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Study of a Lacunary Solid Phase I—Thermodynamic and Crystallographic Characteristics of its Formation

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The dehydration of the barium acid oxalate $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$, depending on the conditions in which it is performed, can lead to two different anhydrous salts. That designated $\alpha H_2C_2O_4 \cdot BaC_2O_4$ has all the features of a stable lacunary phase. Its crystalline structure has been determined and the atomic movements during this structure's formation are described. The other variety $\beta H_2C_2O_4 \cdot BaC_2O_4$ can be prepared either directly from the dihydrate or by transformation of the α form at higher temperature. An infinite number of nonstoichiometric hydrates (designated as $H_2C_2O_4 \cdot BaC_2O_4 \cdot \varepsilon H_2O$ with $0 < \varepsilon < 2$) can be prepared in particular conditions, which identifies the "hydrate–vapor" system studied as divariant. A structural interpretation of this phenomenon is proposed; it takes into account the particular role of water molecules in the coordination polyhedron of the Ba^{2+} cations.

Introduction

During the thermal decomposition of a salt, according to the reaction

$$S_1 \rightarrow S_2 + G$$

both the structure and the composition of the initial crystal (S_1) change to produce a new crystalline phase (S_2) and a gas (G). The processes are therefore more complex than the transformations at constant composition. Several models for the reaction mechanism have been suggested. Among these only two merit consideration. They are distinguished by the mode of formation of the S_2 crystalline structure from that of the solid S_1.

In the first model (*1, 2*) the removal of gas from the S_1 lattice leads to a structurally identical lacunary stacking. The S_2 microcrystals are formed during two further stages which are more or less easily distinguishable: the lacunary phase splits off from the parent crystal then undergoes a rearrangement to give the final S_2 stacking.

In the second (*3, 4*) the new phase S_2 appears as a critical nucleus in the parent phase S_1. This nucleus would have essentially the same lattice as S_2 though its lattice may be strained or defective. The possibility of growth of this nucleus in the initial matrix has been discussed. The strains limit the size of the S_2 domain whose separation from the S_1 matrix gives a microcrystal of the final product.

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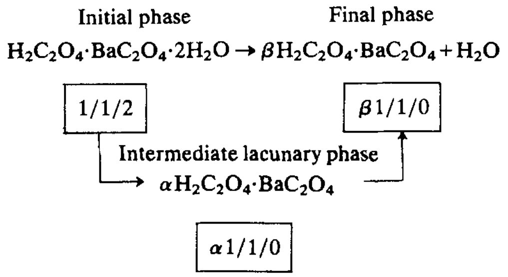
The experimental evidence on which each hypothesis is based is limited; in particular very few experiments have proved the existence of the lacunary intermediate state or the coexistence of the S_2 lattice in that of S_1.

The work described here argues in favor of the first mechanism. The thermal dehydration of acid barium oxalate $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$ to the anhydrous β salt proved to be an entirely typical case of a reaction where a lacunary compound can be isolated: it is the α form of the anhydrous oxalate. For simplicity we have substituted numbered symbols for chemical formulas:



The study of the thermodynamic conditions of lacunary phase formation and the determination of its crystalline structure will lead to a knowledge of the movements of the C_2O_4 groups in the transition from the initial to the anhydrous α1/1/0 stacking. It will also enable us to visualise the possible distribution of point defects in the partial lacunary phase.

Experimental Procedure

Water removal from the initial dihydrate and the modification which it causes in the crystalline structure are studied by thermogravimetry and X-ray diffraction. In the two cases the experimental set-up is designed such that a water vapor pressure and a controlled temperature are established on a finely divided sample (40 mg, 30 μm) (*5*, *6*). The loss of gas can be caused by subjecting the oxalate dihydrate sample, either, to successive and small-increment changes and stabilizations of temperature at constant pressure (isobaric dehydration); or, to successive and small-decrement changes and stabilization of water vapour pressure at constant temperature (isothermal dehydration). In both cases these stabilizations are maintained long enough to be certain of establishing equilibrium.

The oxalate 1/1/2 is obtained very easily as acicular crystals which are well shaped and stable under ambient conditions; study of its structure thus presents little difficulty. In contrast, the preparation of a suitable α1/1/0 specimen is more difficult. Only one mosaic crystal can be obtained. A small dihydrate crystal (about 300 μm section) is placed in a Lindeman tube and very slowly dehydrated (at 30°C and under slowly decreased pressure from 20 torr to 10^{-4} torr), the tube being sealed at the end of the reaction. Under these conditions the "pseudomorph" obtained consists of packing of small coherent diffraction domains which are slightly disoriented [see part II (*7*)].

The recording of reciprocal lattice of 1/1/2 and α1/1/0 oxalate was made with a Weissenberg camera for twelve levels normal to the *c* axis. The atomic coordinates were determined by the heavy atom method (Ba atoms) and calculation of electron density map (C and O atoms). The refinement of atomic positions was made by the least square method, an isotropic temperature factor affecting each atom (*8*).

Results

Phases Diagram

When an isobaric dehydration is carried out, the weight loss curve shows a succession of composition plateaux corresponding to nonstoichiometric hydrates symbolized by 1/1/ε (ε = number of moles of water per mole of anhydrous salt) (*9*). The X-ray diffractograms recorded for each of these plateaux only differ from that of the dihydrate with respect to the progressive displacement of certain peaks and to the variation in their intensities (Fig. 1). When a temperature which varies from 105°C under 2 torr to 80°C under 80 torr is reached (curve L, Fig. 2), the totality of water still bound to the salt is expelled from the sample in only one step; the X-ray diffractogram is then different from those observed hitherto, and is due to the $\beta 1/1/0$ anhydrous salt (Fig. 3).

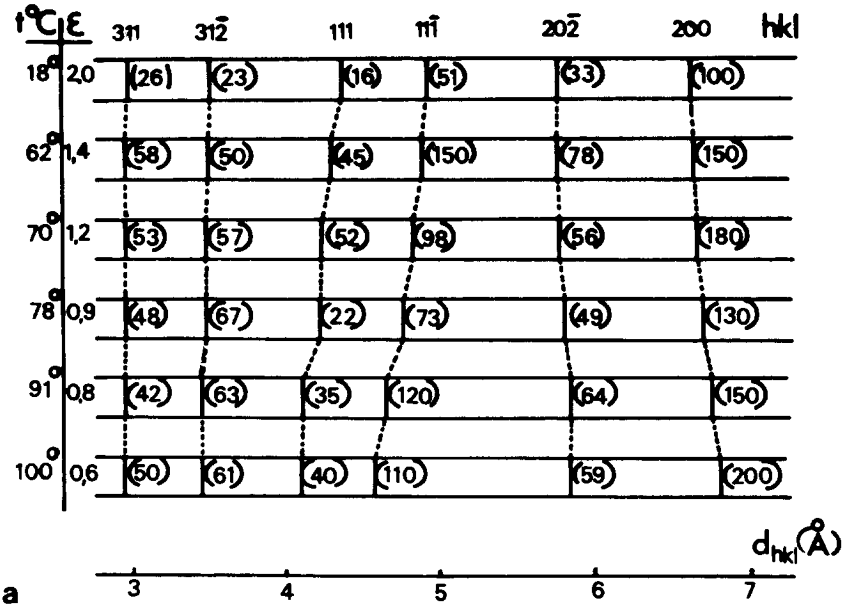


FIG. 1a. Progressive displacement of some characteristic peaks in the X-ray diffractogram recorded during an isobaric dehydration ($P_{H_2O} = 2$ torr). The corresponding intensity is given in parentheses.

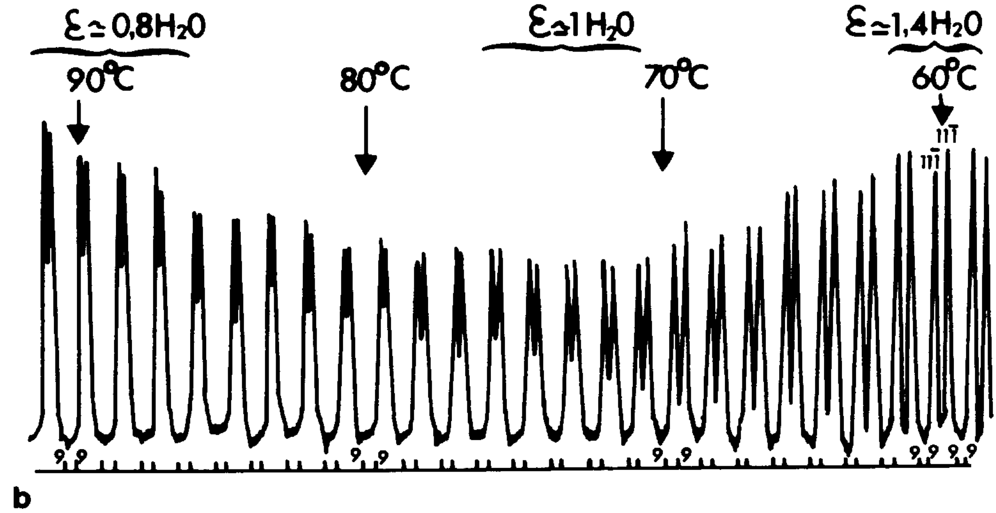


FIG. 1b. Variation of the intensity of the 11$\bar{1}$ peak recorded continuously by scanning forewards and backwards between 9–9.5°θ during an isobaric dehydration ($P_{H_2O} = 2$ torr, heating rate 10°C/hr).

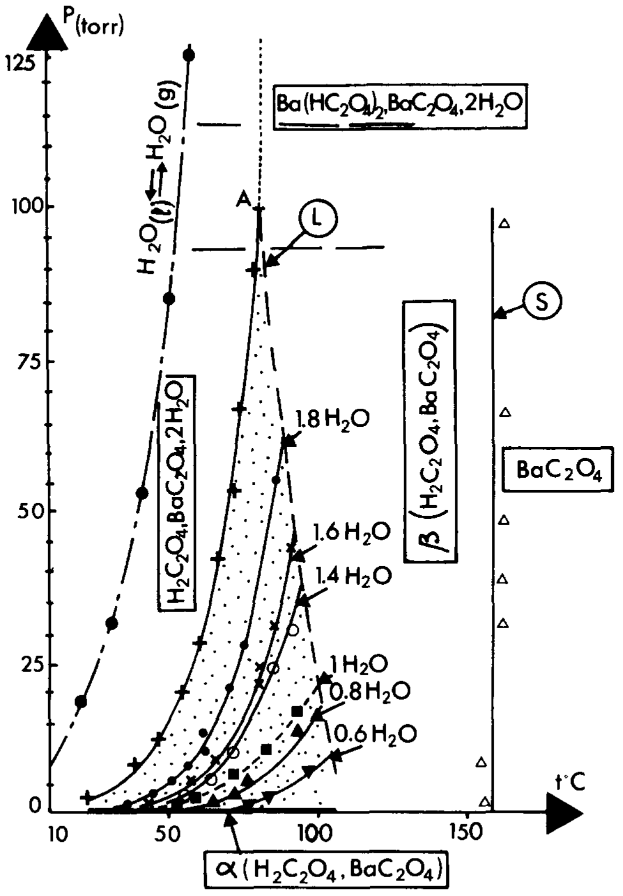


FIG. 2. P(*T*) phases diagram of $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$.

When an isothermal dehydration is carried out it is possible to obtain all hydrates $1/1/\varepsilon$ with ε between 2 and 0. Each thermogram shows a succession of plateaux which correspond to the different stabilizations of pressure. When the pressure is that of ice at −193°C, the α anhydrous salt plateau is reached; its diffractogram has the same form as the dihydrate's but is characterized by maximum displacement of each line. Under these conditions the $\alpha 1/1/0$ oxalate can be obtained at any temperature between 30 and 100°C, but when heated over 120°C gives the $\beta 1/1/0$ form.

These results permit construction of the phase diagram represented by Fig. 2. The zone of stability of the hydrates $1/1/\varepsilon$ is bounded on the left by the domain of existence of the dihydrate and to the right by the curve *L* beyond which the anhydrous phase $\beta 1/1/0$ appears. It is to be noted that within the boundary of this domain there exists a perfect reversibility between dehydration and rehydration. In this zone some isocomposition curves have been presented. The curve corresponding to the composition $\varepsilon = 0$ ($\alpha H_2C_2O_4 \cdot BaC_2O_4$) is represented by the thick line along the temperature axis, as

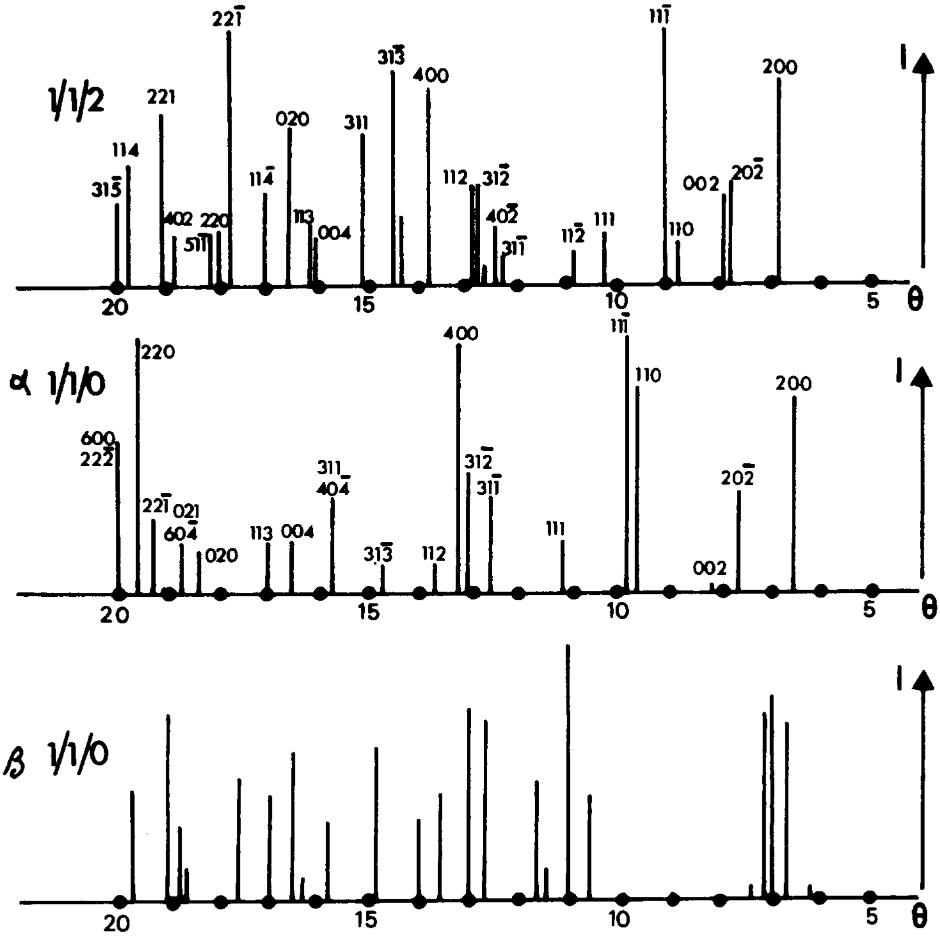


FIG. 3. Schematic X-ray diffractogram of the three phases: $H_2C_2O_4{\cdot}BaC_2O_4{\cdot}2H_2O$; $\alpha H_2C_2O_4{\cdot}BaC_2O_4$; $\beta H_2C_2O_4{\cdot}BaC_2O_4$.

indicated by the results of isothermal dehydration. It is probable that this compound has a zone of stability in the domain of low pressure but we have not been able to define it experimentally.

It may be noted, finally, that if pressures higher than that of the intersection point *A* are applied, the decomposition of the dihydrate is brought about with a liberation all at once of a proportion of the oxalic acid according to the reaction

$$2[H_2C_2O_4{\cdot}BaC_2O_4{\cdot}2H_2O] \rightarrow BaC_2O_4{\cdot}Ba(HC_2O_4)_2{\cdot}2H_2O + H_2C_2O_4{\cdot}2H_2O.$$

Details of this last transformation are given elsewhere (*10*).

Physico-chemical Characteristic of the $1/1/\varepsilon$ Oxalates

Having detailed their conditions of formation we shall deal with the thermodynamic and crystallographic characteristics of nonstoichiometric hydrates, and of the anhydrous phase α.

The thermograms obtained by the method already described enable curves $\varepsilon(P)_T$ and $\varepsilon(T)_P$ to be constructed (Fig. 4) and the isocomposition curves $P(T)_\varepsilon$ can be deduced

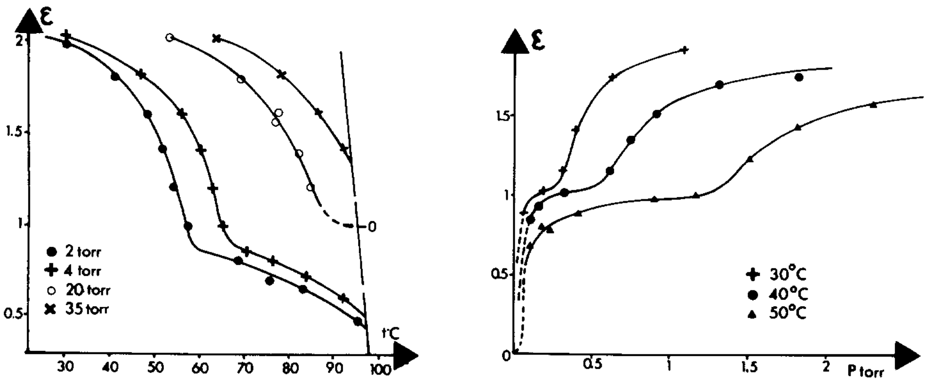


FIG. 4. Isothermal $\varepsilon(P)_T$ and isobaric $\varepsilon(T)_P$ curves show a peculiarity close to the hydration degree $\varepsilon = 1$.

from them (Fig. 2). The isosteric enthalpies and entropies are also calculated.

The most striking feature of these results is the distinct change in the shape of the $\varepsilon(P)_T$ and $\varepsilon(T)_P$ curves for the hydration degree close to $\varepsilon = 1$, and the difference in values of ΔH and ΔS on the two sides of this composition (Table I).

Neither for the $1/1/\varepsilon$ hydrate nor for the anhydrous α salt does there appear a distinct diffraction pattern like that of the dihydrate. This fact, in addition to knowing the reticular constants of the 1/1/2 monoclinic unit cell permit calculation of the a, b, c, β parameters characterizing the $1/1/\varepsilon$ salts and the $\alpha 1/1/0$ form, as well as giving information on their variation as a function of hydration degree. The parameters for the two extreme compounds, 1/1/2 and $\alpha 1/1/0$, are compiled in Table II, and Fig. 5 shows, by way of example, the b parameter variation. The shape of such curve which seems to suggest a divergence from Vegard's law shows, like the $\varepsilon(P)_T$ isotherms, a peculiarity close to $\varepsilon = 1$.

In addition to this particular characteristic, others can be noted which are concerned with the elimination of water: a continuous and large increase, in the a parameter and of the β angle (0.94 Å and 2.80° respectively; a continuous and large reduction in b (0.52 Å); a small decrease in c (0.09 Å); a continuous decrease in volume (53 Å^3); and finally the preservation of the space group and that of the cell contents.

Crystalline Structures of Oxalates 1/1/2 and α1/1/0

Description of the oxalate $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$ structure has already been the object of detailed publications (*8*, *9*) so the two structures will only be compared here in order to bring out the small, structural modifications resulting from complete dehydration.

The mode of stacking is identical: this is shown in Table III where the values are given for fractional coordinates, standard errors, and the thermal agitation factors of the atoms of each oxalate. The first value cor-

TABLE I

ε (mole)	1.8	1.6	1.4	1.2	0.8	0.6
ΔH_{298} (kcal·mole^{-1})	18.2	17.1	17.6	17.1	23.2	23.6
ΔS°_{298} (u.e.)	46	42	42.5	40.6	56	54.4

TABLE II

	a Å	b Å	c Å	β°	V Å³	d	Z	Space group
$H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$	14.45 ±0.03	5.40 ±0.02	12.45 ±0.03	116.00	873	2.66	4	C2/c
$\alpha H_2C_2O_4 \cdot BaC_2O_4$	±15.39 ±0.03	4.88 ±0.03	12.36 ±0.03	118.80	815	2.55	4	C2/c

responds to the oxalate 1/1/2 and the second to the atom considered in the α1/1/0 salt.

In both, the C_2O_4 groups form layers parallel to the (*xoy*) plane at $Z=0$ and $Z=\frac{1}{2}$. The barium atoms are lodged between these sheets. Each layer consists of chains parallel to [120] for the plane passing through the origin, or to $[\bar{1}20]$ for the plane at $z=\frac{1}{2}$. The figures 6a and 6b show the projection of the 1/1/2 stacking on the (*xoz*) plane and that of the $z=0$ (xoy) plane for the α1/1/0 oxalate respectively

In the two stackings the translation unit along these chains consists of two distinct centrosymmetrical C_2O_4 groups: $(C_2O_4)_I$ and $(C_2O_4)_{II}$ connected by a strong hydrogen bond (O_{IVI}–O_{III2} = 2.45 Å). Comparison of values for distances and valency angles of these two groups with information given in the literature for various oxalates and varieties of oxalic acid have permitted their unequivocal identification: $(C_2O_4)_I$ is a $C_2O_4^{2-}$ ion and $(C_2O_4)_{II}$ is an oxalic acid molecule (*10*).

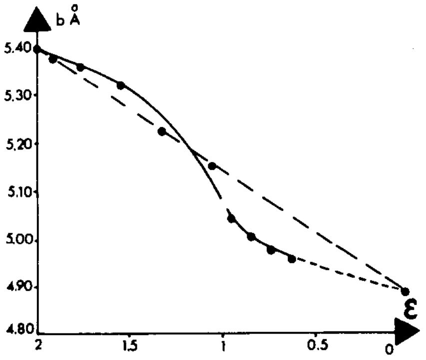


FIG. 5. Variation with the hydration degree ε of the *b* parameter of the monoclinic unit-cell suggest a divergence from Vegard's law.

Taking into account experimental errors due especially to poor recording conditions for the α1/1/0 oxalate structure, one may say that the appearance of vacancies in the 1/1/2 oxalate lattice involves no important modifications either of the characteristic dimensions of the $C_2O_4^{2-}$ ions and $H_2C_2O_4$ molecules (which keep their planar configuration), or of the length of the hydrogen bond which joins them.

The only noticeable change is the reduction of the angle which the two C_2O_4 groups make between them along the chains and which changes from 60° in the 1/1/2 oxalate to 48° in the anhydrous α phase.

The barium atoms ensure cohesion of the two structures. The four Ba^{2+} ions of the unit cell are located in special positions of the *C*2/*c* space group.

In the 1/1/2 oxalate each cation is surrounded by twelve oxygen atoms forming an almost regular icosahedron. Of the six apical independent atoms, two belong to a $(C_2O_4)_I$ ion, two to a $(C_2O_4)_{II}$ molecule, one to a $(C_2O_4)_{II}$ molecule translated from *b*, and one to the water molecule. This distribution shows that the cations ensure cohesion of the structure in two directions, between the chains of oxalate groups within the same layer, and between the adjoining oxalic planes.

In the anhydrous oxalate the barium coordination polyhedron differ from the

TABLE III

Atoms	x	$10^4\sigma x$	y	$10^4\sigma y$	z	$10^4\sigma z$	B(Å^2)	σB (Å^2)
Ba	0.5000	0	0.6661	4	0.2500	0	2.91	0.03
	0.5000	0	0.5718	0	0.2500	0	1.17	0.02
O_I	0.4889	22	0.1275	52	0.1219	31	5.05	0.63
	0.4882	8	0.1571	27	0.1187	13	4.26	0.45
O_{II}	0.3026	22	0.9179	64	0.1352	25	4.53	0.44
	0.3034	11	0.8991	31	0.1463	16	5.59	0.60
O_{III}	0.5772	22	0.7421	63	0.0747	28	4.48	0.49
	0.5756	7	0.7765	24	0.0795	12	3.40	0.44
O_{IV}	0.3615	21	0.6001	54	0.0071	25	4.28	0.49
	0.3561	8	0.6149	21	0.0036	13	3.74	0.50
O_w	0.3153	25	0.4031	75	0.2115	29	5.85	0.68
C_I	0.2349	32	0.8453	71	0.038	50	4.55	0.67
	0.2399	11	0.8243	39	0.0411	18	3.28	0.54
C_{II}	0.4752	28	0.1032	68	0.0195	33	3.61	0.55
	0.4757	11	0.1257	30	0.0178	18	3.20	0.51

preceding icosahedron only by the disappearance of the two water molecules.

In each case, the barium–oxygen distances are in good agreement with those listed in the International Tables for X-ray Crystallography for coordination numbers 12 and 10 of barium with respect to oxygen (*11*).

The dehydration leaves molecule-sized vacancies in the anhydrous framework. Situated in general positions in the dihydrate unit cell, the eight water molecules are equivalent. Study of the environment of one of them (O_{WI}) and of its orientation with respect to the other atoms of the skeleton shows that there is only one hydrogen bond, equal to 2.76 Å which occurs between this molecule and the oxygen O_{III} of the $(C_2O_4)_I$ group. This indicates that the water does not take part in the cohesion of the dihydrate structure.

Examination of the anhydrous salt's structure shows that the sites previously occupied by the water molecules correspond to vacancies forming infinite channels centered on the helicoidal axes. The description of the stacking by means of the polyhedral representation reveals these channels well; the shaded areas of Fig. 7 show their openings on the (010) plane.

The water molecules have thus left the stacking without altering its organization: the later has merely become lacunary.

Discussion

The preceding experimental results have described the behavior of the system "hydrate 1/1/2–H_2Og" which, when subjected to certain conditions of pressure and temperature, leads to divariant equilibria in the sense that the dehydration degree is a function of the temperature at constant pressure and a function of pressure at constant temperature. An infinite number of hydrates $1/1/\varepsilon$ are obtained and in the case of very low pressures, an anhydrous phase, the determination of whose structure shows a

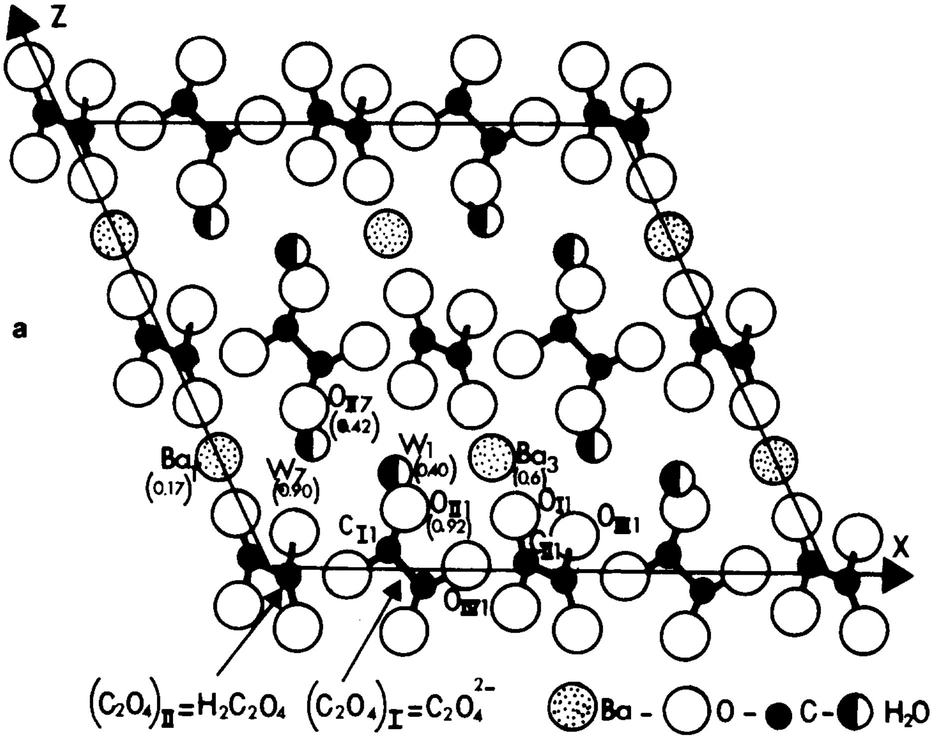


FIG. 6a. Stacking of the 1/1/2 oxalate projected on the (010) plane. Roman and arabian numerals indicate independent and equivalent atoms respectively. The number between parentheses indicates the y fractional coordinate.

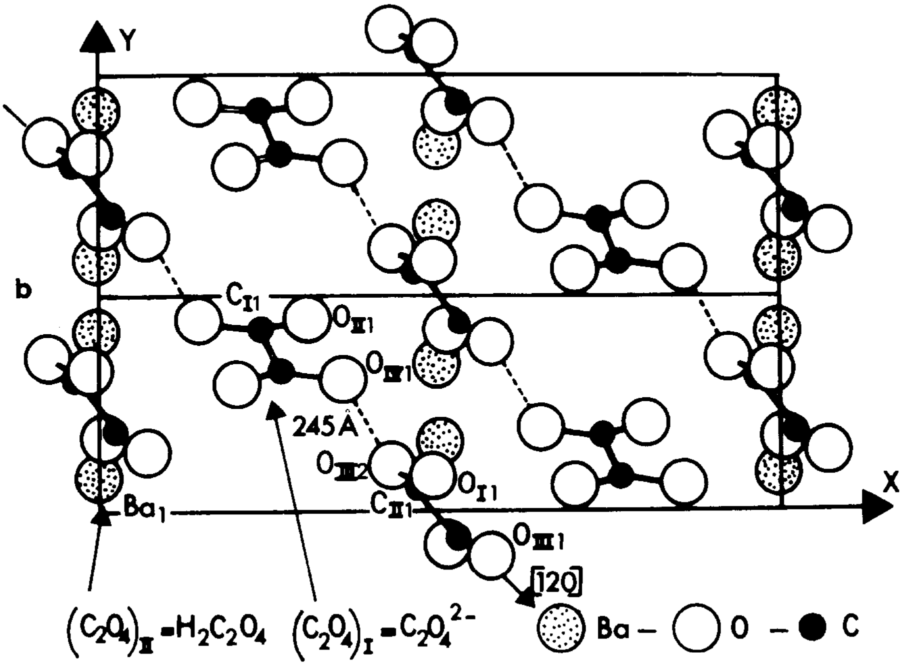


FIG. 6b. Projection on the (001) plane of the characteristic $(H_2C_2O_4–C_2O_4^{2-})_n$ chains in the $z = 0$ (xoy) plane for the α anhydrous oxalate.

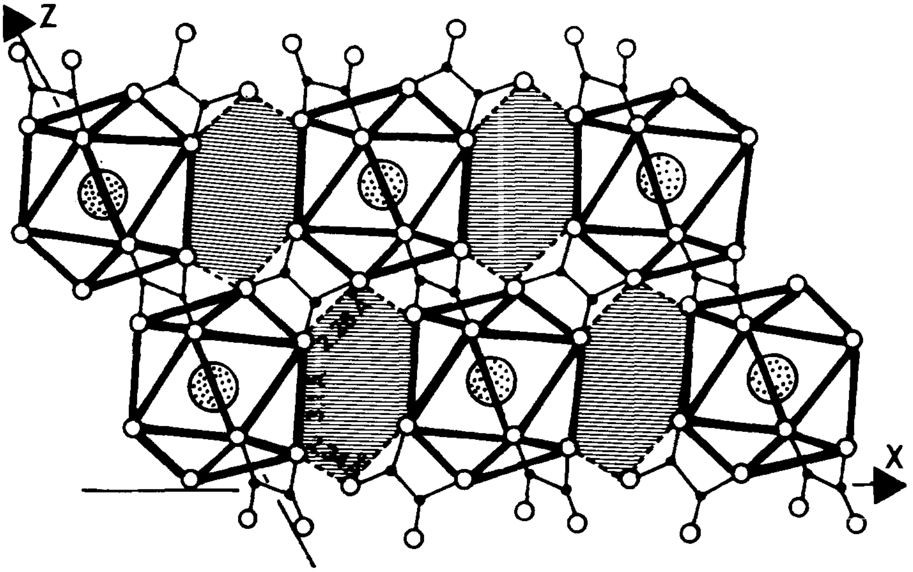


FIG. 7. Stacking of the $\alpha 1/1/0$ oxalate projected on the (010) plane. The shaded areas show the openings on this plane of channels.

lacunary stacking with respect to the initial structure.

This work raises certain questions concerning the mode of evolution of a solid mineral structure which liberates a gas when its stability conditions are modified. The following discussion will provide answers to these questions: first by describing the probable movements of atoms when the lacunary structure appears; next by explaining, by means of thermodynamic models and structural analysis, the existence of divariant equilibria and the limit of the stability domain; finally by proposing a structure corresponding to the 1/1/1 pseudomonohydrate.

Description of Atomic Movements in the Framework during the Formation of the $\alpha 1/1/0$ Phase

The continuous transition from the 1/1/2 to the lacunary stacking involves progressive movements of barium atoms and C_2O_4 groups. They can be described from a knowledge of the atomic positions for the two structures. The displacement of $C_2O_4^{2-}$ ions and of $H_2C_2O_4$ molecules can be assessed by comparing the values of the inclination angle of their mean plane with respect to (010) plane and by comparing their relative position along the characteristic chains of the stackings (Table IV).

Furthermore we have schematized those modifications by projecting on the (010) plane the two extreme positions which each group may occupy around its symmetry center, assuming this to be fixed (Fig. 8). The movement of the ions and molecules result from (a) closure of the angle between the

TABLE IV

	1/1/2	$\alpha 1/1/0$
Tilting angle of the plane of the $H_2C_2O_4$ molecule in comparison with the (010) plane	60°	52°
Tilting angle of the plane of the $C_2O_4^{2-}$ ion in comparison with the (010) plane.	40°	31°
Angle between the plane of the $H_2C_2O_4$ molecule and that of the $C_2O_4^{2-}$ ion along the [120] chains	60°	48°

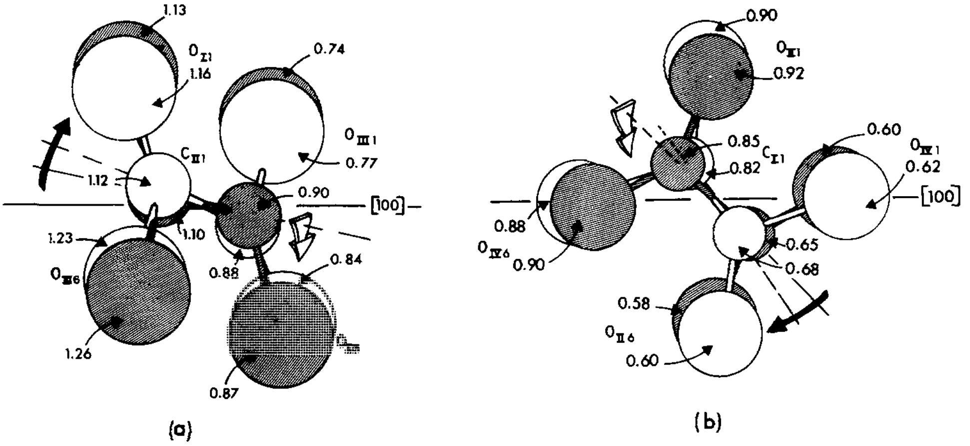


FIG. 8. The tilting–rotating movement of the $H_2C_2O_4$ (Fig. 8a) and $C_2O_4^{2-}$ ion (Fig. 8b).
The atoms in the dihydrate are shaded.
Symbols used are as on Fig. 6.
The large black arrow indicates the rotating movement of the group around the *oy* axis, the large white arrow indicates the tilting movement which causes the angle formed by group plane and the (010) plane to decrease.

(010) plane and group plane and (b) rotation of the group around the *b* axis such that the C–C axis draws nearer to (case of $H_2C_2O_4$) or away from (case of $C_2O_4^{2-}$) the [100] direction.

In order to complete this description, we propose to show that a knowledge of these movements and of the relative disposition of each of the (C_2O_4) groups in the stacking will allow a deduction of the changes in the unit cell parameters observed during the dehydration:

Each kind of group forms layers parallel to the (100) plane which alternate along the *ox* axis (Fig. 6a). Those at $x = 0$ and $x = \frac{1}{2}$ are made up of $H_2C_2O_4$ molecules with barium atoms intercalated in between, while in the others situated at $x = \frac{1}{4}$ and $x = \frac{3}{4}$, $C_2O_4^{2-}$ ions alternate with water molecules. Clearly, the tilting of the (C_2O_4) will induce a contraction of the stacking in the [010] direction (involving reduction of the *b* parameter). At the same time, the tilting together with the rotation must bring about an increase in the *a* parameter since the movement of $C_2O_4^{2-}$ ions (movement of O_{IV} atoms) involves a displacement, in the [100] direction, of the molecules which surround them. On the other hand, the *c* parameter can only be reduced slightly since the displacement of the $H_2C_2O_4$ molecules is limited in this direction by the Ba^{2+} ions and that of the $C_2O_4^{2-}$ ions (displacement of O_{II} atoms) may be very easily achieved in the space made available by the loss of water molecules.

The elimination of water molecules corresponds then to a perfectly topotactic transformation which only involves very reduced movements of atoms remaining in the anhydrous structure.

Interpretation of the Existence of Nonstoichiometric hydrates

We would like to emphasize two unusual results: first, the existence of divariant equilibria even though the water molecules occupy crystallographically defined positions in the structure of the initial dihydrate—second, the abrupt interruption of the divariance domain by a curve (L, Fig. 2) almost parallel to the pressure axis.

We have been able to show that these two results can be explained by a thermodynamic model of the divariance of "hydrate–water vapour" systems, which has been proposed under two virtually equivalent forms (*12–14*).

The first makes use of the thermodynamics of solid solutions and postulates either the existence of an insertion–solid–solution of water in the anhydrous salt, or the existence of a substitution–solid–solution between two hydrated forms of the salt.

The second refers to the concept of stoichiometric difference (quasichemical model). It has recourse to a point defect formulation and gives all the possibilities from the case where water molecules are delocalized, i.e. free to move in the solid, to those where they are localized, i.e. occupy crystallographically precise sites in the structure.

On the other hand, the development of the model by the mathematical study of the $\varepsilon(P)_T$ function and by consideration of all the kinds of reactions competing with the divariant equilibrium (monovariant dehydration or hydration of one of the two constituents of the solid phase, precipitation of a new phase, decomposition of the matrix) has established criteria which, when compared with the experimental results, permit, (a) characterization of the solid which with the gas forms a divariant system, and (b) specification of the characteristic of the phenomenon limiting the divariance both for high and low values of ε.

In our case and whichever of the somewhat different but complementary descriptions of the model one uses; one is led to conclude that the solid phase in equilibrium with vapor consists of either a substitution–solid–solution between the two forms 1/1/2 and α1/1/0, or is a hydrate of localized water molecules; a conclusion which is perfectly consistent with its determined structure. Adopting a quasichemical notation, the divariant equilibrium would be written:

$$(H_2C_2O_4 \cdot BaC_2O_4 2\langle H_2O\rangle)_1 \leftrightarrows 2[H_2O] + (H_2C_2O_4 \cdot BaC_2O_4 \cdot 2\langle\ \rangle)_1$$

The two constituents 1/1/2 and α1/1/0 belong to the same solid phase marked with the index 1. The symbol $\langle\ \rangle$ represents a site in the solid which can be occupied by a water molecule or be empty, in which case it is a vacancy. The symbol [ ] denotes the gaseous state.

The limit L of the divariant domain (Fig. 2) is due to the competition of the preceding reaction with the precipitation of a new solid phase which would be the allotropic β form of the completely dehydrated salt, according to the reaction

$$\underset{\alpha\text{ form}}{(H_2C_2O_4 \cdot BaC_2O_4 \cdot 2\langle\ \rangle)_1} \rightarrow \underset{\beta\text{ form}}{(H_2C_2O_4 \cdot BaC_2O_4)_2}$$

This thermodynamic model enables us then to explain the divariance of the system as well as the limiting phenomena, and to predict the kind of nonstoichiometry. By contrast, it has not been possible to establish an analytical expression of the $\varepsilon(P)_T$ isotherms which takes into account the peculiarity shown by the experimental curves in the neighborhood of the composition $\varepsilon = 1$, However, analysis of the dihydrate structures and of the lacunary anhydrous phase enables us to propose a mode of stacking for the nonstoichiometric hydrates and especially for the 1/1/1 pseudo monohydrate.

Probable Structure for the Lacunary Hydrates 1/1/ε—The case of the 1/1/1 Pseudomonohydrate

This representation of the lacunary hydrates results from the definition of a water vacancy in the oxalate studied. Comparison of the two stackings shows that the water leaves the lattice without any other considerable change in the framework arrangement (mode of stacking, geometry of the coordination polyhedron). The water vacancy is thus defined as a site which occupies the dipole H_2O in the barium coordination polyhedron.

Moreover, the removal of one of the two water molecules from the icosahedron causes the other to leave (*15*); then both sites, keeping their initial structural identity, constitute attraction centers for the dipoles still present in the structure and those of the vapor. Consequently, to the thermodynamic equilibrium there corresponds a statistical equilibrium between the vacancy and the water molecules affecting the entire crystal bulk.

This assumption is consistent with the homogeneous morphological transformations affecting the solid (*7*).

The structure of the lacunary phase $1/1/\varepsilon$ may thus be described as a statistical distribution of "hydrated" polyhedra (coordination 12) and of "anhydrous" polyhedra (coordination 10).

Such considerations enable us to suggest a particular structure when ε is close to 1. Without being that of a defined compound one may consider it to be characterized by a certain extent of order in its vacancies. Indeed, the equilibrium state which occurs in the solid when the concentrations of the free sites and water molecules are equal, does not exclude a corresponding ordered structure in accordance with the lattice symmetry elements.

Such a distribution may be conceived in two ways:

1. *The Water Molecule Occupies the Special Position (1/4, 1/2, 1/4)*

The monohydrate unit-cell contains four water molecules implying that they occupy the (e) special positions in the *C*2/*c* group (Fig. 9). However, calculation of the interatomic distances separating the molecule thus localized and the neighboring oxygen atoms shows that one of them (O_{II7} in the dihydrate structure) in only 2 Å. This distance is much too short for this structural hypothesis to be acceptable.

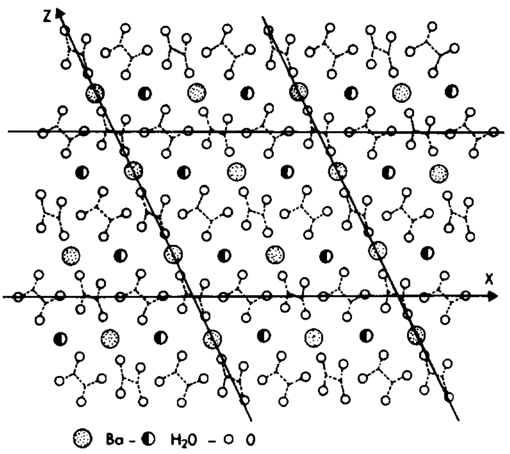


FIG. 9. Structure of the pseudomonohydrate $H_2C_2O_4 \cdot BaC_2O_4 \cdot H_2O$ (projection on the (010) plane). First hypothesis: the water molecule occupies the special position (1/4, 1/2, 1/4).

2. *The Four Water Molecules of the Unit Cell are Shared between the Eight General Positions which they Occupied Initially*

This amounts to considering that each water dipole occupies alternatively one or the other of the two equivalent positions on adjacent polyhedra. An ordered distribution satisfying this dynamic process requires that in the dihydrate structure one icosahedron out of two must be regularly replaced by a ten atom polyhedron (Fig. 10).

The hypothesis of one water molecule statistically distributed between two crystallographic sites is supported by the following arguments: first, in the 1/1/2 oxalate structure (Fig. 6a) the second proton of the molecule W_1 which coordinates the Ba_3^{2+} ion is probably oriented towards oxygen O_{II7} which belongs to the Ba_1^{2+} coordination polyhedron (W_1–$O_{III} = 3.06$ Å) (*8*). Due to thermal agitation and the slight structural modifications resulting from the removal of the first water molecules, the dipole W_1 is equally attracted by one or the other of the

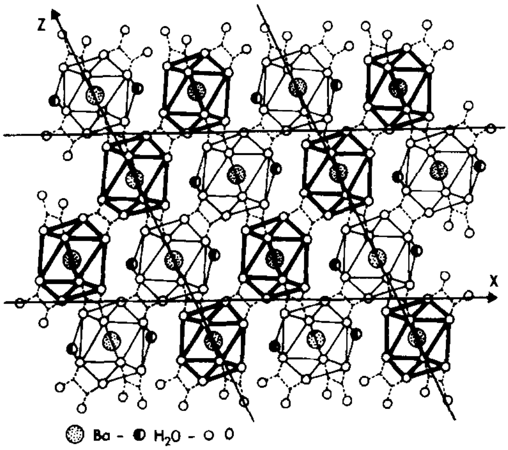


FIG. 10. Structure of the pseudomonohydrate $H_2C_2O_4 \cdot BaC_2O_4 \cdot H_2O$ (projection on the (010) plane). Second hypothesis: the four molecules of the unit cell are shared between the eight general positions which they occupied initially.

two Ba_3^{2+} and Ba_1^{2+} cations. Second, this exchange process appears in other structures [case of Gismondine (*16*) and $\beta FeF_3 \cdot 3H_2O$ (*17*)].

Finally, an argument supporting our pseudomonohydrate structure interpretation relates to the general decrease in intensity of the diffraction peaks for this composition (Fig. 1b). The dynamic process in which the water molecule passes alternately from the two sites is likely to involve a general agitation of the atoms of the structure, which would account for this intensity minimum (following the definition of the corrective term of thermal agitation).

Conclusion

The study of the thermodynamic and crystallographic characteristics of 1/1/2 oxalate dehydration demonstrate the divariance of the system formed by the solid phase and the water vapor.

The condition for isolation of an infinite number of nonstoichiometric hydrates $1/1/\varepsilon$ $(0 < \varepsilon < 2)$ have been specified. The lacunary nature of the anhydrous $\alpha 1/1/0$ salt $(\varepsilon = 0)$ follows unambiguously from the structural analysis which has been made from a totally transformed monocrystal. The atomic movements during this structure's formation are easily described.

The divariance of the "hydrate–vapor" system can be explained by the fact that the loss of water molecules which coordinate the Ba^{2+} cation scarcely affects the coordination polyhedron. The structure of each nonstoichiometric oxalate can therefore be described by a statistical distribution of coordination 12 polyhdra and of coordination 10 polyhedra. The peculiar behavior of the solid when its composition is close to $\varepsilon = 1$ can be interpreted by the appearance of an order in this distribution.

Finally, the formation of the $\alpha 1/1/0$ lacunary structure and its transformation into another more stable form $\beta 1/1/0$ argues in favor of the Freund and Niepce's hypothesis concerning the reaction mechanism of decompositions. In general, the intermediate lacunary phase cannot be observed easily; in the case of the barium acid oxalate, the sequence proposed by these authors is well illustrated.

We shall describe in a following article, the morphological changes during the formation of the $\alpha 1/1/0$ lacunary phase as well as the kinetic characteristics of the corresponding dehydration.

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