JOURNAL OF MATERIALS SCIENCE 13 (1978) 766–776

Three-fold transformation twin in the topotactic decomposition of cadmium carbonate crystals

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A bibliography of the subject gives contradictory results for this topotactic transformation, so a new study was needed. The texture of the "pseudomorphs" which result from the decomposition of cadmium carbonate crystals has been completely investigated. The (0 0 1) plane of $CdCO_3$ does not give the (1 1 1) plane of CdO; the [0 0 1] axis of the carbonate becomes the $[\bar{1}\,4\,0]$ axis of three disjointed sets of oxide crystallites. The oxide crystallites show three orientations at 120° from one another in the carbonate crystal habit around $[\bar{1}\,4\,0]$ axis. Thus, after this three-fold transformation twin, the $[\bar{1}\,4\,0]$ axis seems to be a triad axis for the pseudomorph.

1. Introduction

The present paper is part of an investigation on the structural transformation inherent to a reaction such as: crystalline solid 1 → crystalline solid 2 + gas [1–5]. Such reactions are often "topotactic" [6].

In a topotactic transformation, a monocrystal from the initial material yields a "pseudomorph" (initial crystal shape, i.e. habit, is conserved) containing one or more crystallites of the new phase and having the same three-dimensional orientation with respect to the initial crystal [7]. Both the conservation of atomic piling order [2, 3] and the fact that the chemical entities forming the resulting solid do not diffuse [3] are two major features of the structural transformation process in such a conversion. The latter should be regarded as a mere local rearrangement of the atomic building blocks yielding the new structure.

The decompositions of $Mg(OH)_2$, $Ca(OH)_2$ and $Cd(OH)_2$ of brucite type into the corresponding oxides [1–5] – whose orientation relationships have been known for a long time – were studied. It was also shown that they had the morphological and structural features associated with shear transformations. It was, therefore, interesting to investigate carbonate decompositions giving the same oxides. For $MgCO_3$, $CaCO_3$ and $CdCO_3$ crystallizing with the calcite structure, authors disagree (Section 2) on the problem of orientation relationships. That is why the crystallographic study of this transformation was resumed. Its results were briefly published [8]; they are reported in detail in this paper and discussed with reference to carbonate and oxide crystal structures.

2. Disagreement on orientation relationships

Crystal data of the compounds, orientation and dimension relationships are listed in Table I [9–12]. The structural transformation occurring in the decomposition of calcite-type carbonates was first reported by Dasgupta [9] who studied the decomposition of $MgCO_3$ crystals. Referring to X-ray diffraction patterns, the symmetry of the binary axis in the initial crystals seems to be conserved in the resulting pseudomorph. Dasgupta stated that the hexagonal layers, whose spacing is identical in both crystal structures, are conserved. Accordingly, the large decrease in specific volume results in a contraction of the crystal arrangement parallel to the plane of those hexagonal layers (Fig. 1).

More recently, Singh Dev [10] showed that

TABLE I Crystal data for orientation and dimensional relationships between $CdCO_3$ and CdO.

Crystal data			Orientation and dimensional relationships	
	[11] $CdCO_3$ (c)	[12] CdO(o)	[9] Dasgupta	[10] Singh Dev
Structure type	$CaCO_3$ (calcite)	NaCl	$(0\,0.1)_c \rightarrow (1\,1\,1)_0$	$(1\,0\,\bar{1}\,4)_c \rightarrow (1\,1\,0)_0$
Symmetry	Rhombohedric	Cubic	$[0\,0\,1]_c \rightarrow [1\,1\,1]_0$	$[2\,4\,1]_c \rightarrow [\bar{1}\,1\,0]_0$
Space group	$R\bar{3}c$	Fm3m	$[1\,1\,0]_c \rightarrow [1\,\bar{1}\,0]_0$	$[1\,0\,0]_c \rightarrow [0\,0\,\bar{1}]_0$
a	6.1306 Å	4.6953 Å	$p\,[0\,0\,1]_c = 2.71$ Å → $p\,[1\,1\,1]_0 = 2.71$ Å	$p\,[2\,4\,1]_c = 3.93$ Å $p\,[\bar{1}\,1\,0]_0 = 3.32$ Å
α	47°19′	–	$p\,[1\,1\,0]_c = 4.92$ Å → $p\,[1\,\bar{1}\,0]_0 = 3.32$ Å	$p\,[1\,0\,0]_c = 4.92$ Å $p\,[0\,0\,\bar{1}]_0 = 4.70$ Å
Z	2	4		

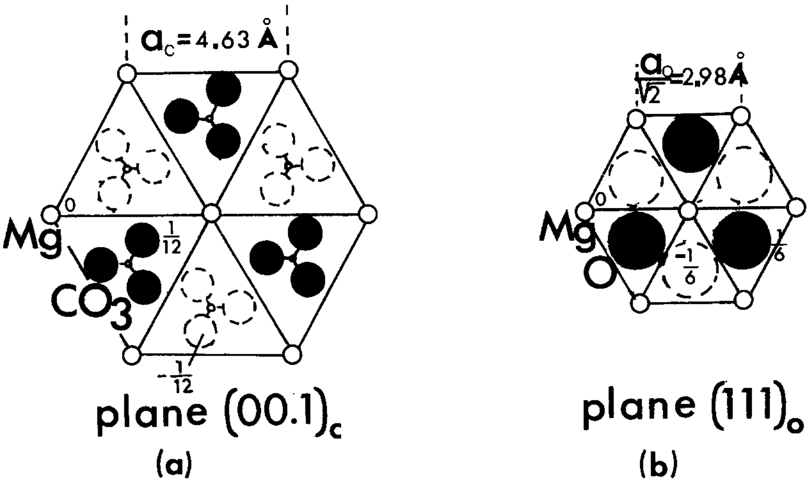

Figure 1 (a) Mg^{2+} cation layer between a set of two CO_3^{2-}-anion layers parallel to hexagonal planes $(0\,0.1)_c$ in $MgCO_3$ structure. (b) Mg^{2+} cation layer between a set of two O^{2-} anion layers parallel to hexagonal planes $(1\,1\,1)_0$ in MgO structure.

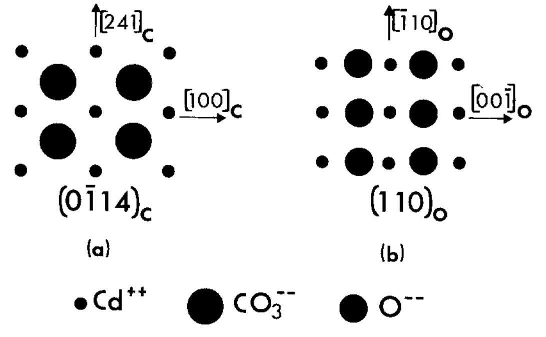

Figure 2 (a) CO_3^{2-} and Cd^{2+} ion layer parallel to $(0\,\bar{1}\,1\,4)_c$ planes in $CdCO_3$ structure. (b) O^{2-} and Cd^{2+} ion layer parallel to $(1\,1\,0)_0$ planes in CdO structure.

the $(0\,\bar{1}\,1\,4)_c$† cleavage faces of calcite and magnesite crystals are converted into the $(1\,1\,0)_0$† plane family of the corresponding oxide (Fig. 2).

Both results are contradictory. Indeed, according to Dasgupta, the triad axis of the carbonate and oxide correspond to one another, which implies that the $(0\,0\,1)_0$ oxide planes correspond to the $(0\,\bar{1}\,1\,4)_c$ carbonate faces. Singh Dev observed $(1\,1\,0)_0$ oxide planes on these faces (Fig. 3).

In a study of the two-fold transformation of calcite crystals into oxide and then into hydroxide [1], preferential orientations which cannot be explained by [9] were found, so a new study was needed.

3. Experimental

3.1. Sample characteristics

Cadmium carbonate crystals prepared by hydrothermic recrystallization [13] were used. They were transparent, more or less truncated rhombohedra (from a few tenths to one or more mm). Crystal face indexation was carried out by optical goniometry (Fig. 4).

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†c = carbonate in hexagonal notation; rh = carbonate in rhombohedral notation; o = oxide.

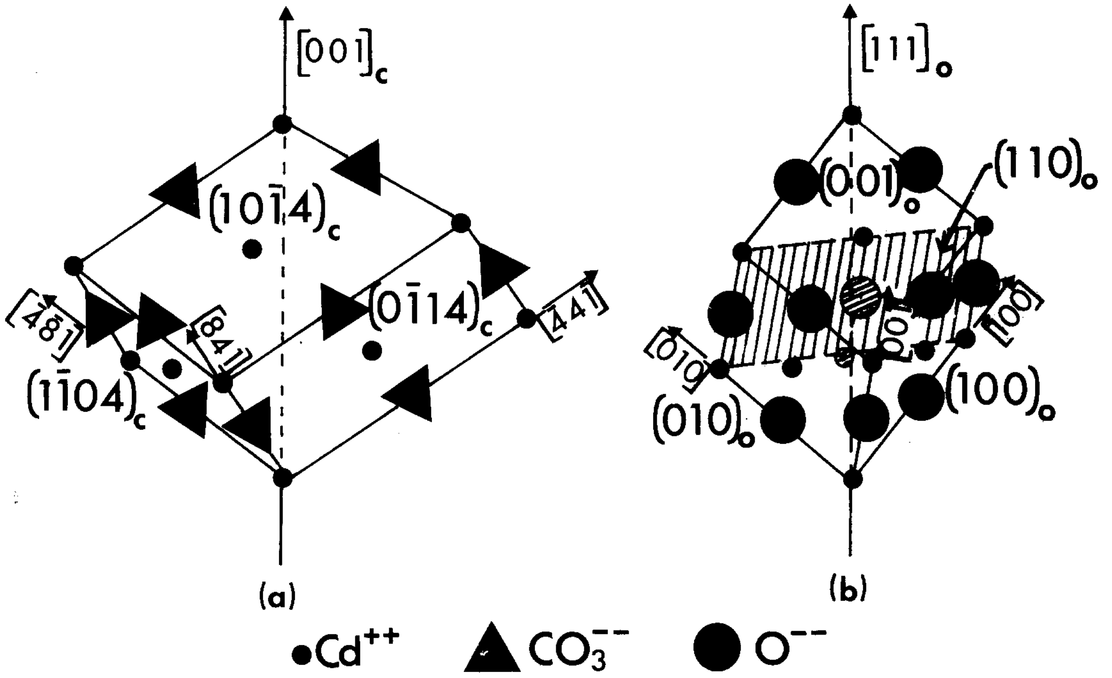

Figure 3 Proposed correlations between (a) $CdCO_3$ structure and (b) CdO structure. Dasgupta [9] :$(1\,0\,\bar{1}\,4)_c \rightarrow (0\,0\,1)_0$; Singh Dev [10] : $(1\,0\,\bar{1}\,4)_c \rightarrow (1\,1\,0)_0$. These two propositions are contradictory.

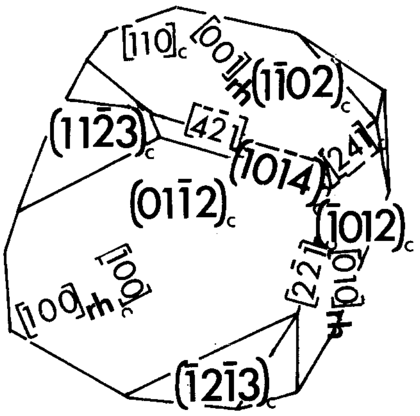

Figure 4 $CdCO_3$ rhombohedric crystal. Faces and axis are indexed respectively $(h\,k\,i\,l)_c$ and $[u\,v\,w]_c$ or $[u\,v\,w]_{rh}$ – $(0\,1\,\bar{1}\,2)_c$-type faces are the most developed.

3.2. Decomposition conditions

Decomposition was effected in a McBain-type thermobalance under vacuum of about 10^{-5} torr, between 300 and 380° C. The crystals were decomposed at various rates and to varying degrees by altering the temperature over this range and the heating time.

3.3. Analysis of the pseudomorphs obtained

They were oriented and observed with a two circle goniometer (TEPSTRA). X-ray diffraction patterns were obtained as follows: (i) the crystal was immobile; (ii) a crystallographic axis of the habit was always oriented along the axis of the cylindrical camera; (iii) another axis was oriented along X-ray beam perpendicular to the camera axis; (iv) cylindrical camera 180 mm; (v) Cu*Kα* filtered radiation; (vi) crystal morphology was examined in SEM (S-410 from Cambridge Instruments Company).

4. Results

A first set of X-ray diffraction patterns was obtained with the $(0\,0\,1)_c$ axis of habit oriented along the rotation axis of a cylindrical camera and one axis of the $(0\,0\,1)_c$ hexagonal plane of habit along the X-ray beam.

4.1. Texture features

A fibre texture was shown by the layer-lines of the patterns (Fig. 5), in which the fibre axis has a "pseudo-triad symmetry". Indeed, two patterns obtained after a 120° rotation of the pseudormorph around the $[0\,0\,1]_c$ axis of the habit were identical

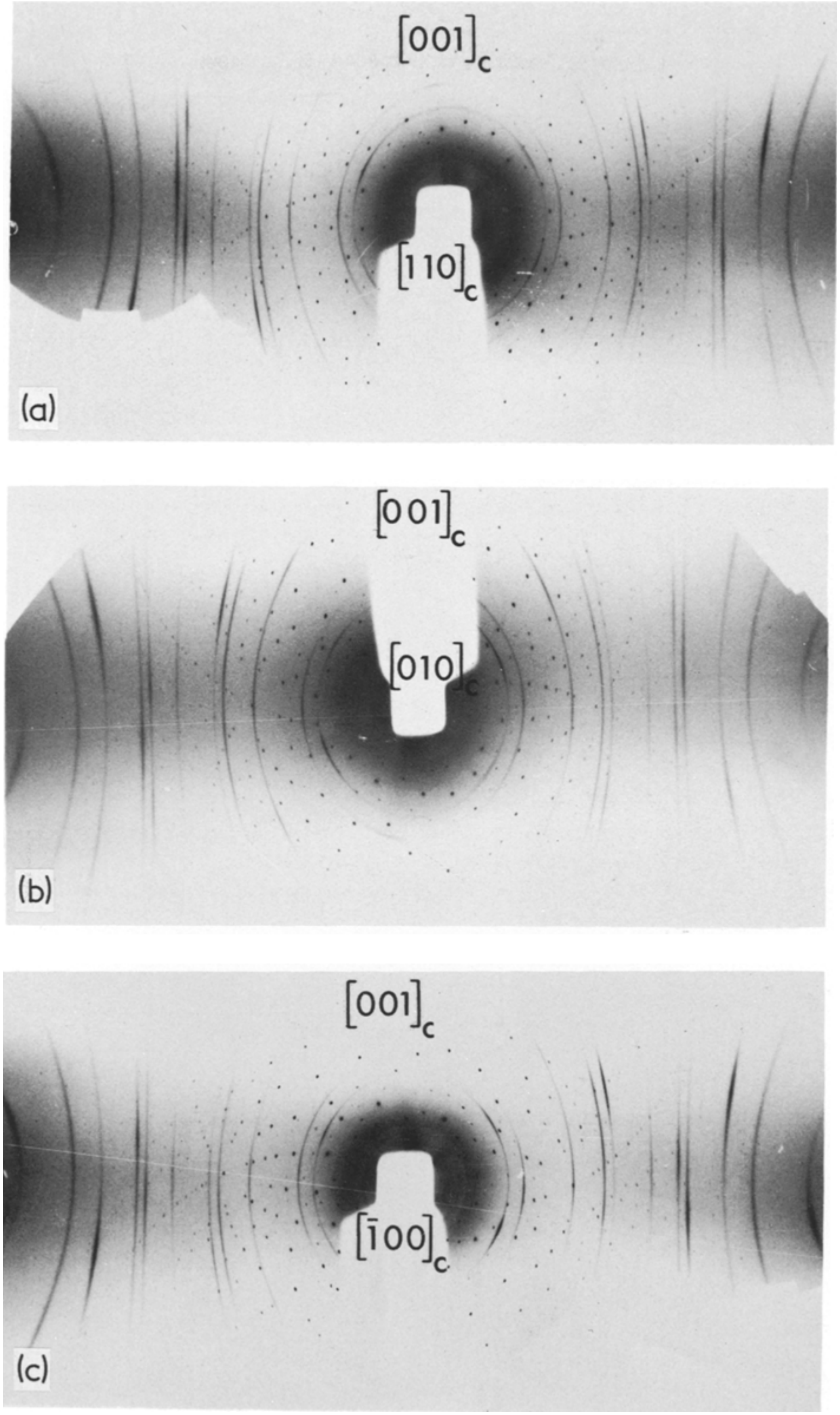

Figure 5 X-ray diffraction patterns of a $CdCO_3$ crystal after decomposition into CdO. The three patterns (a), (b) and (c) were obtained in the following conditions: $[0\,0\,1]_c \parallel$ cylindrical camera rotation axis; $[1\,1\,0]_c$ or $[0\,1\,0]_c$ or $[\bar{1}\,0\,0]_c \parallel$ X-ray beam. These three axis are derived from one another by a 60° rotation around $[0\,0\,1]_c$.

but after a 60° rotation they were not. According to [9] it could be assumed that the fibre axis is a triad axis of the oxide cubic lattice; however, the period deduced from the patterns does not agree with the $a\sqrt{3}$ parameter according to a normal $[1\,1\,1]_0$ axis, but with $a\sqrt{7}$.

4.2. Hypothesis to explain the pseudo-triad symmetry

We assume that it is a plane family, non-rectangular with the triad axis, which is conserved during transformation. The crystal building symmetry of the carbonate is ruled by the $R\bar{3}c$ space group derived from point group $\bar{3}m$; this family necessarily belongs to the $(h\,0\,\bar{h}\,l)_c$ or $(0\,k\,\bar{k}\,l)_c$ type with $l \neq 0$ so that two other families only are equivalent, $(\bar{h}\,h\,0\,l)$ and $(0\,\bar{h}\,h\,l)$ or $(\bar{k}\,0\,k\,l)$ and $(k\,\bar{k}\,0\,l)$. These three families are derived from one another by 120° rotations around $[0\,0\,1]_c$, and each of them can give rise to the $(h'k'l')_0$ family. Thus the oxide crystallites can show three orientations at 120° from one another in the carbonate crystal habit while having the same $[u\,v\,w]_0$ axis along $[0\,0\,1]_c$.

4.3. Indexing the fibre axis

On the 2 0 0 diffraction ring (Fig. 5) there are two spots on the zero-layer line; so the fibre axis must be of $[u\,v\,0]$ type. The angles between the four 1 1 1 spots, which belong to two of the three oxide crystallite "sets", and the angles they make with the fibre axis are seen in a stereographic projection of the CdO lattice directions (Fig. 6). $[u\,v\,0]_0$ is in the equatorial plane and at about 45° and 65° from two $[1\,1\,1]_0$ type axes of the same "set"; $[\bar{1}\,4\,0]_0$ satisfies all these conditions. This direction parameter agrees with the layer lines obtained in all patterns.

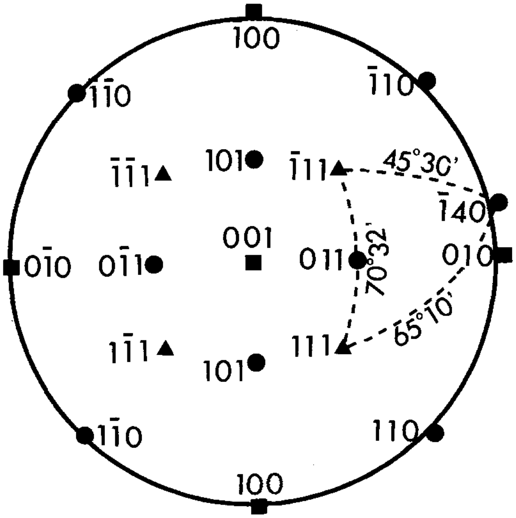

Figure 6 Stereographic projection of CdO axis. Central pole $[0\,0\,1]_0$.

4.4. Crystallite orientations versus the $[\bar{1}\,4\,0]_0$ axis

In accordance with the above assumption, the reciprocal $(\bar{1}\,4\,0)_0^*$ planes of three CdO lattices oriented at 120° from one another around $[\bar{1}\,4\,0]_0$ were drawn. Using the Ewald construction all the diffraction spots of the different patterns could be indexed, which agrees with the above hypothesis. The orientation of the habit was well known for each pattern, so the orientation of $(\bar{1}\,4\,0)_0$ of the three oxide "sets" about $(0\,0\,.\,1)_c$ of the habit was known precisely. The orientation relationships between the lattices of the three

TABLE II Corresponding lattice axis in $CdCO_3$ – CdO transformation

$CdCO_3$ habit	CdO crystallites		
	Set A	Set B	Set C
$[0\,0\,1]_c$	$[\bar{1}\,4\,0]_A$	$[\bar{1}\,4\,0]_B$	$[\bar{1}\,4\,0]_C$
$[\bar{1}\,0\,0]_c$	$[0\,0\,1]_A$		
$[0\,\bar{1}\,0]_c$		$[0\,0\,1]_B$	
$[1\,1\,0]_c$			$[0\,0\,1]_C$
$[\bar{1}\,\bar{2}\,1]_c \equiv [1\,0\,0]_{rh}$	$[1\,4\,0]_A$	$[\bar{1}\,2\,1]_B$	$[\bar{1}\,2\,\bar{1}]_C$
$[2\,1\,1]_c \equiv [0\,1\,0]_{rh}$	$[\bar{1}\,2\,\bar{1}]_A$	$[1\,4\,0]_B$	$[\bar{1}\,2\,1]_C$
$[\bar{1}\,1\,1]_c \equiv [0\,0\,1]_{rh}$	$[\bar{1}\,2\,1]_A$	$[\bar{1}\,2\,\bar{1}]_B$	$[1\,4\,0]_C$

TABLE III Corresponding lattice planes in $CdCO_3 \rightarrow$ CdO transformation. $\Delta\phi$ is the angle between the corresponding planes.

$CdCO_3$ habit	CdO crystallites					
	Set A		Set B		Set C	
	$(h\,k\,l)$	$\Delta\phi$	$(h\,k\,l)$	$\Delta\phi$	$(h\,k\,l)$	$\Delta\phi$
$(0\,0\,0\,1)$	$(\bar{1}\,4\,0)$	0	$(\bar{1}\,4\,0)$	0	$(\bar{1}\,4\,0)$	0
$(0\,1\,\bar{1}\,2)$	$(\bar{1}\,0\,0)$	12°	$(1\,1\,\bar{1})$	20°	$(1\,1\,1)$	20°
$(\bar{1}\,0\,1\,2)$	$(1\,1\,1)$	20°	$(\bar{1}\,0\,0)$	12°	$(1\,1\,\bar{1})$	20°
$(1\,\bar{1}\,0\,2)$	$(1\,1\,\bar{1})$	20°	$(1\,1\,1)$	20°	$(\bar{1}\,0\,0)$	12°
$(\bar{1}\,1\,0\,4)$	$(\bar{1}\,1\,1)$	2°	$(\bar{1}\,1\,\bar{1})$	2°	$(1\,1\,0)$	12°
$(0\,\bar{1}\,1\,4)$	$(1\,1\,0)$	12°	$(\bar{1}\,1\,1)$	2°	$(\bar{1}\,1\,\bar{1})$	2°
$(1\,0\,\bar{1}\,4)$	$(\bar{1}\,1\,\bar{1})$	2°	$(1\,1\,0)$	12°	$(\bar{1}\,1\,1)$	2°
$(0\,\bar{1}\,1\,1)$	$(2\,1\,0)$	0				
$(1\,0\,\bar{1}\,1)$			$(2\,1\,0)$	0		
$(\bar{1}\,1\,0\,1)$					$(2\,1\,0)$	0
$(\bar{2}\,1\,1\,0)$	$(0\,0\,1)$	0				
$(1\,\bar{2}\,1\,0)$			$(0\,0\,1)$	0		
$(1\,1\,\bar{2}\,0)$					$(0\,0\,1)$	0

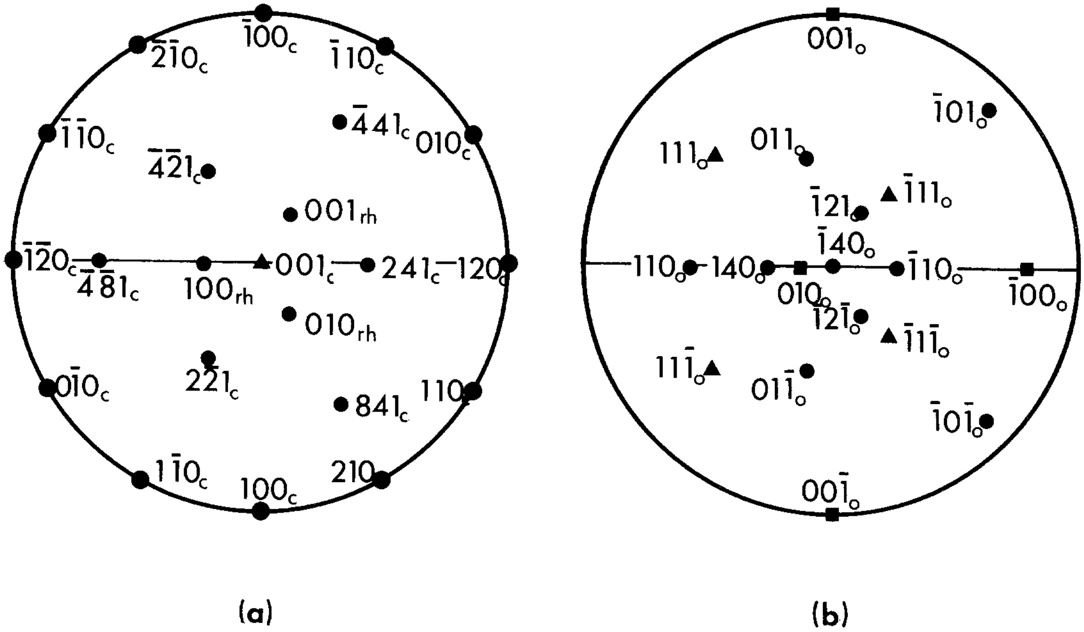

Figure 7 Stereographic projections of $CdCO_3$ axis (a) and CdO axis (b) showing the orientation relationships between both structures in agreement with $[001]_c \parallel [\bar{1}40]_0$ and $[\bar{1}00]_c \parallel [001]_0$.

oxide "sets" termed A, B and C, respectively and the carbonate crystal lattice (Fig. 7) are listed in Tables II and III.

X-ray diffraction patterns showed that the $[\bar{1}21]_0$, $[\bar{1}2\bar{1}]_0$ and $[140]_0$ directions of the oxide were actually oriented along the main axis of the rhombohedral cell of the carbonate.

5. Discussion

5.1. Structural transformation

The specific orientation relationships of the cadmium carbonate transformation into oxide have been given. Their interpretation requires a plane-by-plane comparison of the initial material crystal structures with the resulting compound.

5.1.1. Invariant plane investigation

The first result to check from the structures is the existence of a carbonate plane family, non-perpendicular to the triad axis and liable to be preserved during transformation. This is of major importance for, on the one hand, it underlies the above assumption (see Section 4.2), and on the other, the invariance of a plane family as a coherent or semi-coherent interface between both crystal solids constitutes a fundamental structural feature in a shear transformation.

This plane family must satisfy three conditions:

(1) Its orientation must not have changed, the angular difference $\Delta\phi$ observed between the carbonate plane family and the corresponding oxide family must be very small (Table III).

(2) This plane family must have only two other equivalent families in the carbonate structure

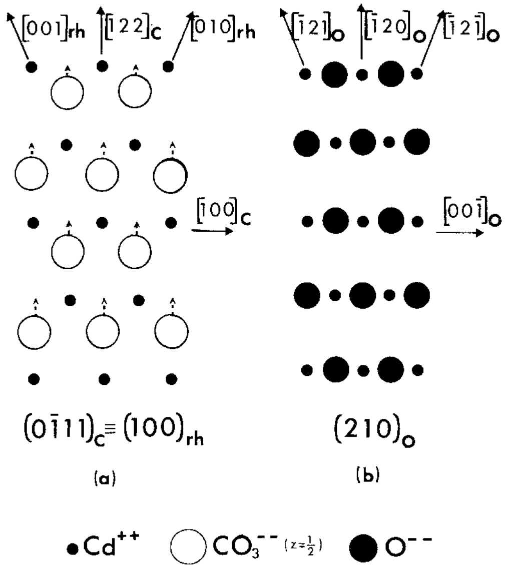

Figure 8 Corresponding atomic arrangements parallel to the $(0\bar{1}11)_c$ $CdCO_3$ plane and the $(210)_0$ CdO plane: $[100]_c = 4.92$ Å → $[00\bar{1}]_0 = 4.70$ Å $[122]_c = 11.33$ Å → $[\bar{1}20]_0 = 10.51$ Å. The arrows (↑) symbolize the translation parallel to the $[241]_c$ axis that brings the into the cation plane.

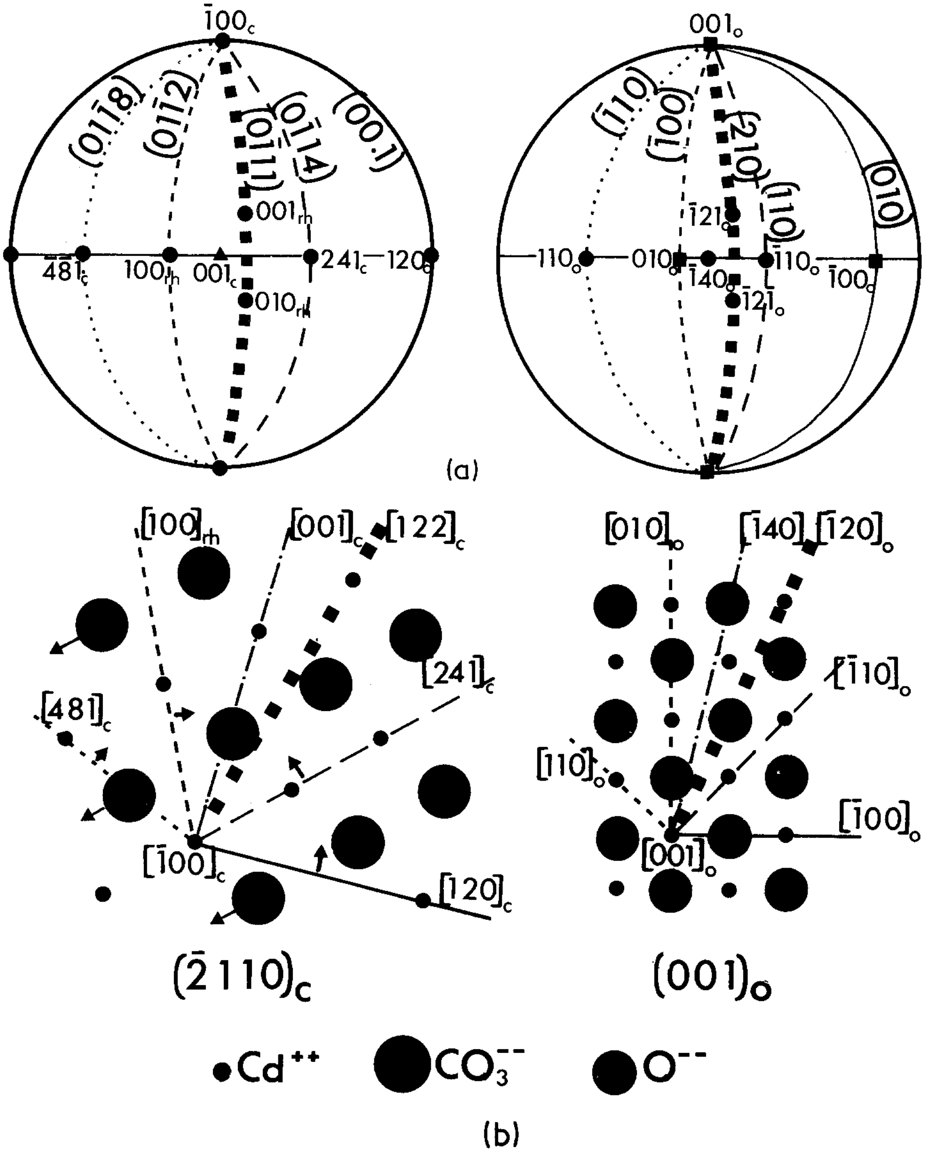

Figure 9 Structural transformation of carbonate into oxide structure. All the corresponding plane families are parallel to the $[\bar{1}\,0\,0]_c$ and $[0\,0\,1]_0$ zone-axes respectively. The substantial contraction of the structure appears in the "bringing together" of these plane families; (a) Stereographic projections parallel to the zone axis on $(0\,0.1)_c$ and $(\bar{1}\,4\,0)_0$ planes respectively. (b) Structure cross-sections perpendicular to the zone axis of $(\bar{2}\,1\,1\,0)_c$ and $(0\,0\,1)_0$ planes respectively. All the atoms are at the same height.

(see Section 4.2); the three plane families, thus are of $(h\,0\,\bar{h}\,l)_c$, $(\bar{h}\,h\,0\,l)_c$ and $(0\,\bar{h}\,h\,l)_c$ type, with $l \neq 0$ (or $(0\,k\,\bar{k}\,l)_c$ $(\bar{k}\,0\,k\,l)_c$ and $(k\,\bar{k}\,0\,l)_c$).

(3) The atomic arrangements in the carbonate plane and in the oxide plane into which the former is converted, should correspond to each other without too much distortion, hence resulting in a coherent or semi-coherent interface between both crystal structures.

Following examination of the above conditions for the various pairs of planes listed in Table III, the $(0\,\bar{1}\,1\,1)_c \equiv (1\,0\,0)_{rh}$ plane family alone proves to be able to be the coherent or semi-coherent interface between both structures during transformation, by becoming the $(2\,1\,0)_0$ family of the oxide (Fig. 8).

5.1.2. Structural transformation investigation

This transformation is shown in Fig. 9. The main carbonate planes and the corresponding oxide planes are drawn in different dotted lines. During transformation, the main plane $(0\bar{1}11)_c$ of the carbonate is preserved and becomes the $(210)_0$ plane in the oxide. The other planes draw nearer to one another around the $[100]_c$ axis parallel to $[00\bar{1}]_0$ and become the corresponding planes in the oxide, which shows the substantial packing of the structure. The tightening of the various plane families is associated with a superimposition of the anion and cation layers towards $[241]_c$ (Fig. 8).

5.2. Crystallite distribution and orientation

Orientation relationships between the carbonate and oxide have been previously established assuming that the carbonate crystal is converted into oxide crystallites with three orientations versus habit. Analysis of the crystal structures enabled us to find both the three equivalent plane families which can become a coherent interface during transformation, and the way in which this structural transformation is able to occur.

Experimental results, however, did not enable us to find out how the oxide crystallites are distributed within the pseudomorph with respect to their orientations and how these crystallites are oriented versus habit faces. Both questions will find an answer by means of a macroscopic, morphological study of partially decomposed crystals.

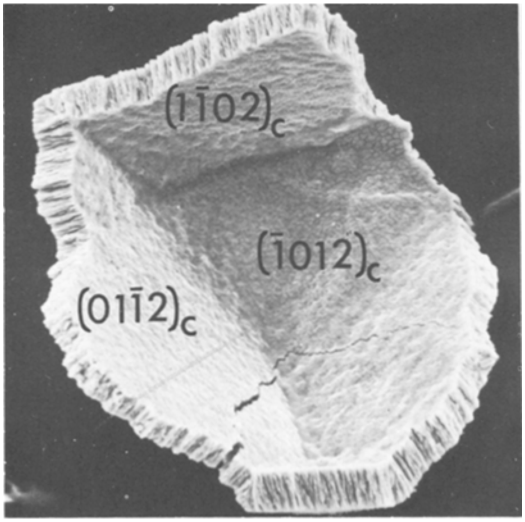

Figure 10 "Oxide cap" removed from a largely decomposed $CdCO_3$ crystal.

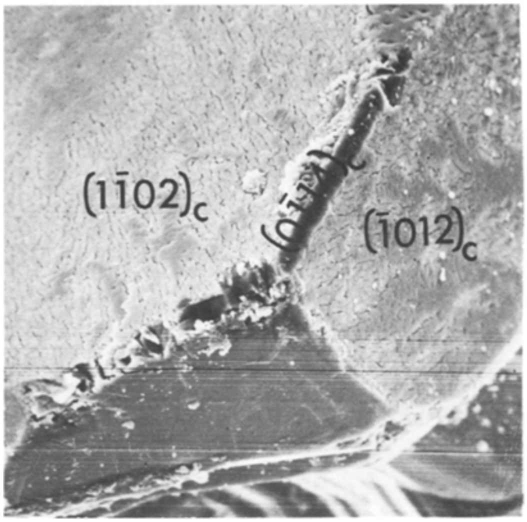

Figure 11 $CdCO_3$ crystal at the very beginning of the reaction —$(01\bar{1}2)_c$-type faces are affected by the reaction whereas the others are not.

5.2.1. *Distribution of the oxide crystallites*

When the crystals are largely decomposed, cadmium oxide layers can be carefully removed while preserving the initial crystal habit (Fig. 10). No fragmentation difference is observed on the faces, however the parallel crackings through the oxide layer are discontinuous at the intersection with certain faces, and show three domains, each characterized by a common cracking direction.

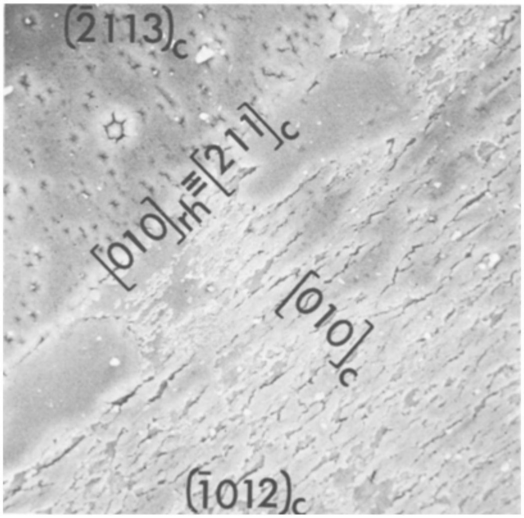

Figure 12 Partially decomposed $CdCO_3$ crystal. $(\bar{2}113)_c$ and $(\bar{1}012)_c$ face aspects lead one to infer a contraction in the $[010]_c$ direction.

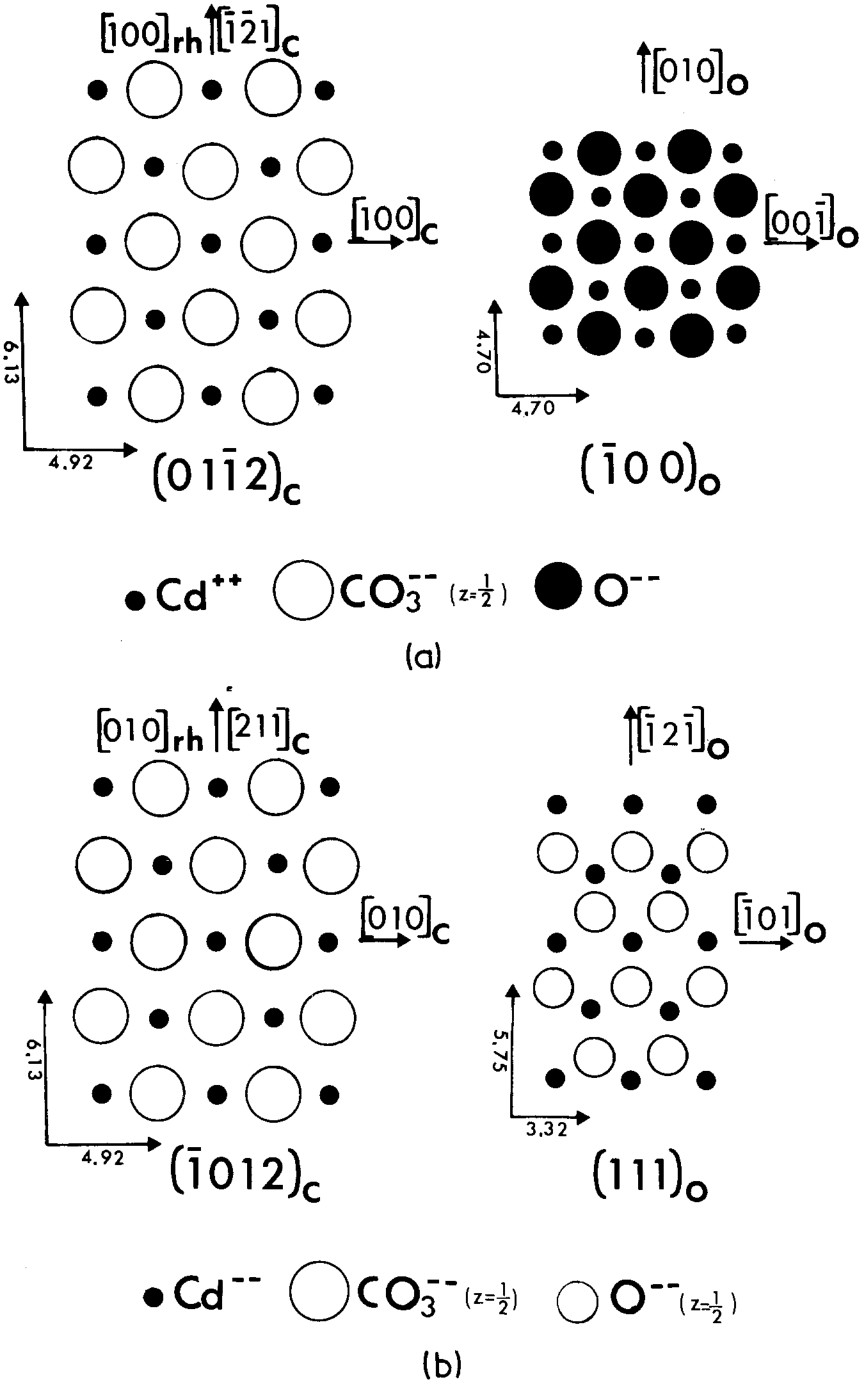

Figure 13 Two non-equivalent possibilities of orientation of the CdO crystallites: (a) Possibility 1: $(1\,0\,0)_0$-type planes are parallel to the $(\bar{1}\,0\,1\,2)_C$-type faces. (b) Possibility 2: $(1\,1\,1)_0$-type planes are parallel to the $(\bar{1}\,0\,1\,2)_C$-type faces. The rectangular translation moduli are given in the corresponding considered planes.

This observation is of major importance. Indeed, the decomposition reaction started on the $(0\,1\,\bar{1}\,2)_c$, $(\bar{1}\,0\,1\,2)_c$ and $(1\,\bar{1}\,0\,2)_c$ faces of the carbonate crystals (Fig. 11). Now the three cracking systems observed seem to be attached to these three natural faces.

As there is a close relationship between the orientation of the oxide crystallites in the habit and the morphological transformation of the crystal, it is reasonable to assume the orientation of the crystallites to be attached to the natural face on which the reaction began. The crystallites of A, B and C, detected by X-ray diffraction then would not be randomly mingled: *the three sets would be disjointed,* (i.e. one crystal domain would have been converted into set A, another into set B and the third into C).

Singh Dev's experimental results [10] substantiate this interpretation. Indeed, X-ray diffractometry carried out on a sufficiently developed natural face shows one orientation of the oxide crystallites only. Had the oxide crystallites from the three sets been randomly intermingled, Singh Dev should have observed, besides the $(1\,1\,0)_0$ planes of the oxide, $(1\,1\,1)_0$-type planes on the $(0\,\bar{1}\,1\,4)_c$ face of the initial crystal (Table III).

5.2.2. Crystallite orientation

In a carbonate crystal domain, the orientation of one of the three crystallite sets versus the natural $(0\,1\,\bar{1}\,2)_c$ face is that listed in Table III: it must be either a $(1\,0\,0)_0$ plane (orientation 1) or a $(1\,1\,1)_0$ plane (orientation 2); both these non-equivalent possibilities are compatible with the orientation relationships discovered and the crystal rearrangement proposed.

Two considerations advocate for one of both possibilities. The observation of the natural, $(\bar{1}\,0\,1\,2)_c$ face of partially decomposed crystals (Fig. 12) implies a greater contraction in the crystal structure towards $[0\,1\,0]_c$, perpendicular to a $[0\,1\,0]_{rh}$ axis of the rhombohedral cell. This agrees with the orientation of the $(1\,1\,1)_0$ crystallite planes along this natural $(\bar{1}\,0\,1\,2)_c$ face (Fig. 13). In addition, Singh Dev [10] showed that the $(1\,1\,0)_0$ planes of the oxide are oriented approximately along a $(0\,\bar{1}\,1\,4)_c$ cleavage face in a calcite crystal. This can be compatible only with the second possibility of orientation (Table III).

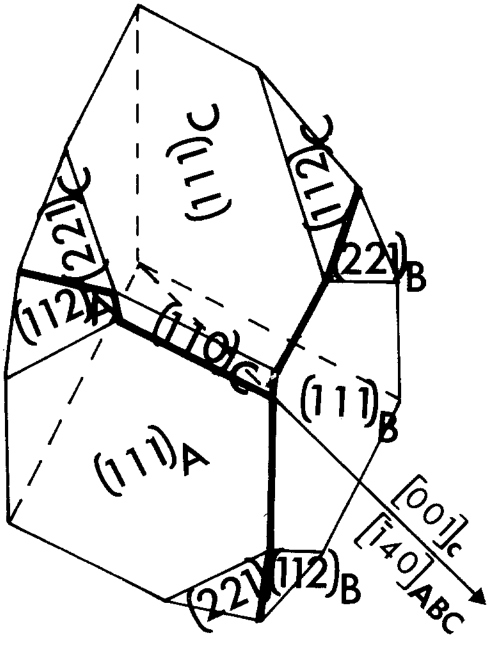

Figure 14 Indexation of the plane families of the three CdO crystallite sets on the $CdCO_3$ habit faces.

Fig. 14, showing the preserved habit of a cadmium carbonate crystal, sums up the results obtained. Plane family indexation of the three oxide crystallite sets is given on the corresponding natural face of the habit in agreement with the above interpretations.

6. Conclusions

X-ray diffraction analysis of the pseudomorph resulting from the decomposition of a cadmium carbonate crystal showed that the transformation is topotactic, but that the resulting orientation relationships are not those to be expected from comparing the crystal structures of the carbonate and the oxide. In fact the plane families parallel to the main planes of the rhombohedral cell are preserved, and each becomes the $(2\,1\,0)_0$ family of the oxide crystallites in the crystallite sets. Indeed, a *three-fold twin of transformation* is suggested, which means that the crystal is not decomposed into oxide crystallites with the same orientation but in three disjointed sets deriving from one another through a process of symmetry in the initial crystal.

The study of this transformation for which it seems that the atomic arrangement is not disrupted – an essential structural feature in a transformation process without diffusion – shows that our present knowledge of crystal arrangements is insufficient to predict the transformation.

In addition to the initial and final configurations, energetic considerations, bonding energies in both arrangements, energies of formation and diffusion of the gaseous entities, and activation energy for intermediate configurations should certainly be taken into account.

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Received 10 June and accepted 16 September 1977.