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Twinning in Relation to Structural Detail in $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$, 'Cadmium Chlorapatite'

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Synthetic $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$ ('cadmium chlorapatite') was found to be twinned by merohedry. Of the two possible forms of twin mirrors, $.m' = \{1\bar{2}10\}$ and $.m' = \{1\bar{1}00\}$, $.m'$ can be ruled out structurally because it requires too short interatomic distances across the expected composition surface, which is made up of planar segments parallel with the faces of $\{1\bar{2}10\}$. The space-group symmetry of the twin is therefore $P6_3/mc'm'$ rather than $P6_3/mm'c'$. Chemically the cadmium analogue of calcium chlorapatite, cadmium chlorapatite is isostructural with calcium fluorapatite, in which the authors observed no such twinning. With the acceptable twin law $.c'm'$ the distance between nearest oxygen atoms across the composition surface would be shorter in calcium fluorapatite (1.8 Å) than it is in cadmium chlorapatite (2.0 Å). Re-positioning displacements of the phosphate groups would also be larger in calcium fluorapatite than in cadmium chlorapatite in the process of twin formation.

Introduction

In a structure investigation of 'cadmium chlorapatite', $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$, with X-ray data (Sudarsanan, Young & Donnay, 1973), it was found that the specimens are twinned by merohedry. The structural detail reported in the previous paper has led us to examine the *atomic arrangement* to try to answer the following questions. Firstly, can one twin law be selected over another possible one, which would be equivalent if only the *lattice* were considered? Secondly, why is this twinning by merohedry less fre-

quently observed in the isostructural calcium fluorapatite?

Nature of the twinning

It is known (see, for instance, Friedel, 1904 or 1926) that twinning by merohedry, found here in cadmium chlorapatite, can occur whenever the point symmetry of the crystal is lower than that of the lattice. For point group $6/m$ the hexagonal lattice, with point symmetry $6/m\ 2/m\ 2/m$, possesses twelve additional symmetry operations, *viz.* two sets of three rotations and three reflections each, expressed by the $2/m$ sym-

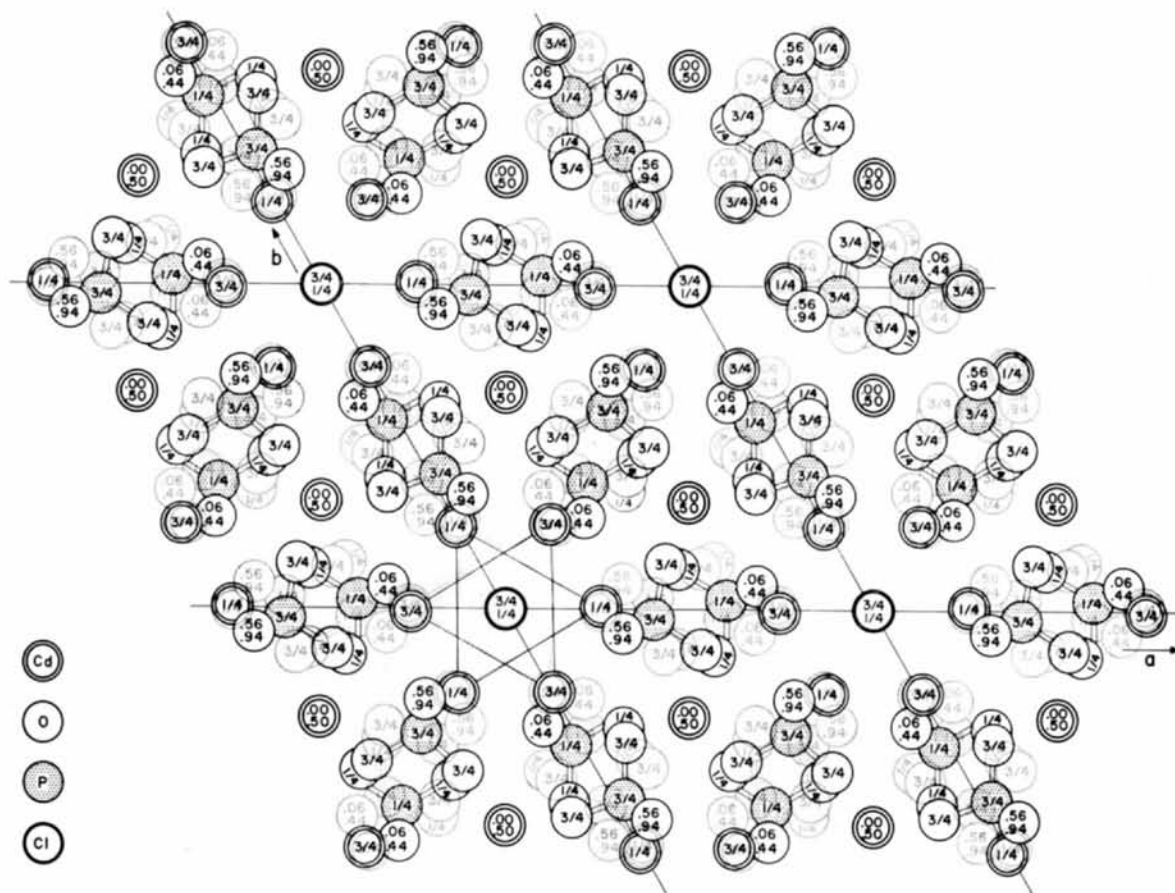


Fig. 2. Superimposed basal plane projections of atomic arrangements in two cadmium chlorapatite crystals twinned by reflection in $. . m'$. In this figure, Cd_I is shown at the average position for the two structures, the individual positions being $z = 0.0053$ and 0.4947 and $z = 0.9947$ and 0.5053 .

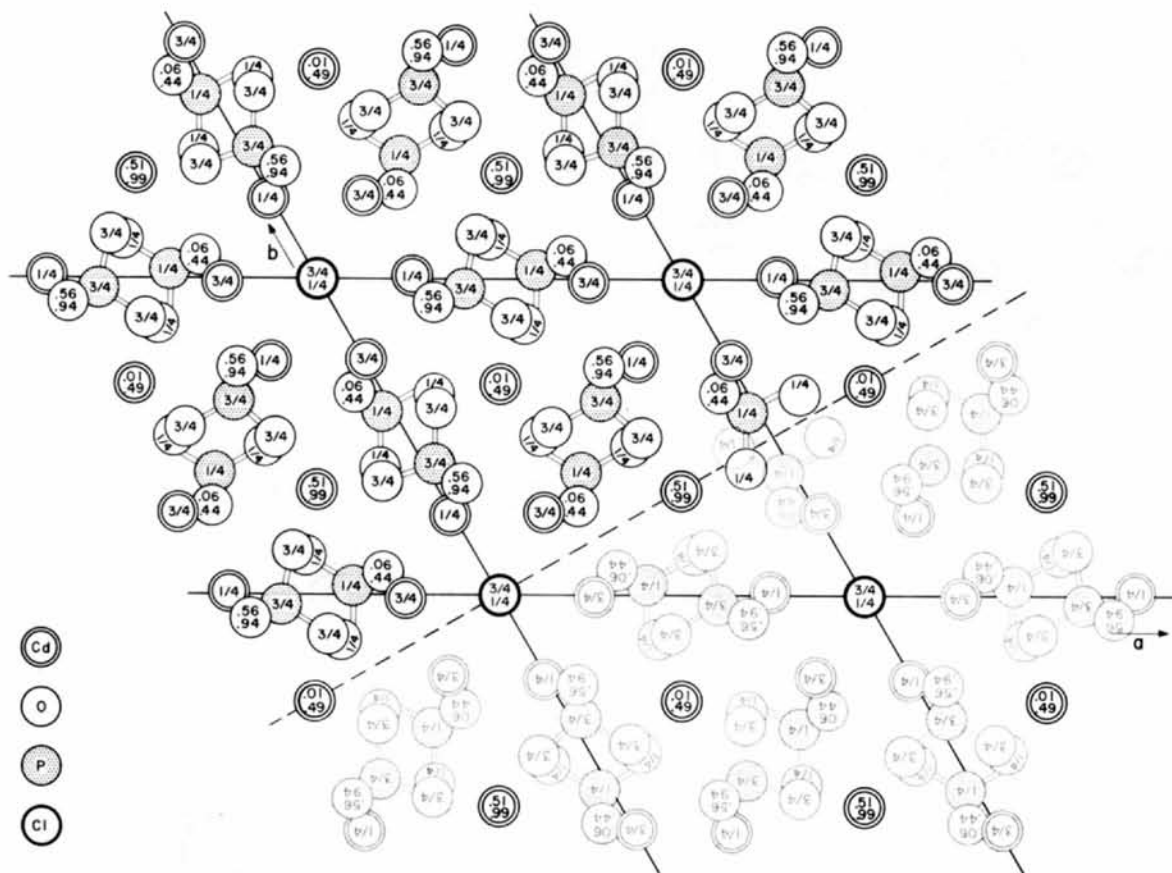


Fig. 3. Atomic arrangements for a $(1\bar{2}10)$ composition plane (dashed line) between crystals twinned by reflection in $.m'$, or glide reflection in $.c'$. (Note that the dashed line is also the trace of one of the $.m'$ twin planes.)

bols in the last two columns of the Hermann-Mauguin notation. Any one of these twelve additional symmetry operations brings the lattice (though not the crystal) to self-coincidence and thus qualifies as a twin operation. In this classical point-group theory of twinning, the twelve simultaneous twin operations produce one and the same twinned orientation, and the twin symmetry is written $6/m\ 2'/m'\ 2'/m'$ in black-white symbolism, where primed elements indicate twin elements (Curien & LeCorre, 1958; Curien & Donnay, 1959).

If, however, the space-group symmetry of the crystal structure, in contradistinction to its point-group symmetry, is taken into account, two distinct twin laws must be recognized; they correspond to the two sets, $.2/m.$ and $.2/m.$, of additional symmetry operations of the lattice.* For simplicity we can designate the twin laws by the twin mirror planes, $.m' = \{1\bar{2}10\}$ and $.m' = \{1\bar{1}00\}$. It is of course understood that the twofold twin axes could equally well be used since the product of a twin reflection ($.m'$ or $.m'$) by the inversion through the symmetry center of the crystal is equal to a 180° twin rotation ($.2'$ or $.2'$). It can likewise be seen (Figs. 1 and 3) that the product of a twin reflection in $.m'$ by a 60° screw rotation around the 6_3 axis of crystal symmetry is equal to a twin glide reflection in $.c'$; similarly the second twin law (Figs. 2 and 4), which we have defined by a reflection in $.m'$, can also be expressed by a glide reflection in $.c'$. Consequently the two distinct twins have the following space-group symmetries: $P6_3/mm'c'$ and $P6_3/mc'm'$.

The experimental means available to distinguish such a twin from a single crystal and to establish whether one or both twin laws are present on a given specimen are somewhat restricted. Since twinning by merohedry brings both the optical indicatrix and the crystal lattice to self coincidence it cannot be detected either by means of optical methods or from observations of the positions of the maxima in X-ray diffraction patterns. The diffracted intensities, however, are affected by twinning through the resultant interchange of atomic coordinates. That fact has been used in the preceding paper (Sudarsanan *et al.*, 1973) to separate the intensity contributions from the two crystals in the twin and, hence, to proceed with the refinement of the structure.

To produce twinned crystal *B* from original crystal *A*, the first twin law, which can be considered a glide reflection in $.c'$, changes x, y, z to $y, x, z + \frac{1}{2}$; the second, defined as reflection in $.m'$, changes x, y, z to y, x, z . As is obvious from these coordinates, the two twin laws differ from each other only in that the first law shifts crystal *B* by $c/2$ with respect to crystal *A*, whereas

the second does not. It follows that the X-ray reflection intensities of the twin will be the same for either twin law operating singly and uniting two crystals, or for both laws occurring jointly and uniting crystal *A* to two antiphase domains, *B* and *B'* (the volume of crystal *A* being kept at the same fraction of the total volume of the twin in all cases). Conditions at the composition surface between the two crystals in the twin, however, are not necessarily the same for both twin laws; the distances of closest approach of atoms of crystal *A* to atoms of crystal *B* can differ. Thus a knowledge of the structural details might enable one of the two twin laws to be ruled out, should this law require improbable closest approaches of atoms across the composition surface. The required detail can be visualized from diagrammatic superpositions of the twin-related structures (Figs. 1 and 2).

Atomic scale aspects of twinning

The composition surface in relation to the twin law

Macroscopically the composition surface can be expected to be irregular, from the well known fact that most twins by merohedry are penetration twins. On the atomic scale, however, any surface that contains three atomic centers not separated by other atoms will, by definition of a plane, comprise a planar segment. The composition surface, whether macroscopically planar or irregular, can be composed of such tiny planar segments. To determine what these segments are, in the case of cadmium chlorapatite, we look for atoms that are restored by the twin operation, that is to say, atoms that occupy the same positions in twinned crystal *B* as they would occupy in original crystal *A* had it remained untwinned.

The Cl atoms constitute lattice complex $00\frac{1}{2}P_c$, which is realized in position $2(a)\bar{6}$ in space group $P6_3/m$. The points of this complex occupy the nodes of a hexagonal primitive lattice whose cell must be doubled in height to match the cell of the space group and must be translated by $c/4$ to coincide with the latter*. This lattice complex is invariant under both twin laws considered above.† It follows that the composition surface will contain Cl atoms, regardless of which twin law is selected.

The Cd₁ atoms form lattice complex $E2z$, which, in this space group, is materialized in position $4(f)3$. The points of $E2z$ are easily visualized as making two vertical dumb-bells centered on the (unoccupied) points of an h.c.p. arrangement *E*; their coordinates are $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4}-0.24)$. [Note that $\frac{1}{4}-0.24$ is the *z* parameter of the $4(f)3$ position.] These points are invariant under the first twin law, $.m'c'$, in which case

* This symbolism, which is used here for the first time to designate simultaneous twin operations, is based on the Hermann-Mauguin symbol for the point symmetry of the lattice. The dots, in such symbols as $.2/m.$ and $.2/m.$, serve to identify the orientation of the symmetry direction $2/m$ with respect to $6/m\ 2/m\ 2/m$.

* In the symbol $00\frac{1}{2}P_c$ the *P* describes the complex, the subscript indicates that *c* must be doubled to go from the complex to the space group, and $00\frac{1}{2}$ represents the shift vector (see, for instance, Hellner, 1965).

† For applications of the concept of lattice complex to the theory of twinning, see for instance Donnay & Curien (1960).

they could be contained in the composition surface (see Fig. 3, where the dashed line is the twin mirror passing through Cl and Cd_I atoms; those parts of the twin plane that do not intersect oxygen atoms could, therefore, become planar segments of the composition surface). If we now consider the second twin law, $.c'm'$, in which the same twin plane is a glide plane c' (Fig. 4), we see that two Cd_I atoms lying on this plane, at heights 0.51 and 0.99, in crystal *A* will have to produce two more Cd_I atoms, at heights 0.01 and 0.49, in crystal *B*, as a requirement of the twin operation. It is, of course, impossible for these four atoms to co-exist: there is room only for two. They could belong to crystal *A* or to crystal *B*, in which case the composition surface would have to twist round them; or, more likely, the cadmium atoms with their centers in the twin plane, being solicited by conflicting forces to locate themselves at 0.51 and 0.49, will settle at 0.50; and likewise those that are to go at +0.01 or -0.01 will settle at 0.00.* It follows that, in the second twin law of cadmium chlorapatite as in the first one, the composition surface can be made up of planar segments, connecting strings of Cl and Cd_I atoms (Fig. 5). Possible planar segments are those belonging to the form $\{\bar{1}\bar{2}10\}$, all of which are parallel to the *c* axis. It is clear that (0001) planar segments are also possible, passing through Cd_I atoms at $z \sim 0$ or $z \sim \frac{1}{2}$. The planar segments available on the atomic scale will enable any composition surface, no matter how irregular on the macroscopic scale, to be accounted for.

The compatibility of the two twin laws with the composition surface in the crystal structure

Consider first the twin law $.m'c'$ (Fig. 3). For a single composition plane ($\bar{1}\bar{2}10$), which is here a twin mirror, oxygen atoms O_{II} with the same *z* coordinate, e.g. $\frac{1}{4}$, approach each other too closely ($\leq 1\text{Å}$) across the composition plane. For a (0001) composition plane, similar close approaches occur. For instance, for (0001) at $z = \frac{1}{2}$, the oxygen atom at 0.34, 0.26, 0.44 in the first crystal comes too close ($\sim 1\text{Å}$) to an oxygen atom at 0.26, 0.34, 0.56 in the second crystal (Fig. 1). For a composition surface made up of planar segments connecting chlorine and cadmium atoms (as shown in Fig. 5 for the other twin law), the following closest approaches across the composition surface are found: 1.8 Å between O_{III} atoms (two such distances per cell), 1.9 Å between O_{II} atoms, and 2.25 Å between Cd_{II} atoms (in metallic cadmium $\text{Cd}-\text{Cd} = 2.98\text{Å}$). For such an irregular composition surface, made up of planar segments that intersect in strings of Cl ions, the angle at which two segments meet may be 60° , 120° or 180° . In the cases of the 60° and 180° angles, the coordina-

tions of the Cl ions would be changed: instead of each Cl ion having three Cd_{II} neighbors at the same level, as in the single crystal, one Cl ion then would have four Cd_{II} neighbors and the other would have two. If the angle of intersection were 120° , each Cl ion would retain coordination number 3, but the Cd_{II} ions with the same *z* value would no longer form an equilateral triangle; they would form a right angled triangle instead, with the Cl ion at the midpoint of the hypotenuse. Such arrangements are clearly energetically different from the coordination scheme in the single crystal and therefore improbable.

Consider now the twin law $.c'm'$ (Figs. 2 and 4). The closest approach across either type of composition plane, ($\bar{1}\bar{2}10$) or (0001), is found to be equal to $\sim 2.0\text{Å}$, between two O_{III} atoms. The radial distribution of the six pairs of PO_4 tetrahedra around a 6_3 axis remains very nearly the same as in the single crystal (Fig. 4, upper left) when the 6_3 axis lies in the composition surface and three of the six pairs belong to crystal *A* and three to crystal *B* (Figs. 4 and 5). The alternation of levels, from $\frac{1}{4}$ to $\frac{3}{4}$, which is achieved by the 60° screw rotation around 6_3 in the single crystal, can be produced by the glide reflection in the $.c'$ twin plane, part of which is a planar segment of the composition surface. The chlorine and cadmium atoms located on this boundary surface continue to have the same kind of nearest neighbors, first coordination numbers and approximate distances from other atoms. The $\text{Cd}_{II}-\text{Cd}_{II}$ distance, in particular, remains the same. We thus see that the second twin law, $.c'm'$, is also acceptable from the point of view of energy considerations: the composition surface respects the integrity of the PO_4 groups (no strong bonds broken or disturbed), the interatomic distances of closest approach across it are not too short, and the first coordination conditions of the boundary atoms remain essentially unaltered (Buerger, 1945).

Rarity of twinning in hexagonal calcium apatites

Twinning by merohedry in calcium apatites is mentioned as 'reported' in Dana's *System of Mineralogy* (Palache, Berman & Frondel, 1951), but it is given after two other twin laws, both of which are characterized as *rare*, so that the implication is clearly made that twinning by merohedry, ($10\bar{1}0$), is doubtful or unconfirmed. Indeed we have not observed it either in any of the tens of samples of calcium fluor-, chlor- and hydroxylapatites we have examined for structure studies.† On the other hand, in the one batch of cadmium chlorapatite available to us, twinning by mero-

* This prediction is made confidently in view of the analogous situation found in marcasite, which twins on (110) and on $\{10\}$, transforming to pyrite under conflicting forces at the intersections of twinning lamellae (Donnay, Kullerud & Donnay, 1971).

† Crystals of calcium chlorapatite are found to be twinned, but according to a different twin law (Mackie, Elliott & Young, 1972). In that case the twin consists of three interpenetrating crystals rotated 120° from each other about the common *c*-axis direction. The twin lattice is the superlattice, based on the double cell $a' = 2a$, $b' = b$, $c' = c$, $\gamma = 120^\circ$, which has hexagonal pseudo-symmetry. This is a case of twinning by reticular pseudo-merohedry, with twin index 2 and obliquity ~ 0 .

hedry was ubiquitous. The best proof of this is that we never found any single crystal for structural work, in spite of all our efforts.

Comparing the structure of cadmium chlorapatite with that of calcium fluorapatite (Young, Sudarsanan & Mackie, 1972), we look for a reason why twinning by merohedry is less frequent, perhaps absent, in the latter. We find that, in both cases, the metal ions undergo almost no re-positioning in twin formation. The displacements required of the other ions are larger in calcium fluorapatite than in cadmium chlorapatite (Table 1). These displacements are likewise larger in calcium hydroxylapatite and chlorapatite. Probably more important, however, is the fact that before allowance for any local elastic accommodation is made, the shortest O–O distance across the composition surface is 2.0 Å for cadmium chlorapatite, but only 1.8 Å for calcium fluorapatite. For repulsive forces dependent on the 6th power of the separation, this amounts to a factor of ~ 2 in O–O mutual repulsive force. However, elastic accommodation of neighboring-atom positions undoubtedly takes place. Taking the normal closest O–O approach to be 2.6 Å for unbonded atoms, one sees that the extent of elastic accommodation required is (2.6–2.0) *vs.* (2.6–1.8) or about one third greater in the calcium fluorapatite case. We conclude that the

required physical accommodation of atomic positions and coordination across the composition surface is significantly larger in the calcium apatites than in cadmium chlorapatite. It is thus taken as the factor that hinders twin formation.

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Table 1. *Displacements of atoms required for twin formation in calcium fluorapatite and cadmium chlorapatite*

Atom	Displacement in $\text{Ca}_5(\text{PO}_4)_3\text{F}$	Displacement in $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$
O _I and O _{II}	1.19 Å	0.96 Å
O _{III}	1.38	1.29
P	0.48	0.44

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Structure Cristalline de La_2GeS_5

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La_2GeS_5 is monoclinic, space group $P2_1/a$ with cell constants $a = 7.893$ (2), $b = 7.641$ (2), $c = 12.702$ (3) Å, $\gamma = 101.39$ (3)° and $Z = 4$. The crystal structure has been determined from General Electric XRD7 diffractometer data using Patterson and Fourier syntheses and refined by a least-squares method. The final R value is 0.053. This structure is made of two kinds of sheets parallel to the plane xOz : alternatively a sheet of tetrahedra $[\text{GeS}_4]_n$ and a sheet $[\text{LaS}]_{2n}$.

Introduction

Une nouvelle famille de combinaisons de terres rares de formule Ln_2SiS_5 et Ln_2GeS_5 a été mise en évidence par Michelet, Perez, Etienne & Darriet-Duale (1970). Ces composés n'existent qu'avec les lanthanides légers:

du lanthane au néodyme dans le cas des dérivés du silicium, avec le lanthane dans le cas du germanium. Beskrovnaïa, Koustovo & Corebnennukov (1971) ont depuis obtenu le composé Ce_2GeS_5 qui paraît isotype de La_2GeS_5 .

Les cristaux de La_2GeS_5 sont préparés suivant les