious restriction in testing possible cases of twinning where the structure would be rotated or reflected about the normal to a contact plane; in such cases the procedure degenerates into a calculation of the atomic density per unit area. Our suggested third stage would handle these cases and would also act as an extension of MATCH2 for general cases.

To compare comparable areas of patterns in A and B, the numbers of occurrences of the motif-defining atoms are scaled by the appropriate integer multiple previously calculated from the ratio of plane areas in A and B. The moduli of the vector sets of the two motifs are then compared. The comparison includes consideration of the charge product of the two atoms which define the ends of the vectors. Thus, charge misfit of greater than 1.5 electrons is at present not permitted in a vector match. Also, vector length misfits greater than 25 percent are not permitted in matches of individual vectors. After these tests have been made between a vector modulus in the motif in compound A and all unmatched vector moduli in a motif in compound B, the best fit of length between the vector in compound A and the corresponding one in compound B is tagged as a match and neither of these vectors will be matched again.

After attempts have been made to match all vector lengths in the two motifs, the fractional vector mismatch $V = 2|L_1-L_2|/(L_1+L_2)$ between "matched" vectors is calculated, together with the fractional charge mismatch $2|C_1-C_2|/(C_1+C_2)$, and the percentage of each vector set matched. Here, L and C are the modulus and charge product, C_iC_j, associated with a vector between atoms i and j. Atoms i and j have been assigned atomic charges, C_i and C_j, respectively. All atom motifs in compound A are compared with all atom motifs in compound B. From each comparison, an inter-motif figure-of-merit quantity is calculated based more or less equally on the average distance mismatch and the number of vectors matched. This quantity, which is designed to be 100 percent for perfect matches, is $[(0.2-T)/0.2]50+(Z_A+Z_B)/4$, where T, the average mismatch of vectors in A ($T=\Sigma v/n$ where

there are n vectors in set A), is compared with 0.2 and effectively constrained to be 0.1 or less for "good" matches, and Z_A and Z_B are the percentages of matched vectors in the vector sets of the motifs in compounds A and B. If the two atoms defining the motifs being compared have different charges they are considered to be mismatched chemically and the percentage quantity defining that match is reduced by 20 percent so that the program will be less likely to match atoms of opposite charge should the vector sets of their motifs accidentally have some correspondence. Such cases would obviously be chemically destabilizing. (We used this feature as an expedient to differentiate between Ca and P by giving Ca a charge of $+2$ and P a charge of -1.)

An attempt is made to match atoms in compound A with atoms in compound B, using the inter-motif figures-of-merit calculated above. Matching between atoms is accomplished by pairing off the atoms in compound A with atoms in compound B in order of descending value of the inter-motif figures-of-merit subject only to the number of occurrences of each atom in the slice. Thus, if an atom in compound A has four total appearances and an atom in compound B has only three occurrences and these atoms have a very high matching quotient, the match will be used until the lower number of occurrences is completely satisfied, that is, three times. The fourth match of the atom in compound A must be accomplished by using some other atom in compound B. In general, this procedure works very well and is correctly able to identify and match, for example, atoms in cation columns in two compounds.

As the atom-matching proceeds, an accumulative sum is made of the associated inter-motif figures-of-merit. When all the atomic occurrences in one of the two compounds have been matched, an inter-plane figure of merit is calculated by dividing the total accumulation of inter-motif quantities by the maximum of the two net areas to give some idea of matching per unit area.

Ambiguities sometimes exist because an atom in one compound may match two atoms in the other compound within the limits of resolution of this procedure. Because of these ambiguities, a general procedure to assemble matching patterns of atoms in slices by considering individual matches is difficult to program. At present, a general procedure seems unnecessary because visual matching of atoms after reference to the plots and the atom-atom environment fits is quick and provides a chance to check on the validity of the calculations at an opportune stage.

5. Merit Figure Upper Bound

Matches in which both the components A and B are the same and which involve the same net appear automatically

if twins are investigated by this procedure. These "identity" matches are important from two points of view:

(1) An identity match of a plane of atoms in the crystal structure with itself provides an upper bound to the inter-plane figure-of-merit derived for structural fits using the MATCH2 program (see ref. [4] and below), because the fit is obviously perfect.

(2) Twinning mechanisms are possible using the same contact plane for both individuals of the twin provided a layer of the structure can be transformed into itself or into another layer without transforming the crystal into itself, as the examples of Dornberger-Schiff show [5].

6. Twinning in Ca₅(PO₄)OH

In $Ca_5(PO_4)_3OH$, 15 matching nets (specified in table 1) were obtained for possible cases of twinning, subject to the constraints that the maximum length of a net-defining vector is less than 20 Å, that angles between the vectors defining two matched nets agree within 10° and that matches containing nets both of which are within 2° of being parallel to paired nets already found are removed from the final list. The rationale for these criteria is explained more fully in reference [4]. An additional match, (103) on line 8 in table 1, is a special case (see below). The first 8 entries in table 1 are identity matches.

Figures of merit for the degree of structural fit were calculated for these 16 net matches using the positions of calcium and phosphorus atoms in the $Ca_5(PO_4)_3OH$ structure. A slice thickness of 2 Å through the structure was specified, i.e., the atoms making up the composition of a possible contact plane were allowed to be distributed over a 2 Å thick slice of the structure rather than on a two-dimensional plane. Slices were considered to be centered on all atoms in turn; redundant slices were removed from further consideration. The calculated inter-plane figures of merit for the possible twinning modes are given together with other details in table 1. From this table we see that the highest inter-plane merit figure and hence the best structural match for $Ca_5(PO_4)_3OH$ is for the net based on component vectors [001] and [100], with vector components in terms of edges of the unit cell. This corresponds to a contact plane of (010). (Point group 6/m, on which the space group $P6_3/m$ of $Ca_5(PO_4)_3OH$ is based, specifies that there are 6 equivalent compositional planes which include the c axis ±[001]; {100} is the representation of these 6 planes, which include (010) given on line 1 of table 1 as a direct quote from the output of the MATCH2 program.)

Because of the lack of information on the relative orientations of the planes, our current mode of calculation gives no means of assessing the probability of twinning when a net is compared with itself. Such an identity match

obviously gives a perfect fit with itself. (Twinning would require rotation of one of the two slices before juxtaposition.) Inter-plane merit figures derived from perfect fits are obviously related to the density of atoms in the slice per unit area of the slice, since all individual inter-atom figures-of-merit are 100 (each atom fits perfectly with itself). This limitation applies only to identity matches, which themselves are found only in twinning, and would be removed if the third stage of the calculations (MATCH3) were completed. The present procedure is applicable to cases of twinning where the twinning operation brings two slices not related by point-group symmetry into contact.

This approach provides a filter through which possible cases of twinning and epitaxy are passed and obvious misfits are discarded. There is always the possibility that new tests will discard some of the surviving cases. The need for a third stage (as described in ref. [4]) is demonstrated by the findings of Donnay, Sudarsanan, and Young [6] on $Ca_5(PO_4)_3OH$ and $Cd_5(PO_4)_3Cl$. Twinning on (100), called twinning by merohedry in reference [6], is essentially non-existent in the hexagonal form of $Ca_5(PO_4)_3OH$ (where some OH is substituted by F to destroy the sense of the OH chain directions) but is ubiquitous in $Cd_5(PO_4)_3Cl$ and in the monoclinic form of $Ca_5(PO_4)_3OH$ (no F impurity) (Elliott, Mackie and Young [7] and Skinner, Dickens, and Jordan [8]) which is said to twin by reticular pseudo-merohedry. Both cases give high merit figures using our approach, but in the case of $Ca_5(PO_4)_3OH$, twinning on (100) is not favored because of O...O inter-phosphate group contacts [6].

With the above in mind, we cannot say at this stage whether the first 8 cases (all identity matches) in table 1 are feasible cases of twinning or not. *Their figures of merit mainly provide context in which to judge the non-identity cases, 9 to 16 in table 1, and the cases of epitaxy reported later in this paper.* Based on the three highest inter-plane merit figures of 9.26, 7.96 and 7.82, we judge at this point that twinnings and epitaxies involving merit figures less than 6.0 would be unlikely to occur for $Ca_5(PO_4)_3OH$.

Donnay, Sudarsanan, and Young [6] infer from their own experience and from context taken from Palache, Berman and Frondel [9] that twinning in $Ca_5(PO_4)_3(F,OH)$ is rare at best and is based on the twin planes (111) and (103). The plane (111) is represented in table 1 by the symmetrically equivalent form $(0\bar{1}1)$. The inter-plane merit figure for $(0\bar{1}1)$ is 7.96. The (103) family of planes were not generated in our usual procedure because the $\pm[30\bar{1}]$ vector, which would normally be used to define the plane, is longer (29.07 Å) than our upper limit of 20 Å. Results for (103) were calculated separately and appear on line 8 in table 1; the highest merit figure is 6.27.

The merit figure approach using only Ca and P atoms thus appears to possess some validity as a necessary but

TABLE 1. *Twinning possibilities for apatites.*

	Contact planes		d-spacings, Å	Net vectors		Sort key	Disloc/cm²	Inter-plane merit figure	Atoms involved[a] in slices for Ca$_5$(PO$_4$)$_3$OH	Area A, Å²	Area B, Å²
	A	B		A	B						
1	(010)	(010)	8.15,8.15	[100,001]	[100,001]	0.015	0.0	9.26	2Ca(1),2Ca(2),2P	64.8	64.8
2	(001)	(001)	6.88,6.88	[100,210]	[100,210]	0.019	0.0	7.82	3Ca(2),3P	76.8	76.8
3	(0$\bar{1}$1)	(0$\bar{1}$1)	5.26,5.26	[100,211]	[100,211]	0.028	0.0	7.96	2Ca(1),3Ca(2),3P	100.5	100.5
4	($\bar{1}$20)	($\bar{1}$20)	4.71,4.71	[001,210]	[001,210]	0.033	0.0	7.13	4Ca(2),4P	112.2	112.2
5	($\bar{1}$21)	($\bar{1}$21)	3.89,3.89	[101,210]	[101,210]	0.042	0.0	7.36	2Ca(1),2Ca(2),6P	136.0	136.0
6	($\bar{2}$31)	($\bar{2}$31)	2.81,2.81	[102,211]	[102,211]	0.061	0.0	6.92	3Ca(1),5Ca(2),5P	187.8	187.8
7	(2$\bar{4}$1)	(2$\bar{4}$1)	2.23,2.23	[210,102]	[210,102]	0.080	0.0	6.75	4Ca(1),6Ca(2),6P	237.2	237.2
8	(103)	(103)	2.21,2.21	[010,30$\bar{1}$]	[010,30$\bar{1}$]	0.080	0.0	6.27[b]	4Ca(1),6Ca(2),5P	239.2	239.2
9	(010)	($\bar{1}$20)	2.21,2.21	[001,100]	[001,210]	0.176	1.55×10¹⁴	4.83	10Ca(1),10Ca(2),10P 12Ca(2),12P	64.8	112.2
10	(01$\bar{1}$)	($\bar{2}$31)	5.26,2.81	[211,100]	[102,211]	0.247	7.27×10¹⁰	5.38	4Ca(1),6Ca(2),6P; 4Ca(1),6Ca(2),4P	100.5	187.8
11	(010)	($\bar{1}$11)	8.15,5.26	[101,100]	[101,211]	0.306	1.84×10¹³	6.10	6Ca(1),6Ca(2),6P; 4Ca(1),6Ca(2),6P	64.8	100.5
12	(010)	(2$\bar{4}$1)	4.08,2.23	[102,100]	[210,102]	0.311	7.77×10¹⁰	3.55	4Ca(1),4Ca(2),4P; 4Ca(1),6Ca(2),6P	129.6	237.2
13	(0$\bar{1}$1)	(001)	5.26,6.88	[100,211]	[100,210]	0.321	2.66×10¹³	5.58	6Ca(1),9Ca(2),9P; 12Ca(2), 12P	100.5	76.8
14	(001)	(1$\bar{2}$0)	6.88,4.71	[210,100]	[210,211]	0.364	1.52×10¹³	4.88	9Ca(2),9P; 8Ca(2),8P	76.8	112.2
15	(010)	($\bar{1}$21)	8.15,3.89	[101,100]	[101,210]	0.417	5.39×10¹³	5.54	4Ca(1),4Ca(2),4P; 4Ca(1),3Ca(2),3P	64.8	136.0
16	($\bar{2}$31)	(001)	2.81,6.88	[102,211]	[210,100]	0.419	2.26×10¹⁰	4.81	8Ca(1),12Ca(2),8P; 15Ca(2), 15P	187.8	76.8

Criteria: net vectors <20 Å; lengths of corresponding vectors agree within 15 percent; corresponding angles in networks agree within 10°.

Contact planes are given in Miller index (intercept) notation. Net vectors r_A and r_B given in terms of unit cell translations; α_A is angle between vectors r_{A1} and r_{A2}; α_B is similarly defined in net B. The sort key used in these calculations was

$$||r_{A1}|-|r_{B1}||/[(|r_{A1}|+|r_{B1}|)/2] + ||r_{A2}|-|r_{B2}||/[(|r_{A2}|+|r_{B2}|)/2] + |\alpha_A-\alpha_B|/[(\alpha_A+\alpha_B)/2] + 0.15[\text{maximum (area a, area b)}-25]/400.$$

"Disloc" is an estimate of the additional number of dislocations due to misfit introduced at the interface assuming no elastic strain in either component, i.e.,

$$\text{Disloc} = 10^{16}(||r_{A1}|-|r_{B1}||\cdot||r_{A2}|-|r_{B2}||\sin[(\alpha_A+\alpha_B)/2])/(|r_{A1}|\cdot|r_{A2}|\cdot|r_{B1}|\cdot|r_{B2}|).$$

[a] Only Ca and P atoms used.
[b] This match included because of statement in Frondel et al. [9]; length of 30$\bar{1}$ vector is 29.07 Å (outside usual range). Other merit figures for this match were 5.37, 5.31, 5.23, and 5.22, corresponding to different sets of parallel planes.

incomplete criterion for ranking twinning possibilities. Although we considered fits in only two dimensions, the eight cases of possible merohedry (first 8 lines in table 1) have the highest merit figures (≥ 6.27), consistent with the conventional twinning view of coincident lattices. It is noteworthy that identity matches do not require the misfit dislocations usually necessary [10] to accommodate dimensional misfit between different substrates. It is also noteworthy that in some twins the thickness of the boundary layer may reflect a gradual change over many unit cells (see reference 11 for a specific example) and may show the effect of elastic strain. It is not obvious in such cases that the relationship between individuals of the twin can be described in terms of a coincident lattice.

7. Epitaxy Between $Ca_5(PO_4)_3OH$ and Other Calcium Ortho-Phosphates

The calcium phosphates we have considered here as possibilities for forming epitactical relationships with $Ca_5(PO_4)_3OH$ are $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ [12,13], $CaHPO_4 \cdot 2H_2O$ [14], $CaHPO_4$ [15], $Ca(H_2PO_4)_2 \cdot H_2O$ [16,17], $Ca_4O(PO_4)_2$ [18], β-$Ca_3(PO_4)_2$ [19] and $Ca_5(PO_4)_2SiO_4$ [20] (see table 2 for common names). These materials comprise the more stable and common calcium phosphates.

Table 2 contains the matched nets obtained using only metric criteria with the constraints described earlier. The large number of acceptable matches is partly a result of the generous constraints, but also results from ignoring structural aspects.

Table 3 contains details of the first five matching nets for each case, ranked by sort key [4]. An estimate of the dislocation density due to misfit in the absence of all elastic strain is provided. An estimate of the corresponding misfit dislocation density is given by

$$(||\mathbf{r}_{A1}| - |\mathbf{r}_{B1}||)(||\mathbf{r}_{A2}| - |\mathbf{r}_{B2}||) \sin$$
$$\frac{\alpha_A + \alpha_B}{2} / (|\mathbf{r}_{A1}|)(|\mathbf{r}_{A2}|)(|\mathbf{r}_{B1}|)(|\mathbf{r}_{B2}|).$$

where α_A is the angle between vectors $\mathbf{r}_{A1}$ and $\mathbf{r}_{A2}$ in net A and α_B is the angle between vectors $\mathbf{r}_{B1}$ and $\mathbf{r}_{B2}$ in net B. The formula is exact if $\alpha_B = \alpha_A$. Although this estimate of misfit dislocation density ignores any relaxation due to elastic strain in the contact layer, its use does enable a comparison with the normal density range of 10^2-10^{12} dislocations/cm^2 for homogeneous materials [21]. The type of dislocation is unspecified but may be of the edge or screw type or a combination of the two. Van der Merwe has calculated [22] that elastic strain may be invoked to take up dimensional misfit when the epitactical film is less than ~ 20 Å thick, but that the accommodation mechanism is

TABLE 2. *Total number of matching nets between* $Ca_5(PO_4)_3OH$ *and several other calcium ortho-phosphates.*

$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	(Octacalcium phosphate)	11
$Ca_4O(PO_4)_2$	(Tetracalcium phosphate)	82
$CaHPO_4^a$	(Dicalcium phosphate)	332
$CaHPO_4 \cdot 2H_2O^b$	(Dicalcium phosphate dihydrate)	229
$Ca(H_2PO_4)_2 \cdot H_2O$	(Monocalcium phosphate)	405
β-$Ca_3(PO_4)_2$	(Beta-tricalcium phosphate)	8
$Ca_5(PO_4)_2SiO_4$	(Silico-carnotite)	56

Matches satisfy metric requirements only, i.e., corresponding distances in net agree within 15 percent, angles within 10°, all distances < 20 Å. Results obtained with program MATCH1.

[a] Distances agree within 10 percent; angles within 4°; all distances < 21 Å.

[b] Distances agree within 15 percent; angles within 4°; all distances < 21 Å.

inclusion of dislocations at the interface for films > 200 Å. At this stage, we may say that the most favorable case of epitaxy in which all the misfit is taken up by dislocations will require an additional 10^8 dislocations/cm^2 at the interface, to be compared with dislocation densities of 10^2 to 10^{12} dislocations/cm^2 in homogeneous solids. A dislocation density of 10^{12} dislocations/cm^2 corresponds to an inter-dislocation spacing of ~ 100 Å, i.e., ~ 30 ions for close-packed Ca and PO_4 ions.

For each of the seven pairs of compounds, the structure-matching procedure was applied to the 10 matching nets determined from the sort key to be the most probable candidates for epitaxy. The Ca and P positions in the crystal structures were used to specify their gross structural details. The matching nets with the highest merit figures are given in table 4. Table 4 also shows the contact planes, the sort order, and the atoms found to be involved in the structural matches. The number of each type of atom is given for equivalent areas of the contact planes. In all cases, a 2 Å thick slice was used and all subsets and redundancies were removed, e.g., 2Ca(2),2P, being a subset of a parallel slice 2Ca(1),2Ca(2),2P in $Ca_5(PO_4)_3OH$, was not considered in the (010) *vs.* (100) matching of $Ca_5(PO_4)_3OH$ with $Ca_8H_2(PO_4)_6 \cdot 5H_2O$.

Reasons for considering only Ca and P positions in the crystal structure include (i) reducing the computational expense to manageable proportions, (ii) allowing the program to fit in the computer ($> 65K$ of storage may otherwise be required although an overlay scheme has now reduced the importance of this second consideration), and (iii) specifying only the major features of the structure because dislocations and elastic strain at the interface may change the local details somewhat. One assumption when only Ca and P atoms are included is that these atoms are sufficient to specify the major features of the structure.

	Contact planes		Net vectors		Sort key	Disloc.
	A	B	A	B		
$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	(010)	(100)	[001,100]	[001,010]	0.035	1.28×10^{10}
	(010)	($\bar{1}$10)	[001,100]	[001,110]	0.082	3.58×10^9
	(010)	(010)	[001,100]	[001,100]	0.119	2.83×10^{10}
	($\bar{1}$20)	($\bar{1}$10)	[001,210]	[001,110]	0.226	1.09×10^{11}
	(2$\bar{4}$1)	(100)	[210,102]	[012,0$\bar{1}$2]	0.246	7.25×10^8
$Ca_4O(PO_4)_2$	(010)	(010)	[100,001]	[001,100]	0.051	1.30×10^{10}
	(010)	(110)	[100,001]	[001,1$\bar{1}$0]	0.058	2.59×10^9
	(010)	($\bar{1}$10)	[100,001]	[001,110]	0.058	2.59×10^9
	($\bar{1}$21)	($\bar{1}$01)	[101,201]	[101,111]	0.072	3.23×10^9
	($\bar{1}$21)	(101)	[101,210]	[10$\bar{1}$,11$\bar{1}$]	0.103	2.12×10^{10}
$CaHPO_4^b$	(0$\bar{1}$0)	($\bar{1}\bar{1}$2)	[100,001]	[1$\bar{1}$0,111]	0.062	8.84×10^8
	(1$\bar{2}$0)	(311)	[211,001]	[$\bar{1}$12,0$\bar{1}$1]	0.085	1.80×10^9
	(010)	(001)	[001,100]	[100,010]	0.092	1.77×10^{10}
	(1$\bar{2}$0)	($\bar{1}$3$\bar{2}$)	[211,001]	[$\bar{1}$12,111]	0.098	1.87×10^9
	(01$\bar{1}$)	($\bar{1}$0$\bar{1}$)	[211,100]	[$\bar{1}\bar{2}$1,010]	0.106	1.23×10^{10}
$CaHPO_4 \cdot 2H_2O^c$	(010)	(3$\bar{1}\bar{1}$)	[102,100]	[01$\bar{1}$,112]	0.129	2.23×10^8
	(010)	($\bar{3}$11)	[102,100]	[011,$\bar{1}$1$\bar{2}$]	0.129	2.23×10^8
	(010)	(100)	[001,100]	[010,001]	0.130	2.31×10^{10}
	($\bar{2}$31)	(011)	[102,211]	[$\bar{1}\bar{1}$1,11$\bar{1}$]	0.132	9.08×10^{10}
	($\bar{2}$31)	(0$\bar{1}$1)	[102,211]	[111,$\bar{1}$11]	0.132	9.08×10^{10}
$Ca(H_2PO_4)_2 \cdot H_2O$	(010)	(1$\bar{3}\bar{1}$)	[100,001]	[101,$\bar{2}$11]	0.053	1.33×10^{13}
	(1$\bar{2}$0)	(1$\bar{4}$1)	[210,001]	[212,$\bar{1}$01]	0.098	5.95×10^9
	(01$\bar{1}$)	(021)	[211,100]	[2$\bar{1}$2,0$\bar{1}$2]	0.103	5.33×10^6
	(01$\bar{1}$)	(001)	[211,100]	[100,3$\bar{1}$0]	0.116	2.90×10^{10}
	(01$\bar{1}$)	(25$\bar{1}$)	[211,100]	[$\bar{2}$11,3$\bar{1}$1]	0.119	6.38×10^9
β-$Ca_3(PO_4)_2$	(010)	(001)	[100,001]	[120,100]	0.113	1.24×10^{10}
	(1$\bar{2}$0)	(001)	[210,001]	[120,100]	0.176	3.34×10^{10}
	(10$\bar{2}$)	(001)	[211,201]	[210,110]	0.184	1.14×10^{10}
	($\bar{1}$11)	(001)	[101,211]	[110,210]	0.190	5.87×10^{10}
	(001)	(001)	[100,210]	[110,210]	0.232	3.11×10^{11}
$Ca_5(PO_4)_2SiO_4$	(010)	(0$\bar{1}$1)	[001,100]	[100,011]	0.075	2.77×10^{10}
	(1$\bar{2}$0)	(001)	[210,001]	[010,100]	0.104	9.55×10^{10}
	(1$\bar{2}$0)	(1$\bar{1}$0)	[210,001]	[110,001]	0.110	1.98×10^{10}
	(010)	(010)	[100,001]	[001,100]	0.111	2.25×10^{11}
	(1$\bar{2}$0)	(100)	[210,001]	[010,001]	0.118	2.87×10^{10}

Contact planes given in Miller index (intercept) notation. Net vectors given in terms of unit cell translations. Sort key and "Disloc" defined in table 1.

[a] According to sort key; best five taken for each case. Usual criteria: distances agree within 15 percent; angles within 10°; all distances <20 Å. Results obtained with program MATCH1.

[b] Distances agree within 10 percent; angles within 4°; all distances <21 Å.

[c] Distances agree within 15 percent; angles within 4°; all distances <21 Å.

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TABLE 4. *Details of matches for best inter-plane merit figures (>4.5) between* $Ca_5 \cdot (PO_4)_3OH$ *and several other calcium phosphates.*

	Contact planes A	Contact planes B	Sort key	Sort order	Merit figure	Atoms A	Atoms B	Disloc	Areas A	Areas B
$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	(010)	(100)	0.035	1	8.32	2Ca(1),2Ca(2),2P	Ca(1),Ca(2),Ca(5),Ca(8),P(9),P(12)	1.28×10^{10}	64.8	64.9
	($\bar{1}11$)	(100)	0.306	8	6.17	4Ca(1),6Ca(2),6P	3Ca(1),3Ca(2),3Ca(5),3Ca(8),3P(9),3P(12)	4.63×10^9	100.5	64.9
	(010)	(010)	0.119	3	4.74	4Ca(1),4Ca(2),4P	Ca(1),Ca(2),Ca(3),Ca(4),Ca(7),Ca(8),P(10),P(12),P(13)	2.83×10^{10}	64.8	134.0
	(010)	($\bar{1}10$)	0.082	2	4.66	4Ca(1),4Ca(2),4P	Ca(3),2Ca(4),Ca(5),2Ca(6),P(9),P(13)	3.58×10^{10}	64.8	129.1
$Ca_4O(PO_4)_2$	(010)	(010)	0.051	1	7.98	2Ca(1),2Ca(2),2P	Ca(5),Ca(6),Ca(7),Ca(8),P(3),P(4)	1.30×10^{10}	64.8	66.4
	(010)	(010)	0.051	1	7.70	2Ca(1),2Ca(2),2P	Ca(1),Ca(2),Ca(3),Ca(4),P(1),P(2)	1.30×10^{10}	64.8	66.4
			11 more matches between 4.90 and 4.50							
$CaHPO_4$	(010)	(001)	0.092	3	5.84	4Ca(1),4Ca(2),4P	3Ca(1),3Ca(2),3P(1),3P(2)	1.77×10^{10}	64.8	45.8
	(010)	(100)	0.112	9	5.42	6Ca(1),6Ca(2),6P	4Ca(1),4Ca(2),4P(1),4P(2)	3.88×10^{10}	64.8	92.2
$CaHPO_4 \cdot 2H_2O$	(010)	($10\bar{1}$)	0.138	10	2.85	6Ca(1),12Ca(2),9P	4Ca,4P	3.41×10^{10}	64.8	96.5
	(010)	($10\bar{1}$)	0.138	10	2.80	12Ca(1),12Ca(2),6P	4Ca,4P	3.41×10^{10}	64.8	96.5
$Ca(H_2PO_4)_2 \cdot H_2O$	($01\bar{1}$)	(001)	0.116	4	2.73	4Ca(1),6Ca(2),6P	3Ca(1),3P(1),3P(2)	2.90×10^{10}	100.5	66.4
β-$Ca_3(PO_4)_2$ [a]	($1\bar{2}2$)	(001)	0.375	8	5.65	4Ca(1),6Ca(2),6P	6Ca(3),2Ca(4),2Ca(5),2P(2)	6.44×10^{10}	190.2	94.4
	(001)	(001)	0.190	4	5.27	2Ca(1),3Ca(2),3P	3Ca(3),Ca(4),Ca(5),3P(2)	5.87×10^{10}	100.5	94.4
	($0\bar{1}1$)	(001)	0.364	7	5.08	2Ca(1),3Ca(2),3P	3Ca(3),Ca(4),Ca(5),3P(2)	6.80×10^{10}	100.5	94.4
	(001)	(001)	0.232	5	4.89	3Ca(2),3P	3Ca(3),Ca(4),Ca(5),3P(2)	3.11×10^{11}	76.8	94.4
$Ca_5(PO_4)_2SiO_4$	(010)	(010)	0.111	4	6.70	2Ca(1),2Ca(2),2P	2Ca(2),2Ca(3),2G	2.25×10^{11}	64.8	68.3
	($1\bar{2}2$)	(010)	0.141	7	6.25	4Ca(1),6Ca(2),6P	6Ca(2),6Ca(3),6G	2.31×10^{10}	190.2	68.3
	($0\bar{1}1$)	(010)	0.151	9	5.65	4Ca(1),6Ca(2),6P	6Ca(2),6Ca(3),6G	6.14×10^{10}	100.5	68.3
	(010)	($0\bar{1}1$)	0.075	1	5.60	4Ca(1),4Ca(2),4P	4Ca(1),3Ca(3),4G	2.77×10^{10}	64.8	124.8
	(010)	($0\bar{1}0$)	0.075	1	5.40	4Ca(1),4Ca(2),4P	2Ca(2),2Ca(3),2M,2G	2.77×10^{10}	64.8	124.8
			5 more matches between 5.02 and 4.59							

Results obtained with program MATCH2. Thickness of slice through structure = 2 Å total (1 Å out from central plane). Motif radius = 6.0 Å. Input was results of MATCH1 calculations (tables 2 and 3). Atoms were included in an atom's motif when their distance to the motif-defining atom was within factor of 1.25 of nearest distance for atoms of that type to central atom. Vectors in different motifs must match within 15 percent in length and have the same sign for the charge product of the atoms defining the vector before they can be considered to be matched. Compound A is $Ca_5(PO_4)_3OH$. Compound B is specified at the left hand side of table 4.

Contact planes and sort key are as given in table 3. The ordinal number of the match in the output from MATCH1 (sorted on the sort key) is given in the sort order column.

[a] Merit figure includes allowing for only half occupancy of Ca(4) site.

This will not be true if for example a structure contains an appreciable number of water molecules, as in the hydrated layer of $Ca_8H_2(PO_4)_6 \cdot 5H_2O$. However, the merit figures will be meaningful if the major features of at least one of the structures are adequately represented by Ca and P positions. This is the case for the apatitic layer of $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ and is especially true for $Ca_5(PO_4)_3OH$ itself. Inclusion of the other structural features, such as the oxygen atoms in $Ca_5(PO_4)_3OH$, may mitigate against matches with high merit figures for Ca and P alone, but will probably not produce a higher merit figure (suitably scaled if necessary) than that obtained with Ca and P. A previously-mentioned example of obtaining a high merit figure with near zero probability of twinning when the oxygen atoms are considered [6] is the (100) plane of $Ca_5(PO_4)_3Cl$.

8. Feasible Cases of Epitaxy

Figure 3 shows the frequency of occurrence *vs.* interplane merit figure for the 364 inter-plane merit figures obtained in this study. Few cases of epitaxy have inter-plane merit figures greater than our proposed threshold value of 6.0. Those that do involve epitaxy between $Ca_5(PO_4)_3OH$ and $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, $Ca_5(PO_4)_3OH$ and $Ca_4O(PO_4)_2$, and $Ca_5(PO_4)_3OH$ and $Ca_5(PO_4)_2SiO_4$.
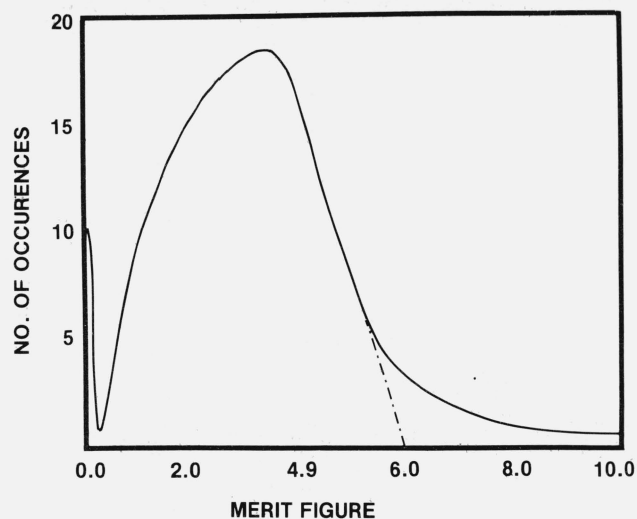

FIGURE 3. *Distribution of number of occurrences versus interplane figure-of-merit for calculations described in this paper.*

Table 5 shows the detailed atom:atom matching for the highest inter-plane merit figures for the various cases of epitaxy considered. For the $Ca_5(PO_4)_3OH/CaH_2(PO_4)_6 \cdot 5H_2O$ case with an inter-plane merit figure of 8.32, the detailed atom-atom matching is reasonable both chemically (as indicated by the magnitudes of the individual atom-atom matches and by visual inspection of the structures) and

TABLE 5. *Inter-motif figures of merit and correspondence of atoms for best fit cases in table 4.*

$Ca_8H_2(PO_4)_6 \cdot 5H_2O$ inter-plane merit figure = 8.32						
$Ca_5(PO_4)_3OH$	Ca1 [1]	Ca2 [1]	Ca5 [1]	Ca8 [1]	P9 [1]	P12 [1]
Ca1 [2]	97.8(2)	98.1(1)	79.5	75.0	37.2	51.4
Ca2 [2]	82.2	81.9	97.1(3)	89.5(4)	43.6	51.2
P [2]	59.8	59.4	51.2	52.1	70.9(6)	86.0(5)
$Ca_4O(PO_4)_2$ inter-plane merit figure = 7.98						
$Ca_5(PO_4)_3OH$	Ca5 [1]	Ca6 [1]	Ca7 [1]	Ca8 [1]	P3 [1]	P4 [1]
Ca1 [2]	84.8	81.2	93.3(2)	93.3(1)	56.2	53.8
Ca2 [2]	81.0(6)	81.5(5)	78.6	78.9	56.9	57.9
P [2]	62.8	65.6	55.4	55.9	89.5(4)	91.7(3)
$Ca_4O(PO_4)_2$ inter-plane merit figure = 7.70						
$Ca_5(PO_4)_3OH$	Ca1 [1]	Ca2 [1]	Ca3 [1]	Ca4 [1]	P1 [1]	P2 [1]
Ca1 [2]	94.6(1)	86.8(4)	84.9	77.3	28.0	54.7
Ca2 [2]	78.0	74.6	82.1(5)	92.0(3)	26.6	56.3
P [2]	57.4	50.7	58.1	47.6	63.5(6)	92.7(2)

CaHPO$_4$ inter-plane merit figure = 5.84				
$Ca_5(PO_4)_3OH$	Ca1 [3]	Ca2 [3]	P1 [3]	P2 [3]
Ca1 [4]	67.4(8)	68.6(5,6,7)	52.3	53.1
Ca2 [4]	62.7(9,10)	62.7	46.7(11,12)	47.7
P [4]	55.1	53.4	77.2(4)	77.5(1,2,3)

CaHPO$_4$ inter-plane merit figure = 5.42

Ca$_5$(PO$_4$)$_3$OH	Ca1 [4]	Ca2 [4]	P1 [4]	P2 [4]
Ca1 [6]	62.9	<u>67.1</u>(7,8,9,10)	<u>43.2</u>(15,16)	43.6
Ca2 [6]	<u>63.4</u>(11,12,13,14)	64.5	38.6	39.1
P [6]	50.6	49.6	<u>74.1</u>(5,6)	<u>74.2</u>(1,2,3,4)

CaHPO$_4$·2H$_2$O inter-plane merit figure = 2.85

Ca$_5$(PO$_4$)$_3$OH	Ca [4]	P [4]
Ca1 [6]	46.3	<u>69.8</u>(1,2,3,4)
Ca2 [12]	<u>68.8</u>(5,6,7,8)	47.2
P [9]	0.0	27.0

Ca(H$_2$PO$_4$)$_2$·H$_2$O inter-plane merit figure = 2.73

Ca$_5$(PO$_4$)$_3$OH	Ca1 [3]	P1 [3]	P2[3]
Ca1 [4]	<u>64.3</u>(1,2,3)	41.6	34.9
Ca2 [6]	52.3	32.3	34.2
P [6]	38.7	<u>58.7</u>(7,8,9)	<u>59.7</u>(4,5,6)

β-Ca$_3$(PO$_4$)$_2$ inter-plane merit figure = 5.65

Ca$_5$(PO$_4$)$_3$OH	Ca3 [6]	Ca4 [2]	Ca5 [2]	P2 [6]
Ca1 [4]	<u>77.6</u>(1,2,3,4)	62.1	59.5	35.0
Ca2 [6]	<u>75.2</u>(5,6)	66.9[a](12,13)	<u>57.2</u>(15,16)	36.1
P [6]	52.6	37.0	27.9	<u>72.2</u>(7,8,9,10, 11,12)

Ca$_5$(PO$_4$)$_2$SiO$_4$ inter-plane merit figure = 6.70

Ca$_5$(PO$_4$)$_3$OH	Ca2 [2]	Ca3 [2]	G [2]
Ca1 [2]	77.6	<u>77.6</u>(3,4)	49.3
Ca2 [2]	<u>77.7</u>(1,2)	75.0	44.6
P [2]	43.8	57.4	<u>73.6</u>(5,6)

Ca$_5$(PO$_4$)$_2$SiO$_4$ inter-plane merit figure = 6.25

Ca$_5$(PO$_4$)$_3$OH	Ca2 [6]	Ca3 [6]	G [6]
Ca1 [4]	75.2	<u>82.0</u>(1,2,3,4)	53.5
Ca2 [6]	<u>77.8</u>(11,12,13, 14,15,16)	74.4	52.5
P [6]	39.9	54.3	<u>80.8</u>(5,6,7,8,9,10)

Atom labels are for crystallographically different atoms, i.e., those which have different chemical environments. These labels are given as Ca(1) etc. in table 4 and as Ca 1 etc. here. Thus Ca 1 [2] means that two Ca 1 atoms have been included in the slice. The atoms in Ca$_5$(PO$_4$)$_3$OH are given down the left hand side of each small table and the atoms in the other compound are given along the top. Individual atom-atom matchings were accomplished by considering the highest individual inter-motif figures-of-merit and the number of each atom type available. The individual inter-motif figures-of-merit used in calculating the inter-plane merit figure are underlined. The order in which the matches were made is given in parentheses, e.g., 98.1 (1) was the first atom match used for Ca$_5$(PO$_4$)$_3$OH/Ca$_8$H$_2$(PO$_4$)$_6$·5H$_2$O.

[a] Must be reduced by 50 percent in summing for merit figure because only half of the Ca(4) sites are occupied.

spatially, as is shown by the map in figure 4. The epitactical relationships involving all atoms in the crystal structure is shown in three dimensional form in figure 5. Evidence for this case of epitaxy was found first by Brown et al. [23] and later by Brown et al. [24]. Figures 6 and 7 show the detailed atom:atom matching in the contact slices for the two significant matches between Ca$_5$(PO$_4$)$_3$OH and Ca$_4$O(PO$_4$)$_2$. The fit is obviously good in both cases. These cases have not yet been found in practice.
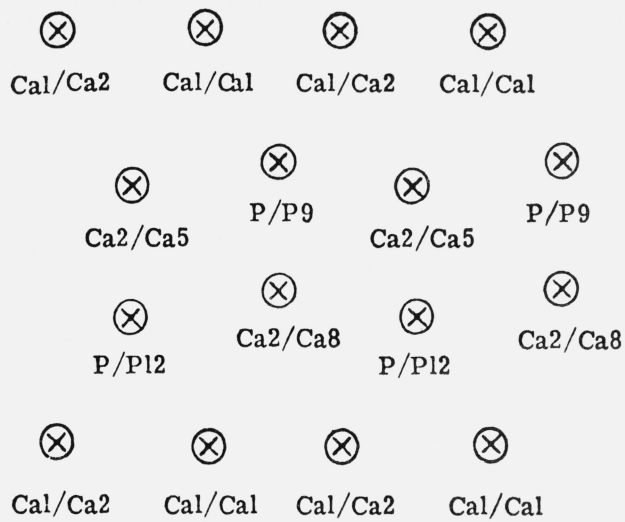
⊗ ⊗ ⊗ ⊗
Cal/Ca2   Cal/Cal   Cal/Ca2   Cal/Cal

⊗   ⊗   ⊗   ⊗
P/P9   P/P9
Ca2/Ca5   Ca2/Ca5

⊗   ⊗   ⊗   ⊗
          Ca2/Ca8   Ca2/Ca8
P/Pl2   P/Pl2

⊗   ⊗   ⊗   ⊗
Cal/Ca2   Cal/Cal   Cal/Ca2   Cal/Cal

FIGURE 4. *Epitaxy between contact planes* (010) *in* $Ca_5(PO_4)_3OH$ *and* (100) *in* $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ *for merit figure* 8.32.

First set of labels signifies atoms in the former at location X; second set of labels signifies atoms in the latter at location O. In this case the relative atomic positions are essentially superimposed.
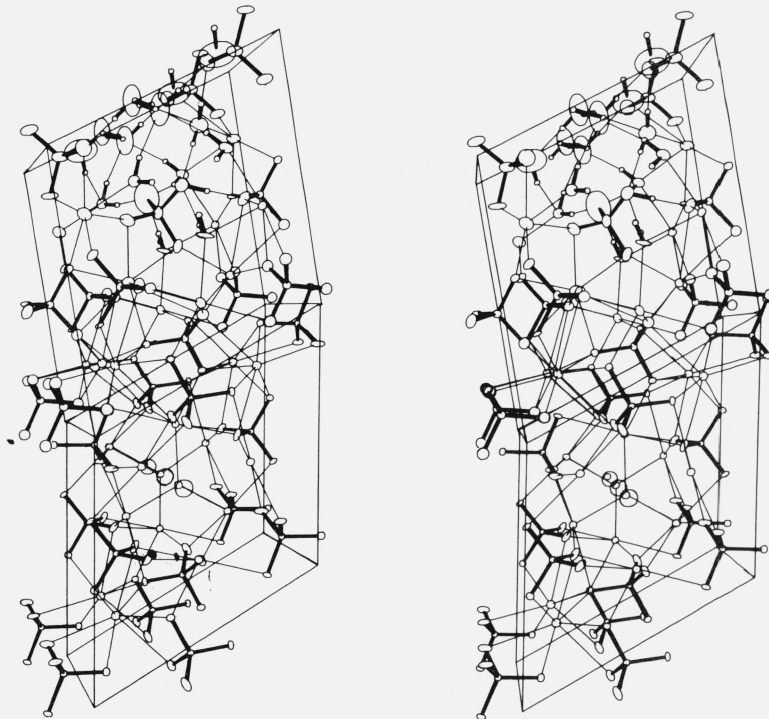
FIGURE 5. *A stereoscopic illustration of epitaxy between* $Ca_5(PO_4)_3OH$ *and* $Ca_8H_2(PO_4)_6 \cdot 5H_2O$.
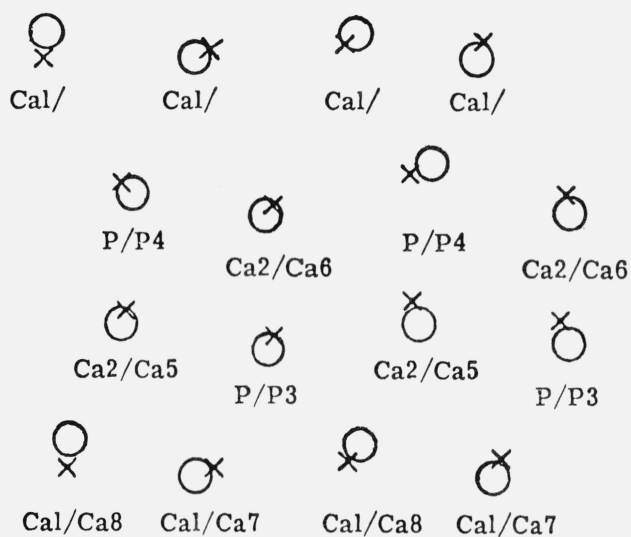
FIGURE 6. *Epitaxy between contact planes* (010) *in* $Ca_5(PO_4)_3OH$ *and* (010) *in* $Ca_4O(PO_4)_2$ *for merit figure* 7.98.
Labelling as in figure 4.

FIGURE 8. *Epitaxy between contact planes* (010) *in* $Ca_5(PO_4)_3OH$ *and* (100) *in* $Ca_5(PO_4)_2SiO_4$ *for merit figure* 6.70.
Labelling as in figure 4. The fit over the whole surface is not particularly good. G refers to a general position in $Ca_5(PO_4)_2SiO_4$ which is occupied by both P and Si atoms.

FIGURE 7. *Epitaxy between contact planes* (010) *in* $Ca_5(PO_4)_3OH$ *and* (010) *in* $Ca_5(PO_4)_2SiO_4$ *for merit figure* 7.70.
Labelling as in figure 4.

9. Unlikely Cases of Epitaxy

The next highest inter-plane merit figures (table 5) involve epitaxy between $Ca_5(PO_4)_3OH$ and $Ca_5(PO_4)_2SiO_4$. Comparison of the correspondences in table 5 for the inter-plane merit figure 6.70 reveals a need for visual supervision of the procedure (suitable plots are produced by the computer program). In table 5, Ca(1) in $Ca_5(PO_4)_3OH$ is matched with Ca(3) in $Ca_5(PO_4)_2SiO_4$, while Ca(2) in the former is matched with Ca(2) in the latter. Figure 8 shows that this is unrealistic. The matches Ca(1):Ca(2) at 77.6 and Ca(2):Ca(3) at 75.0 could have been taken instead with
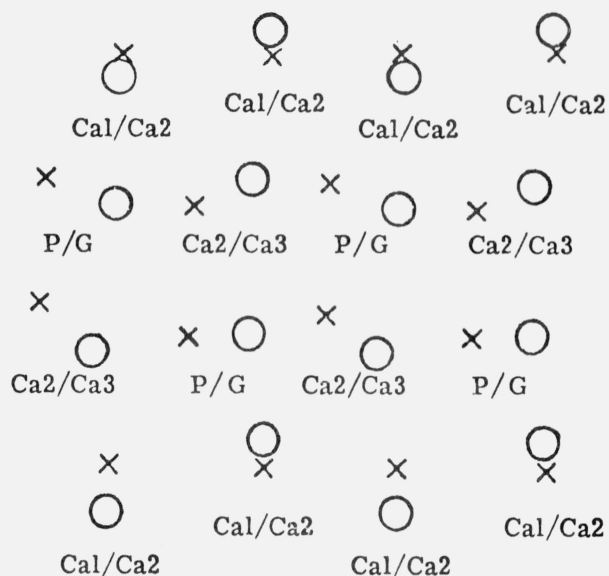
essentially no change in the overall merit figure. (There is some uncertainty in the matching process where individual atom matches are within ~5 units of one another.) Figure 8 also shows that this match is unlikely to produce a viable case of epitaxy because the atomic patterns taken as wholes over the contact planes rather than an atom environment at a time can be seen not to match especially well. We have a choice of matching the Ca strings running horizontally at the top and bottom of figure 8 or matching the Ca/P and Ca/G strings in the middle of figure 8.

Figure 9 contains the atoms involved in the second case of possible epitaxy in table 5 for $Ca_5(PO_4)_3OH$ and $Ca_5(PO_4)_2SiO_4$. There is no obvious correspondence between the atomic patterns.

According to our filtering procedure, the best case for $CaHPO_4 \cdot 2H_2O$ is a lowly 2.85. The possibilities suggested by Francis and Webb [25] for epitaxy between $Ca_5(PO_4)_3OH$ and $CaHPO_4 \cdot 2H_2O$ did not survive the filtering process in the generation of matching nets because the differences in their net angles are ~10°, whereas a maximum of 7° had to be used to cut the number of matching nets down to manageable proportions (<1000). Their possibilities were treated as special cases and are shown as such in table 6. The fact that the highest merit figure is only 3.84 suggests on a quantitative basis that experimental realization of these hypothetical cases is very unlikely, and that growth of an extensive, oriented and cohesive film of $Ca_5(PO_4)_3OH$ on $CaHPO_4 \cdot H_2O$ (or *vice versa*) is not a significant factor in the
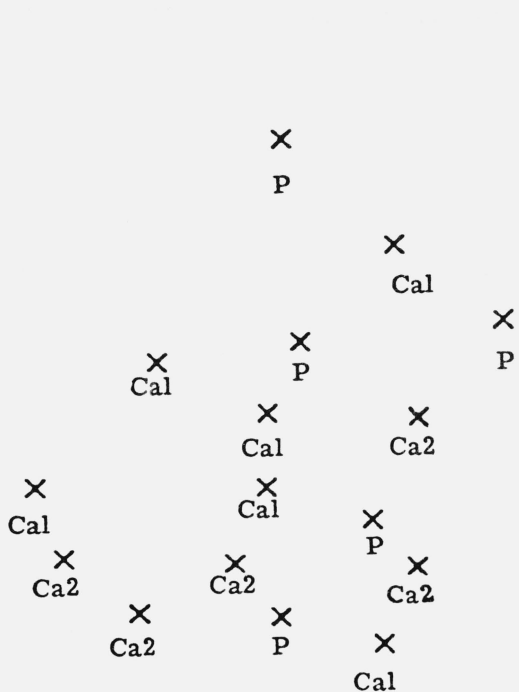
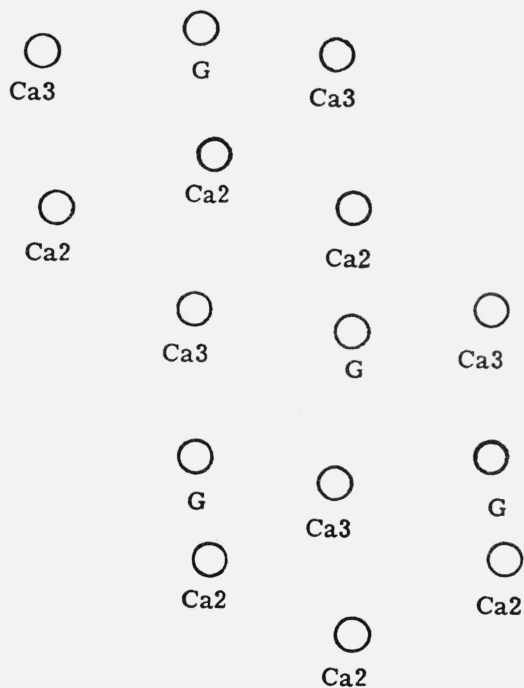FIGURE 9a. *Atomic arrangement on* $(1\overline{2}\overline{2})$ *plane of* $Ca_5(PO_4)_3OH$.

FIGURE 9b. *Atomic arrangement on* (010) *plane of* $Ca_5(PO_4)_2SiO_4$.
G refers to a site which is occupied by both P and Si atoms.

TABLE 6. *Francis and Webb suggestions for*
$Ca_5(PO_4)_3OH/CaHPO_4\cdot2H_2O$ *epitaxy.* *

| Contact planes | | Net | vectors | Lengths and angles | | | | | | Sort | Areas,Å^2 | | Disloc., |
A	B	A	B	A		B		A	B	key	A	B	cm^{-2}
1 (010)	(010)	[101,001]	[100,001]	11.66Å	6.88Å	5.81Å	6.24Å	53.84°	63.58°	0.276	64.79	32.47	3.60×10^{12}
2 (110)	(110)	[1$\overline{1}$0,001]	[$\overline{1}$10,001]	16.31Å	6.88Å	16.25Å	6.24Å	90.00°	80.85°	0.236	112.21	100.12	2.20×10^{11}

Atom matching *

Matching Net 1				Matching Net 2
Merit figure = 3.84		Merit figure = 3.52		Merit figure = 2.55
Ca [2]	P [2]	Ca [2]	P [2]	
Ca 2 [2] 68.5 (1,2)	32.4	Ca 1 [2] 56.0 (3,4)	28.6	Ca [4]
P [2] 48.7	56.1 (3,4)	Ca 2 [2] 51.8	29.9	Ca 1 [4] 71.4 (1,2,3,4)
		P [2] 41.4	58.2 (1,2)	

A colums–$Ca_5(PO_4)_3OH$; B columns–$CaHPO_4\cdot2H_2O$

*$Ca_5(PO_4)_3OH$ atoms vertical, $CaHPO_4\cdot2H_2O$ atoms horizontal. Subsets accepted in these calculations.

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biological growth of $Ca_5(PO_4)_3OH$-like material. The atomic correspondencies given in table 6 and as placed in our unpublished plots are very poor.

Similar results [26] suggest that $Ca(H_2PO_4)_2 \cdot H_2O$, found to be the predominant new solid phase formed in acid-etching of teeth, probably does not enter into an epitactical relationship with $Ca_5(PO_4)_3OH$. β-$Ca_3(PO_4)_2$ and $CaHPO_4$ have about the same merit figure for epitaxy with $Ca_5(PO_4)_3OH$. The case judged to be most likely from the present procedure for $CaHPO_4$ was also suggested from visual inspection of the structures by Brown et al. [1]. Our present results suggest that the action of depositing $Ca_5(PO_4)_3OH$ on $CaHPO_4$ [27] and $Ca(H_2PO_4)_2 \cdot H_2O$ on $Ca_5(PO_4)_3OH$ arises strictly from heterogeneous nucleation of the surface phases on solid particles, the various nuclei forming an incoherent film which then mechanically blocks access from the surrounding solution to the interior of the particles. It is also doubtful at this point whether β-$Ca_3(PO_4)_2$ will enter into an epitactical relationship with $Ca_5(PO_4)_3OH$.

10. Merit Figure Required for Epitaxy

We can now provide some context to aid in the assessment of merit figures. A distribution of the 364 merit figures obtained in this study was given in figure 3. The maximum, centered about a merit figure of approximately 3.0, may be ascribed to random matches. Our previous lower bound of 6.0 leaves only a few cases for serious consideration. The lower bound for reasonable expectation of epitaxy in these calculations is 7.70, found for $Ca_5(PO_4)_3OH/Ca_4O(PO_4)_2$. A lower bound of 6.0 is therefore a reasonably conservative estimate, and it is in keeping with an extrapolation of the upper side of the maximum in figure 1 to zero cases. Note, however, that the magnitudes of the merit figures depend on the percentages of the structures used and are related to the number of atoms in a slice per unit area of that slice. Therefore each investigation must provide context in which to judge the magnitudes of the merit figures. It is good practice to calculate figures of merit for some random matches to provide information on the merit figure distribution.

11. Implications of Quantitative Estimations of Epitaxy

Quantitatively evaluating both the atomic correspondence and the misfit of the net angles and repeat distances associated with the contact planes provides insight into the nature of the overgrowth and its properties. Well matched atomic patterns indicate the possibility of the formation of a extensive coherent film under conditions where both members of the epitactical pair are stable. Such a film would be well attached with a small surface area, and would be as kinetically reactive as macroscopically-sized samples of the pure substance. It would be the favored choice and perhaps even unavoidable. Such cases would be important in nonstoichiometric precursor formation and ubiquitous twinning. On the other hand, cases with poorly matched patterns would be expected to provide a mixture of phases or thin, mechanically weak films spreading through dendritic growth. Such films would have high surface area and hence enhanced kinetic reactivity. They would be important only under drastic conditions of crystallization.

12. Summary

A procedure for generating and examining possible cases of epitaxy and twinning has provided a general and quantitative estimate of the relative probabilities of occurrence. The present procedure filters out unlikely candidates leaving the more probable cases for detailed examination. Such examination should include an assessment of the compatibility of the complete crystal structures in the vicinity of the contact plane. Realistic evaluation of the relative probability of occurrence for examples of twinning which have the same contact plane for both components of the twin will require that twinning operations be performed on large structural slices before their compatibility is evaluated. Up to this point such twinning modes have mainly been used here to provide upper bounds for the merit figures.

Our examination of possible $Ca_5(PO_4)_3OH$ twins suggests that twinning on the same contact plane is more likely than twinning that results from different contact planes for each twin component. The twinning mode using the same contact plane requires no dislocations due to misfit at the interface and favors coherent growth. Relative merit figures suggest that twinning on (111) is more likely than twinning on (103). Unfortunately there is not enough experimental data available to check this prediction.

Evaluation of proposed epitaxies between $Ca_5(PO_4)_3OH$ and other calcium phosphates indicates that the highest probabilities for epitaxy are between $Ca_5(PO_4)_3OH$ and $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, $Ca_5(PO_4)_3OH$ and $Ca_4O(PO_4)_2$, and $Ca_5(PO_4)_3OH$ and $Ca_5(PO_4)_2SiO_4$. Of these, the first is the most likely and is probably unavoidable under conditions where $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ is stable, the second has not yet been found, and the last is unlikely as suggested by figures 2-7. Possible epitaxies between $Ca_5(PO_4)_3OH$ and $CaHPO_4$ or β-$Ca_3(PO_4)_2$ are significantly less likely than epitaxy between $Ca_5(PO_4)_3OH$ and $Ca_4O(PO_4)_2$ on the basis of relative merit figures.

Epitaxy tests between $Ca_5(PO_4)_3OH$ and $CaHPO_4 \cdot 2H_2O$ or $Ca(H_2PO_4)_2 \cdot H_2O$ gave merit figures which suggest that these cases are no better than a random match. Any deposition of these phases on one another will form incoherent films which then mechanically block access of the surrounding solution to the interior.

similar as possible. There is some iteration in origin shift between the two structures to minimize the mismatch.

Much of the above procedure is working correctly in a prototype program. Copies of all programs mentioned in this paper are available from the authors.

13. Note on Matching of Complete Patterns

To consider identity matches in twinning and the interlocking of complete interfacial planes in epitaxy and twinning, a third step in this series is desirable. That step would use as a starting point the planes found here and would attempt to estimate the degree-of-fit between slices through the complete structures, including for example the oxygen atoms in calcium phosphates. The procedure could be as follows: cell parameters, symmetry elements and atomic positions are used to generate a full unit cell of atoms in orthogonal coordinates for each of the two crystal structures to be compared. Unit cell vectors defining the slices through the structure, usually obtained from MATCH1 and MATCH2, or possibly from inspection of the structure, are used by the program to calculate various statistics (as described for MATCH1) for the planes. The normals to these planes are used to bring the two structures into alignment so that the planes to be compared are parallel to one another. The structures are rotated about the plane normals according to the requirements of superimposing a short $(\geqslant 3)$ list of "matching atoms" usually obtained from MATCH2. The mirror images of one of the initial structures is also considered if the trial atoms can not be matched. Various diagnostic messages concerning any misfits are provided.

An attempt is then made to optimize the superposition of the slices in the two structures. The distances between "matching" atoms with the same alphabetic label (e.g., Ca) are calculated and, before being summed, are weighted by a heuristically designed quantity incorporating the product of the assigned atomic charges. The two slices are maneuvered over one another until the weighted sum of distances over all matching atoms is a minimum.

The contents of the slice are then filled out using the complete crystal structure. Atoms in rigid bodies such as PO_4 are given their complete rigid body. Finally, the completed slices are maneuvered over one another and various merit figures are provided. These figures are based on charge and distance mismatch when the two slices are superimposed. The requirement is that the two slices be as

14. References

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