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Polymorphism and Anion Rotational Disorder in the Alkaline Earth Carbonates

J. J. LANDER

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(Received December 26, 1948)

X-ray diffraction methods have been developed for the study of materials at high temperatures under controlled atmospheres, and an investigation of the high temperature phases of the alkaline earth carbonates has been made. BaCO_3 was found to change from orthorhombic (aragonite type) to hexagonal (calcite type) at 803°C , and to cubic (sodium chloride type) at 976°C . SrCO_3 was found to change from orthorhombic (aragonite type) to hexagonal (calcite type) at 912°C . A few experiments with mixtures, which go through similar transitions, are described.

These transitions are related to the rotational activity of the carbonate ions and consideration of the nature of the transitions leads to a description of the probable rotational behavior of these ions in the various phases.

PART I. EXPERIMENTAL X-RAY DIFFRACTION STUDY

ONE of the earliest cases of polymorphism investigated by means of x-ray diffraction is that of CaCO_3 . Calcite (rhombohedral) and aragonite (orthorhombic) are well understood from the crystallographic point of view but a complete identification of vaterite (hexagonal) has not been reported. Aragonite is presumably the stable form at low temperatures and high pressures. It is rapidly and irreversibly converted to calcite at about 470°C . Vaterite is so unstable that large crystals have not been obtained. A fourth modification has been reported by Boeke.¹ He observed a reversible change in heat content of calcite at 975°C but found that the optical properties did not change in the transition.

Strontianite, isomorphous with aragonite, is the only form of strontium carbonate which has been observed at room temperature. Boeke² reported a transition to a hexagonal form occurring at 929°C on heating and at 920°C on cooling. These transition temperatures are very sensitive to impurities. For example, he had reported earlier that the temperature of transition on heating was 830°C , and this lower result he thought due to admixed CaCO_3 .

Witherite, isomorphous with aragonite, is the only form of barium carbonate which has been observed at room temperature. Boeke reported (reference 2) that witherite changes to a hexagonal form at 811°C and to a cubic form at 982°C . On cooling a hysteresis of about 50°C was observed in the case of the first transition. He also found that the admixture of 30 mole percent CaCO_3 lowered the orthorhombic to hexagonal transition temperature by about 150°C . However Cork and Gerhard,³ having completed an x-ray study of BaCO_3 at temperatures up to 1000°C stated, "In pure BaCO_3 no change in structure occurred, but the lattice enlarged."

* Presented at the First International Congress of Crystallography, held at Harvard University, July 28 to August 3, 1948.

¹ H. E. Boeke, *Neues Jahrb. Min. Geol. I*, 91 (1912).

² H. E. Boeke, *Chem. Zentr. I*, 1909 (1913).

³ J. M. Cork and S. L. Gerhard, *Am. Min.* **16**, 71 (1931).

Since the existence of at least one of these alkaline earth carbonate modifications has been questioned, and since in any case the crystallographic data given by Boeke are necessarily meager (he was limited to optical techniques), the x-ray diffraction study reported herein has been made. The results, besides being of general chemical interest, are of immediate importance to determinations of rates of decomposition and of equilibria between carbonate and oxide. Moreover they appear to provide an interesting set of examples of order-disorder transitions produced by anion rotational oscillation in the solid state, and this aspect of their behavior will be considered in detail in Part II.

Experimental Procedure

The crystallographic data reported below were obtained with x-ray diffraction accessories designed for the study of materials at high temperatures in controlled atmospheres or in a vacuum.⁴ Transition temperatures were observed precisely and rapidly with an x-ray spectrometer and one of these accessories. More detailed information was obtained from powder patterns for which $\text{CuK}\alpha$ radiation and a nickel filter were used. Some of these patterns are reproduced in Figs. 1, 2, and 3.

The transition temperatures reported are averages of results obtained with the spectrometer as well as from measurements of rates of heating and cooling. Agreement to $\pm 5^\circ\text{C}$ was obtained for corresponding points in all cases except that of the cubic transition of BaCO_3 for which an initial set of runs in the spectrometer gave too low a value. In this method a very small amount of material is used and one cannot be sure that its quality is as pure as that of the source. For this reason the transition temperatures were also measured using much larger samples and the usual differential method of observing heating and cooling rates as a function of temperature. The results of these measurements have been given heavier weight in the reported results.

⁴ J. J. Lander, *Rev. Sci. Inst.* **20**, 82 (1949).

The carbonates were obtained from batches of exceptionally high purity with respect to the cation. They had been dried at room temperature after precipitation from water solution. In all experiments at higher than ambient temperature of the laboratory they were maintained in 99.8 percent pure CO_2 at one atmosphere. Noticeable decomposition to oxide did not occur below 1300°C in the case of BaCO_3 or of SrCO_3 but occurred at about 900°C in the case of CaCO_3 . There was no noticeable reaction with the platinum supports.

Experimental Results with BaCO_3

Aragonite Type

As received barium carbonate gave only a few extremely broad features. After heating to 200°C an identifiable witherite pattern was obtained. The pattern of Fig. 1(a) was obtained from material at room temperature after it had been heated to 700°C . The lines are quite sharp and the pattern is identical with that

obtained from a powdered crystal of witherite.⁵ Measurements of a pattern from the former material into which sodium chloride was ground to serve as standard are given in Table I. The lattice constants $a_0=5.30\text{\AA}$, $b_0=8.88\text{\AA}$ and $c_0=6.42\text{\AA}$ are believed to be accurate to 0.2 percent. They are compared in Table II with those found by Wilson,⁶ by Cork and Gerhard (reference 3), and by Colby and LaCoste.⁷

Figure 1(b) is a pattern obtained from BaCO_3 at 750°C . Most of its features correspond with those of 1(a), however it will be found that a few lines are markedly displaced. Measurements of the most accurately determinable spacings, given in Table I, reveal an unusually large expansion along the c_0 direction, the direction normal to the plane of the carbonate ion. In order to obtain more accurate values for the changes in cell constants produced by heating from 20°C to 750°C the x-ray spectrometer was used. This method gives a greater relative accuracy than can be obtained

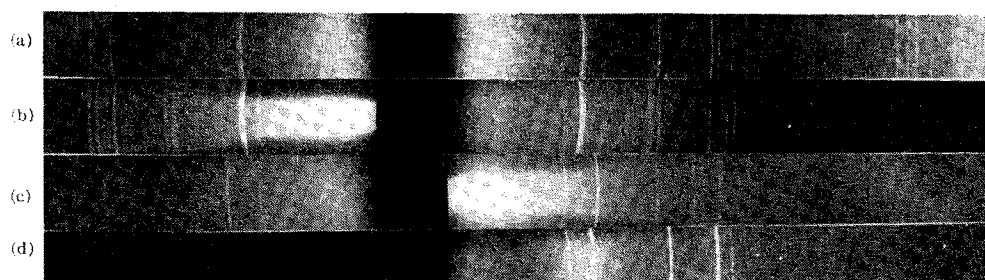


FIG. 1. Patterns from BaCO_3 : (a) orthorhombic form at 20°C after heating to 700°C ; (b) the same at 750°C ; (c) hexagonal form at 830°C ; (d) cubic form at 960°C after heating to 980°C .

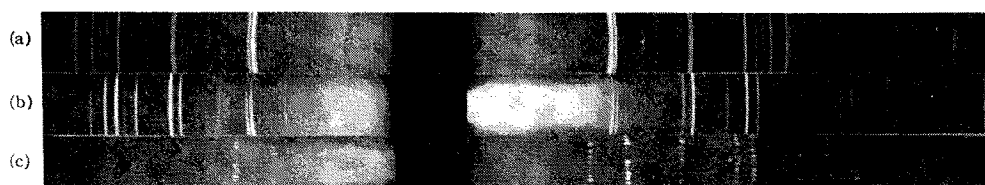


FIG. 2. Patterns from SrCO_3 : (a) orthorhombic form at 20°C after heating to 700°C ; (b) hexagonal form at 860°C ; (c) hexagonal form at 920°C .

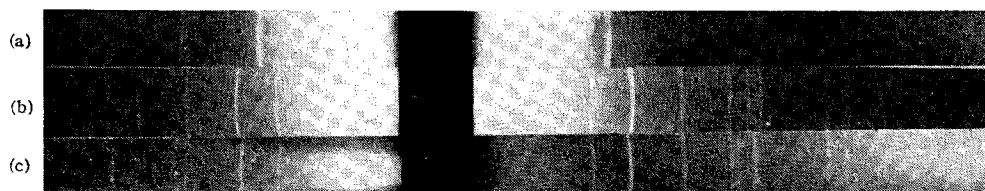


FIG. 3. "Triple carbonate" patterns: (a) orthorhombic form, no heat treatment; (b) hexagonal form at 750°C ; (c) hexagonal form at 20°C after heating to 750°C .

⁵ Crystals of witherite were obtained from Wards Natural Science Museum. They contained about one percent of strontium.

⁶ T. A. Wilson, Phys. Rev. **31**, 305 (1928).

⁷ M. Y. Colby and L. J. B. LaCoste, Zeits. f. Krist. **90**, 1 (1935).

TABLE I. X-ray data from aragonite-type carbonates.

hkl	BaCO ₃ at 20°C			BaCO ₃ at 750°C		SrCO ₃ at 20°C			Triple Carbonate at 20°C	
	<i>I</i> (obs.)	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>I</i> (obs.)	<i>d</i> (obs.)	<i>d</i> (calc.)	<i>I</i> (obs.)	<i>d</i> (obs.)
110	$\frac{1}{2}$	4.54	4.55	4.52	4.57	$\frac{1}{2}$	4.32	4.34	$\frac{1}{2}$	4.38
020	$\frac{1}{2}$	4.45	4.44	4.45	4.46	$\frac{1}{2}$	4.18	4.18	$\frac{1}{2}$	4.22
101	4.10	4.15	$\frac{1}{2}$	3.90	3.88
111	10	3.70	3.71	3.71	3.76	10	3.50	3.51	10	3.56
021	3	3.65	3.65	3.66	3.70	5	3.42	3.48	5	3.49
002	1	3.22	3.21	3.31	3.32	2	2.98	3.00	1	3.08
012	$\frac{1}{2}$	3.02	3.02	3.09	3.11	2	2.81	2.82	1	2.89
102	2.80	2.82	1	2.58	2.58	$\frac{1}{2}$	2.64
031	1	2.66	2.69	2.69	2.72	2	2.54	2.53	3	2.57
200			2.65	2.66	2.66			2.54		
112	2	2.62	2.62	2.69	2.69	3	2.46	2.47	3	2.52
022			2.60	2.66	2.66			2.44	5	2.48
130	2	2.59	2.58	2.59		3	2.44	2.43		
210	2.54	2.55	$\frac{1}{2}$	2.25	2.25	$\frac{1}{2}$	2.28
220	1	2.28	2.28	2.27	2.28	$1\frac{1}{2}$	2.17	2.17	$\frac{1}{2}$	2.19
040	$\frac{1}{2}$	2.22	2.22	2.22	2.23	$\frac{1}{2}$	2.090	2.092	1	2.128
221	4	2.15	2.15	2.15	2.16	5	2.040	2.041	7	2.073
041	2	2.101	2.103	2.110	2.110	3	1.973	1.973	5	2.015
202	2	2.052	2.050	2.075	2.076	3	1.936	1.938	3	1.975
132	3	2.020	2.012	2.040	2.043	4	1.893	1.894	5	1.938
113	4	1.937	1.936	2.000	1.991	3	1.816	1.816	5	1.862
023	1	1.804	1.803	$\frac{1}{2}$	1.822
222	$\frac{1}{2}$	1.858	1.857	$\frac{1}{2}$	1.758	1.758	1	1.793
042	$\frac{1}{2}$	1.827	1.827	1.850	1.848	$\frac{1}{2}$	1.716	1.716	$\frac{1}{2}$	1.750
310	$\frac{1}{2}$	1.731	1.732	1.736	1.739	$\frac{1}{2}$	1.660	1.660	1	1.680
240	$\frac{1}{2}$	1.705	1.702	1.705	1.708	$\frac{1}{2}$	1.617	1.612	$\frac{3}{2}$	1.645
311	$1\frac{1}{2}$	1.672	1.673	1.683	1.683	2	1.602	1.600	3	1.622
241	$1\frac{1}{2}$	1.645	1.645	1.653	1.654	2	1.562	1.560	3	1.586
151	2	1.626	1.628	1.639	1.639	2	1.537	1.535	3	1.567
004	$\frac{1}{2}$	1.606	1.606	$\frac{1}{2}$	1.500	1.500	$\frac{1}{2}$	1.541
223	$\frac{1}{2}$	1.558	1.558	1.595	1.590		1.473	1.471	1	1.505
330	$\frac{1}{2}$	1.517	1.517	1.522	1.523	1	1.468
114	1	1.420	1.417	$1\frac{1}{2}$	1.453

by measurement of the photographic patterns.** Displacements of the lines due to the 221, 132, and 113 planes were observed. The cell constants at 750°C given in Table IV were obtained in this manner.

Calcite Type

The pattern of Fig. 2(c) was produced by BaCO₃ at 830°C. Measured values for intensities and spacings are given in Table III as well as spacings calculated for a calcite-type structure with $a_0 = 5.205\text{\AA}$ and $c_0 = 10.55\text{\AA}$. The spacings which occur are those of the rhombohedral division of the hexagonal system and the observed intensities are in qualitative agreement with intensities calculated for the calcite structure in which scattering by the carbonate ion is neglected. For such a structure the intensities of all lines which appear are equal to a constant multiplied by the plane multiplicity and the angular scattering function. In the case of calcite it has been shown that carbonate ions are ordered in the manner shown in Fig. 4, and therefore the smallest rhombohedral cell contains two molecules. However, such ordering would be more difficult to observe in calcite-type structures containing much heavier metal

ions and at comparatively high temperatures. The hexagonal indexing of Table III assumes the smaller rhombohedral cell which contains one molecule and it is to be noted that all the observed features can be indexed on this basis, but the absence of reflections such as the 210, from which the ordering of carbonate ions can be inferred, is not accepted herein as evidence of disorder in either hexagonal BaCO₃ or SrCO₃. It is not unlikely that a more thorough study, preferably with monochromatic radiation, would decide this important point.

The transition temperature observed on heating was 803°C and that on cooling was 750°C. It was found that both transitions occurred abruptly. Material was held for an hour with no observable change at temperatures which, when shifted in the right direction by 10°C, produced the transitions in a matter of seconds.

Lower transition temperatures were obtained by adding CaCO₃, as was observed by Boeke. Approximately 2 mole percent lowered the temperatures of transition by approximately 25°C. Measurements of the transition in air also yielded lower results, presumably caused by a small amount of decomposition.

Sodium Chloride Type

The pattern reproduced in Fig. 1(d) was obtained from BaCO₃ at 960°C after heating to 980°C. Spacings in intensities correspond to those of the sodium chloride-

** The back-reflection technique would yield much more accurate results but could not be used because of the diffuseness of the features in the back reflection region. However, to obtain the highest precision, coefficients of linear expansion should be measured directly, for example, by interferometric measurements of single crystals.

type cubic structure with a_0 equal to 6.96Å. It is to be noted that the unit rhombohedral cell of calcite can be regarded as a distorted sodium chloride-type cell. Conversely a sodium chloride-type structure can be regarded as a special case of the calcite-type structure and may be given a similar indexing. The constants for the orthohexagonal cell (which is based on a (111) plane of the cubic cell) of cubic BaCO_3 are given in Table IV. This method of representing constants facilitates comparison among the polymorphic forms.

Tests to 1300°C revealed no further change in structure and none is to be expected.

The transition from hexagonal to cubic occurred at 976°C and the reverse transition about 20°C lower. Both were abrupt. Admixture of 2 mole percent CaCO_3 was observed to raise the temperatures of transition by about 20°C, and, as will be described below, it was found that large amounts of SrCO_3 or CaCO_3 tend to stabilize the hexagonal form.

Experimental Results with SrCO_3

Aragonite Type

Natural crystals were not obtained. As received, the powder gave a recognizable strontianite pattern. After heating to 700°C and cooling slowly the pattern of Fig. 2(a) was obtained. The close correspondence between this and the witherite pattern is obvious. Observed spacings and intensities are given in Table I as well as spacings calculated with $a_0=5.08\text{Å}$, $b_0=8.36\text{Å}$ and $c_0=6.00\text{Å}$. As in the case of BaCO_3 an unusually large thermal expansion along the c_0 axis was observed. The results of measurements of the change in lattice constants made with the spectrometer are given in Table IV.

Calcite Type

The intensities and indexing of spacings of the pattern of Fig. 2(c), produced by SrCO_3 at 920°C, parallel those found for hexagonal BaCO_3 and therefore the structure is that of calcite with anions possibly disordered. The calculated spacings given in Table III were obtained with a_0 equal to 5.092Å and c_0 equal to 9.53Å.

The orthorhombic to hexagonal transition occurred at about 912°C. Boeke obtained 929°C. Transitions were abrupt and admixture of 2 mole percent CaCO_3 lowered the temperatures of transition by about 40°C.

TABLE II. Reported lattice constants of aragonite type BaCO_3 and SrCO_3 .

Material	a_0	b_0	c_0	Reference
BaCO_3 (20°C)	5.30	8.88	6.42	Lander
BaCO_3 (20°C)	5.252	8.828	6.544	Wilson
BaCO_3 (20°C)	5.28	8.83	6.39	Colby and LaCoste
BaCO_3 (20°C)	5.256	9.172	6.412	Cork and Gerhard
SrCO_3 (20°C)	5.08	8.36	6.00	Lander
SrCO_3 (20°C)	5.12	8.40	6.08	Wilson

TABLE III. X-ray data from calcite-type carbonates.

hkl	BaCO_3 at 830°C			SrCO_3 at 920°C			Triple Carbonate at 20°C		
	I	$d(\text{obs.})$	$d(\text{calc.})$	I	$d(\text{obs.})$	$d(\text{calc.})$	I	$d(\text{obs.})$	$d(\text{calc.})$
10.1	7	4.12	4.14	5	3.98	4.00	5	3.96	3.99
00.3	3	3.48	3.52	—	—	—	—	—	—
01.2	10	3.40	3.42	10	3.22	3.18	10	3.17	3.18
11.0	6	2.59	2.60	5	2.53	2.54	5	2.58	2.56
10.4	6	2.27	2.28	5	2.094	2.098	—	—	—
02.1	5	2.20	2.20	3	2.140	2.140	5	2.155	2.155
11.3	2	2.09	2.09	(5)	1.993	2.000	2	1.988	1.994
20.2	2	2.07	2.07	—	—	—	2	1.988	1.994
01.5	2	1.910	1.910	2	1.752	1.749	$\frac{1}{2}$	1.692	1.692
00.6	$\frac{1}{2}$	1.760	1.758	$\frac{1}{2}$	1.593	1.589	$\frac{1}{2}$	1.525	1.525
02.4	$\frac{1}{2}$	1.711	1.713	1	1.622	1.618	$\frac{1}{4}$	1.592	1.592
21.1	2	1.682	1.682	3	1.639	1.643	1	1.648	1.648
12.2	$1\frac{1}{2}$	1.622	1.622	2	1.573	1.573	$\frac{3}{4}$	1.573	1.575
20.5	$\frac{1}{2}$	1.538	1.539	$\frac{1}{2}$	1.446	1.441	—	—	—
03.0	$\frac{1}{2}$	1.503	1.503	1	1.470	1.471	$\frac{1}{4}$	1.478	1.478
11.6	1	1.456	1.457	$\frac{1}{2}$	1.349	1.347	$\frac{1}{2}$	1.311	1.311
21.4	(1)	1.429	1.430	1	1.366	1.365	$\frac{1}{2}$	1.352	1.351
10.7	—	—	1.429	—	—	—	—	—	—
30.3	$\frac{1}{2}$	1.382	1.382	$\frac{1}{2}$	1.334	1.334	$\frac{1}{2}$	1.311	1.330
12.5	$\frac{1}{2}$	1.323	1.325	$\frac{1}{2}$	1.255	1.254	—	—	—
01.8	$\frac{1}{4}$	1.266	1.266	—	—	—	—	—	—
22.0	—	—	—	$\frac{1}{4}$	1.273	1.272	$\frac{1}{2}$	1.281	1.280

Heating to 1300°C produced no further change in structure. It is possible that a transition to a cubic form exists at a higher temperature and would be observed in experiments carried out with the material under a high pressure of CO_2 .

Experimental Results with CaCO_3

CaCO_3 was examined in the temperature range between 20°C and 900°C with the spectrometer. No transition was observed. At 900°C decomposition set in, the equilibrium pressure of CO_2 being about one atmosphere. Thus it was impossible to check the result obtained by Boeke at 975°C with the available equipment.

Lattice constants at 20°C and at 750°C are given in Table IV. These were obtained from measurements made of line displacements with the spectrometer. From these data the average coefficient of linear expansion in the c_0 direction is calculated to be 25×10^{-6} per °C and in the a_0 direction -2×10^{-6} per °C. Geiss⁸ measured these coefficients by a direct method in the range 0° to 80°C and obtained $(25.57 + 0.016t) \times 10^{-6}$ for the first and $(-5.05 + 0.008t) \times 10^{-6}$ for the second. Obviously third-order terms, negative in each case, must be added to cover the range 0° to 800°C. However, these terms cannot be obtained very precisely from the x-ray data reported here.

Experimental Results with a Triple Carbonate

A mixture of 46 percent BaCO_3 , 46 percent SrCO_3 and 8 percent CaCO_3 (percentages by weight) obtained by precipitation from a solution of the three metallic ions gave the barely recognizable aragonite-type pat-

⁸ Geiss, Ann. d. Physik 76, 403 (1925).

TABLE IV. Orthorhombic and hexagonal cell constants.

Material	Temp. (°C)	Structure*	a_0	b_0	c_0	Volume in Å ³ per mole
BaCO ₃	20	Orthorhombic	5.30	8.88	6.42	76.0
BaCO ₃	750	Orthorhombic	4.32	8.92	6.64	78.6
BaCO ₃	830	Hexagonal	5.205	9.02	10.55	82.6
BaCO ₃	960	Cubic	4.92	8.52	12.05	84.2
SrCO ₃	20	Orthorhombic	5.08	8.36	6.00	63.7
SrCO ₃	850	Orthorhombic	5.10	8.39	6.19	66.2
SrCO ₃	920	Hexagonal	5.092	8.82	9.53	71.4
CaCO ₃	20	Hexagonal	4.97	8.64	8.51	61.1
CaCO ₃	750	Hexagonal	4.976	8.64	8.67	62.0

* In the hexagonal and cubic structures a_0 , b_0 and c_0 refer to the orthorhombic cells and these cells contain eight molecules, whereas the orthorhombic cells contain four molecules. Anion disorder is implied by the values of c_0 given for all hexagonal cells. This is not valid in the case of CaCO₃ and may not be for the others. For an ordered cell this dimension is actually $2 \times c_0$.

tern reproduced in Fig. 3(a). After heating to 700°C and cooling to room temperature the material gave a good pattern very similar to those of Figs. 1(a) and 2(a). Observed intensities and spacings are given in Table I and the calculated lattice constants are $a_0 = 5.14$ Å, $b_0 = 8.52$ Å and $c_0 = 6.16$ Å.

Calcite Type

A pattern of hexagonal "triple carbonate" was obtained from the material at 750°C, and it was found that this structure was retained on cooling to room temperature at a moderate rate. However by very slow cooling the aragonite structure was obtained. The hexagonal patterns are reproduced in Fig. 3 and the observed intensities and spacings of the room temperature pattern are given in Table III. The spacings calculated from $a_0 = 5.12$ Å and $c_0 = 9.15$ Å agree very well with the observed values. The expansion between 20°C and 750°C along the c_0 direction, as measured with the spectrometer, was 3.8 percent whereas in the a_0 direction it was 0.4 percent.

Examination with the spectrometer revealed that the transition from orthorhombic to hexagonal on heating occurred rapidly at 710°C ($\pm 5^\circ$) and again it was found that the hexagonal structure was retained when the material was cooled at a moderate rate. Thus the structure of the "triple carbonate" may be either orthorhombic or hexagonal depending on the heat treatment, and this may be true of a wide range of mixtures of two or more of the carbonates.

Huber and Wagener⁹ made an x-ray examination of mixtures of the alkaline earth carbonates, and they report complete solution and the orthorhombic structure for mixtures of BaCO₃ or SrCO₃ with less than about 20 mole percent CaCO₃.

R. Faivre has made x-ray studies of mixtures of SrCO₃ with CaCO₃ and of BaCO₃ with CaCO₃.¹⁰ After heating to 900°C he found miscibility and the ortho-

rhombic structure for mixtures containing more than 50 mole percent SrCO₃ in CaCO₃ but a solubility limit of 11 percent was observed for SrCO₃ in the calcite form of CaCO₃. He also found that BaCO₃ takes up 35 percent CaCO₃ without change in structure but when more than this amount was present he observed the hexagonal structure.

Volume Considerations

The volumes in cubic angstroms per molecule of the alkaline earth carbonates at various temperatures are listed in Table IV and are plotted in Fig. 5. The full lines indicate average volume expansions and for the hexagonal forms of BaCO₃ and SrCO₃ and the cubic form of BaCO₃ they are estimates made on the assumption that the coefficients of volume expansion are the same as those of the orthorhombic forms. X-ray measurements were made but the temperature ranges are too small to obtain very accurate results. However, such measurements did prove that the expansions cannot be much larger than those estimated. The volume increases at the transition points are believed to be accurate to about 10 percent. The discontinuity indicated for CaCO₃ at 975°C is based on the assumption that the transition observed by Boeke is accompanied by a marked expansion along the c_0 axis.

PART II. ANION ROTATIONAL DISORDER

Introduction

A large number of transitions in solids have been associated with increased rotational activity of asymmetric ions or asymmetric molecular groups. In general it is expected that rotation remains effectively hindered

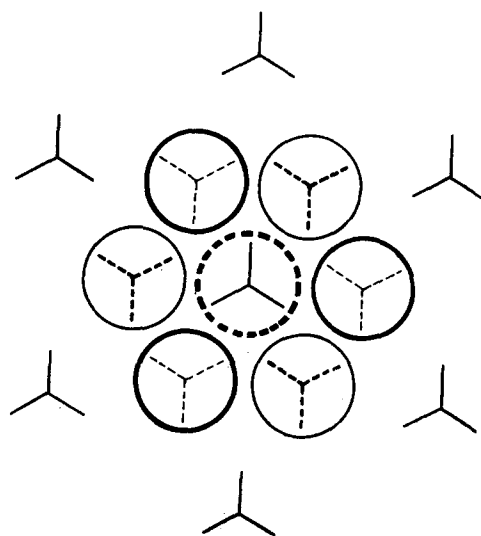


FIG. 4. Projection, along trigonal axis, of a carbonate ion and its nearest neighbors of both kinds in the ordered calcite structure. Circles represent metal ions, full lines a central plane and adjacent planes, dotted lines more distant planes, heavy lines upper planes and light lines lower planes.

⁹ H. Huber and S. Wagener, *Zeits. f. tech. Physik* **23**, 1 (1942).

¹⁰ R. Faivre, *Comptes Rendus* **219**, 73 (1944); **222**, 227 (1946).

above the transition temperature. Extensive investigations by means of the nuclear magnetic resonance method provide the most conclusive experimental evidence for this point of view.^{11,12}

In the argument which follows, and which concerns the alkaline earth carbonates, stress is placed on the possibility of a transition being determined or characterized by an increase in the number of configurations of rotational oscillation available to the carbonate ion. For example, constrained to a plane with a field of threefold symmetry, three configurations of rotational oscillation are available to the ion. If the symmetry of field changes to sixfold, six configurations are available. A transition which involves such an increase in configurations apparently takes place with a large increase in ionic rotational activity; but considerations of detailed dynamical behavior such as relative amplitudes of modes of oscillation, the persistence of ordered domains, and average rotational frequencies are not a part of the formal argument of this paper. An increase in the number of available configurations is described as a decrease in order, and it is assumed that the increase proceeds stepwise. It is recognized that this treatment represents a limited aspect of both disordering processes and changes in structure.

It is not at all obvious that the transition phases of barium and strontium carbonate are disordered and no direct experimental evidence for disorder has been offered. Moreover it is to be noted that in the related aragonite to calcite transition of CaCO_3 one type of ordered anion configurations simply gives way to another, there being no decrease in order since the number of configurations available to an anion is three in each case. Nevertheless it is argued that the transitions to hexagonal forms of barium and strontium carbonate are quite different in character. Furthermore the very interesting results of an x-ray study of NaNO_3 made by L. A. Siegel,¹³ and described below, indicate in detail the probable behavior of the hexagonal phases of the carbonates.

Comparison of Alkaline Earth Carbonates with Alkaline Nitrates

The alkali nitrates undergo transitions similar to those observed in the alkaline earth carbonates and it is to be noted that the nitrate ion is almost identical with the carbonate ion morphologically. Both ions are clover-shaped and only very careful x-ray examination reveals dimensional differences. KNO_3 is orthorhombic (aragonite structure) at room temperature but changes to a disordered hexagonal (calcite) structure at 127.7°C .¹⁴

NaNO_3 is hexagonal (calcite structure) at room temperature and it undergoes a transition at 275°C .

¹¹ Bitter, Alpert, Poss, Lehr, and Lin, *Phys. Rev.* **71**, 738 (1947).

¹² N. L. Alpert, *Phys. Rev.* **75**, 398 (1949).

¹³ Presented at the First International Congress of Crystallography, held at Harvard University, July 28 to August 3, 1948.

¹⁴ Kracek, Barth, and Ksanda, *Phys. Rev.* **40**, 1034 (1932).

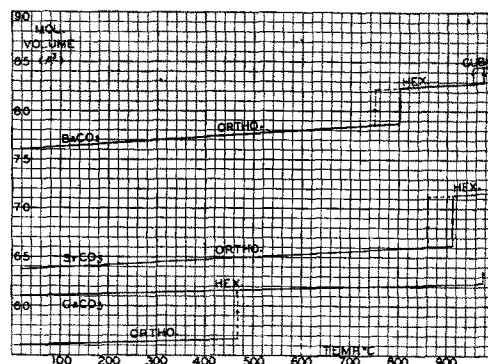


FIG. 5. Volumes per molecule in cubic angstroms plotted against temperature.

X-ray examination indicated that the nitrate ions rotate above the transition temperature but that no other change in structure takes place.¹⁵ A large expansion along the trigonal axis accompanies the transition (see Table V). In this case the more accurate analysis made by L. A. Siegel results in a more detailed description of the rotational behavior of the nitrate ion.

NH_4NO_3 undergoes six-phase transitions.¹⁶ A cubic form of the CsCl type is observed between 125.2 and 169.5°C , a tetragonal form between 84.2 and 125.2°C , an orthorhombic form between 32.3 and 84.2°C , etc. Free rotation about three mutually perpendicular axes was assumed to explain the x-ray data obtained from the cubic form, but apparently rotation was not required to interpret data obtained from the other modifications. A transition to a CsCl-type cubic phase is also exhibited by CsNO_3 (at 170°C), RbNO_3 (210°C) and by TlNO_3 (at 170°C). Finbak and Hassel¹⁷ made a study of these materials as well as of NH_4NO_3 and they pointed out that the cell dimensions of the cubic phases were too small to permit perfectly free rotation of any reasonably sized nitrate ions. However they did not assign more probable locations to the nitrate ions.

It is apparent that the phase transitions of alkali nitrates and of alkaline earth carbonates have a number of features in common. The temperature range of the transitions of interest in the case of the carbonates is quite different, but this is to be expected as a result of the stronger electrostatic and repulsive forces acting between the doubly charged ions. If anion rotational disorder exists in the hexagonal and the cubic forms of the carbonates, the analogy is almost complete. Pertinent crystallographic data are collected in Table V.

The cubic phases listed in Table V are too dense to contain anions occupying a volume corresponding to that of spheres circumscribed about a reasonably sized anion. The case of NH_4NO_3 has been discussed by Fin-

¹⁵ Kracek, Posnjak, and Hendricks, *J. Am. Chem. Soc.* **53**, 1183, 2609, 339 (1931).

¹⁶ Hendricks, Posnjak, and Kracek, *J. Am. Chem. Soc.* **54**, 2766 (1932).

¹⁷ C. Finbak and O. H. Hassel, *Zeits. f. physik Chemie* **B35**, 25 (1937).

TABLE V.

Material	Str.	Temp. (°C)	a_0	b_0	c_0	r_M
BaCO ₃	Ortho.*	20	5.30	8.88	6.42	1.35
BaCO ₃	Hex.	750	5.20	9.02	10.55	1.35
BaCO ₃	NaCl	950	4.92	8.52	12.05	1.35
SrCO ₃	Ortho.	20	5.08	8.36	6.00	1.13
SrCO ₃	Hex.	920	5.09	8.82	9.53	1.13
CaCO ₃	Ortho.	20	4.94	7.94	5.72	0.99
CaCO ₃	Hex.	20	4.96	8.49	2×8.48	0.99
NaNO ₃	Hex.	20	5.06	8.76	2×8.39	0.95
NaNO ₃	Hex. (rot.)	275	5.08	8.80	8.82	0.95
KNO ₃	Ortho.	20	5.42	9.17	6.45	1.33
KNO ₃	Hex. (rot.)	127	5.27	9.13	9.54	1.33
NH ₄ NO ₃	Hex.	-18	5.75	9.96	2×7.95	1.48
NH ₄ NO ₃	CsCl (rot.)	126	6.22	7.62	7.62	1.48

* Cell constants are for orthorhombic or orthohexagonal cells. Unless a_0 for hexagonal cells is multiplied by 2, disorder is implied. Metal radii r_M are from L. C. Pauling [*The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940), p. 346]. The approximate C-O distance is 1.31 and the N-O distance is 1.21. Dimensions are in Å units. Where the structure is marked (rot.) the original data were interpreted as evidence for free rotation by Kracek *et al.*

bak and Hassel and a simple calculation leads to this conclusion in the case of BaCO₃. The shortest Ba-O distance calculated for the hexagonal phase is 2.65. Allowing 1.35 for the radius of the barium ion leaves 1.30 for the outer radius of an oxygen ion in the carbonate ion. Since the hexagonal (calcite) structure is simply a distortion of the cubic (NaCl) structure, it is expected that the value for the outer radius of the oxygen ion will not change much in the transition. From the above values the diameter of the sphere circumscribing the carbonate ion is calculated to be 5.22 and the diameter of the barium ion to be 2.70. Thus the unit cell edge for the sodium chloride structure, assuming completely free rotation, might be expected to be 7.92. The observed value is 6.96, about 12 percent lower, and therefore, on the average, carbonate groups do not occupy a maximum volume. This argument suggests an assignment of positions which do not have spherical symmetry (free rotation about three mutually perpendicular axes).

It is to be noted that an approach to spherical symmetry can be obtained with an ordered arrangement of nitrate groups in which the anions are distributed with planes perpendicular to the four trigonal axes of a cube. The alkaline earth nitrates actually crystallize in a CaF₂-type cubic structure and an ordered arrangement has been assigned to the nitrate ions with planes perpendicular to the four trigonal axes.¹⁸

Mechanisms for Disorder in a Calcite-Type Structure

In calcite-type structures containing a planar anion with threefold symmetry the ordered arrangement of Fig. 4 is generally observed. All anions in a given plane have the same orientation, but are rotated through 60° with respect to all anions in the two adjacent planes. Only three equivalent positions are available to a given

anion. This ordering is not due to the metal ions. With respect to these alone the potential field in the plane of any anion has sixfold symmetry, which leaves six equivalent positions for all anions. Order is created by the anions themselves in setting up maximum distances between nearest oxygen ions. The metal ions offer a considerable barrier to the rotation of a single anion, but it is conceivable that a relative minimum exists in potential energy for the position obtained by rotating through 60°. An important consequence of such a rotation is that the energy levels of similar wrong orientations for all neighboring anions are temporarily lowered, so that there is a tendency for one such transition to produce another nearby.

This model of disorder is analogous to that for order-disorder in some alloys in which no gross change in structure takes place. A qualitative treatment of the Bragg-Williams type, which assumes complete disorder and neglects differences in vibrational entropy, is easily adapted to the situation. In the partially disordered crystal of N anions there are $2N$ non-equivalent orientations, therefore the maximum entropy change is $k \ln 2^N$. The change in internal energy is proportional to the energy V_0 required to disorder an anion in the completely ordered crystal. It follows that the critical temperature is proportional to V_0 . Since the ordered and disordered orientations are identical with respect to metal ions V_0 is determined, to a first approximation, by the "repulsive" interactions between oxygen ions. It is obvious that with increasing cell size the distances between oxygen ions increase and therefore that V_0 decreases. Thus critical temperatures should decrease in the series CaCO₃, SrCO₃, and BaCO₃. Moreover if the critical temperature of one of the series is known, then these temperatures may be calculated readily for the rest of the series, since some of the factors which are difficult to evaluate can be eliminated as a result of similarity in structure and other properties. If the Born-Mayer¹⁹ equation be used to calculate V_0 it is found that

$$V_0 = A \sum_s a_s e^{-r_s/\rho},$$

where A contains factors which should have identical values for the members of the series, a_s is the number of identical distances r_s between interaction centers for oxygen ions, and ρ is a constant which should be about 0.34×10^{-8} cm. The ratio of two critical temperatures is given by

$$T/T' = [\sum_s a_s e^{-r_s/\rho}] / [\sum_s a_s e^{-r'_s/\rho}],$$

in which the constant of proportionality in the expression for the critical temperature is also eliminated. If the disordered structure for CaCO₃ is more stable above 975°C, then with reasonable values for r_s and r'_s it has been calculated that BaCO₃ should disorder at a temperature about 400°C lower. The critical temperature

¹⁸ Strukturbericht, Band II, p. 73.

¹⁹ M. Born and J. E. Mayer, Zeits. f. Physik 71, 1 (1932).

The argument that disorder, if it exists, is of the type described by Siegel may be supported by a con-

Rotational Disorder in Cubic Structures

The transitions of BaCO_3 and NH_4NO_3 to cubic structures remain to be considered. It has been argued that anion-free rotation about all axes is improbable but it was pointed out that a cubic structure may result from an arrangement of these anions with planes perpendicular to the four trigonal axes (body diagonals) of a cube. In the case of BaCO_3 with the NaCl structure the projection along the trigonal axis of any anion so

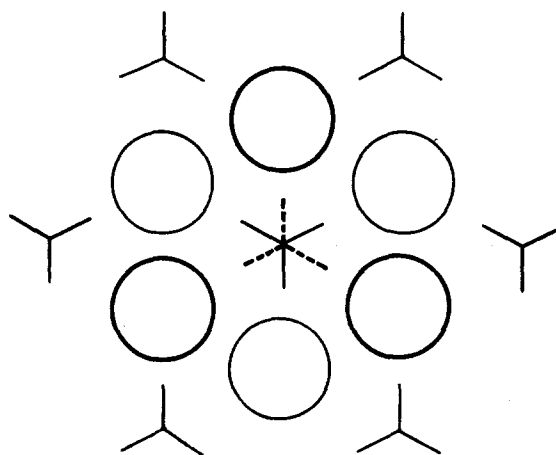


FIG. 6. Projection, along pseudotrigonal axis, of a carbonate ion and its nearest neighbors of both kinds in the aragonite structure. Light circles represent metal ions at the zero level and heavier circles metal ions at one-half. The three carbonate ions along the center line are at approximately one-third and those above and below at approximately one-sixth. The carbonate ions represented by the dashed lines are at approximately five-sixths and minus one-sixth.

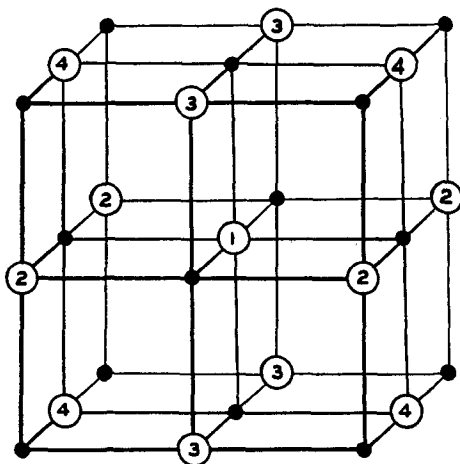


FIG. 7. Representation of a possible structure for cubic BaCO_3 . Carbonate ions are indicated by the open circles and numbers refer to the four ways of orienting an ion with its plane perpendicular to a trigonal axis. This cell is ordered with respect to these orientations.

oriented on a Cl lattice point and of its nearest neighbor cations is identical with a similar projection for the hexagonal calcite-type structure. Such an ordered arrangement has, of course, less rotational order than the ordered hexagonal arrangement, but two additional types of disorder may exist. Disorder may arise in a manner similar to that described above for the hexagonal structure in which disordering was brought about by increased rotational activity of an anion in its plane, in which process six rotational configurations, probably of the aragonite type, become available; and disorder may also arise by rotations to wrong trigonal axes, that is, by rotations about axes lying in the planes of the ions.

Consider a likely ordered arrangement of a type which should result in the cubic NaCl structure. Such an arrangement is represented in Fig. 7. The open circles represent carbonate ions. The four orientations with the plane of the ion perpendicular to a trigonal axis may be distributed in any fashion on the four carbonate sites of an elementary cube but once this is done the requirement that the unit cubic cell be repeatable in space fixes the distribution. Note that no two nearest neighbors are identically oriented.

If one calculates minimum oxygen to oxygen and oxygen to metal ion distances for this arrangement, assuming only rotation about the axis perpendicular to the plane of anions, one finds that these distances are larger than the corresponding distances calculated for a disordered hexagonal structure and therefore one concludes that if the hexagonal phase is disordered with respect to rotation of an anion in its plane, according to the first or the second mechanism discussed above, then the cubic phase is also disordered with respect to the same rotational mode and probably according to the corresponding mechanism. One might argue that oxygen to oxygen interactions are so much smaller than

in the hexagonal phase that an approach to completely free rotation may take place, but the amplitudes of rotational oscillations in directions perpendicular to the plane of an anion must be large, as is indicated by the transition to the cubic structure, and an adequate estimate of the various interactions must take this into account.

The cubic phase of BaCO_3 may be disordered with respect to the four orientations of anions on the body diagonals. Such a disordering process might appear as a separate transition and be characterized by an increase from one to four in the number of equivalent orientations of the axis of the ion.

Summary and Conclusion

Transitions in the solid state of both the first and the second kinds which are obviously due to increased rotational activity of an asymmetric ion are well known. In general the experimental evidence favors a theory of disordered configurations of rotational oscillation, and this theory is assumed *a priori*. The high temperature transitions of the alkaline earth carbonates apparently fall into this classification. No direct experimental evidence has been offered in proof of this argument. It is supported (1) by analogy with the behavior of alkali-nitrates, (2) by the evidence of increased rotational activity offered by the very large coefficients of thermal expansion in the direction perpendicular to the plane of the carbonate ion in both orthorhombic and hexagonal forms, (3) by the anomalous heat in CaCO_3 at 975°C , (4) by the existence of plausible mechanisms for rotational disorder which may be, in effect, first approximations to the rotational activity of the anions in these substances, and (5) by the transition of BaCO_3 to a cubic structure, which transition clearly implies an advance stage of rotational disorder.

For these reasons, and since no evidence for order exists, it has been argued that the hexagonal phases of both BaCO_3 and SrCO_3 and also of CaCO_3 above 975°C are disordered, the most likely mechanism being one in which the number of equivalent orientations obtained by rotation of a carbonate ion in its plane changes from three to six. These may be assigned in two different ways, and the more likely is that observed by Siegel in NaNO_3 . It also seems probable that the cubic phase of BaCO_3 is disordered in the same sense, but cubic symmetry implies a rotation of the axis of the carbonate ion. The four body diagonals of a cube provide four preferred orientations for the axis of the ion. An ordered arrangement exists and also one of disorder in which case the configurations of rotational oscillation of an ion in this mode increase from one to four.

The configurations of rotational oscillation available to an asymmetric ion or molecule are an important property of transitions involving rotational disorder.

The transitions described above appear to be relatively simple from this point of view. In an extreme type of disorder the configurations may be uniformly distributed in space, but the most extreme case is one of free or nearly free rotation in space in which case con-

figurations of rotational oscillation are no longer significant. It is doubtful that a precise determination of the rotational behavior of BaCO_3 or SrCO_3 can be made by means of x-ray diffraction studies if the transition forms are disordered.

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Rotational Absorption Spectrum of HDO*

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The 2_2-2_1 , 3_0-3_1 , $4_{-3}-3_1$, and the 5_0-5_1 rotational absorption transitions of HDO have been observed and identified on the basis of their Stark effect. By comparing the theoretical and experimental Stark shift, the dipole moment for all these transitions has been measured as 1.84 ± 0.01 . The effective HOD angle is also determined as $104^\circ \pm 30'$ and the parameter of asymmetry, κ , as about -0.696 . The line breadth $\Delta\nu$ at one atmosphere is $0.38 \pm 0.04 \text{ cm}^{-1}$. None of these quantities is in disagreement with independent determinations.

INTRODUCTION

THE intermediate heavy water molecule, HDO, has not been studied as fruitfully as have the H_2O and D_2O isotopic forms. The pure rotational spectrum of the intermediate molecule observed in the infra-red is, of course, hopelessly complicated by absorption due to the inevitable H_2O and D_2O impurities. However, King, Hainer, and Cross¹ (KHC) have reanalyzed existing vibration-rotation data and on the basis of a rigid rotor model have published a table of expected absorption frequencies in the microwave region.

One might expect that little could be said about the HDO molecule if these absorption frequencies were measured since, for example, centrifugal distortion of the energy levels would obscure any relation between the absorption frequencies and the molecular structure. It is inevitable that with a molecule as complicated as HDO, an asymmetric top, those rotational energy levels having magnitudes of several hundred wave numbers may not be calculated exactly from measured energy-level differences of the order of one wave number.

On the other hand, such measurements are of value in determining the usefulness of a rigid rotor analysis of infra-red data, and in supplementing infra-red data used in assigning term values. Stark effect measurements also provide additional structure data in the case of HDO, as we shall show below. A study of the absorption due to HDO in the microwave region can thus be of use, although application of the data is certainly more limited than in the case of a linear or a symmetric top molecule.

EXPERIMENTAL MEASUREMENTS

The sweep spectroscope and frequency standard used in these measurements have been described elsewhere.² Since KHC have pointed out that centrifugal distortion effects cancel out rather well in $\Delta J=0$ transitions, these transitions were first studied. The 5_0-5_1 ** line at 22307.67 Mc/sec has been reported by Townes and Merritt,³ and by us.⁴ To obtain a more accurate analysis the Stark effect for this transition was remeasured, and two other transitions, the 2_1-2_2 and the 3_0-3_1 were also measured at 10,278.99 Mc/sec and 50,236.90 Mc/sec, respectively. The Stark measurements on these lines enable positive identification to be made.

INTERPRETATION RESULTS

The theoretical Stark effect may be calculated for these transitions to compare with the observed perturbation. For perturbation energies ($\mu \cdot E$, where μ is the electric dipole moment, E is the electric field) much less than the energy difference between the asymmetric-top term values, the Stark effect is a second-order perturbation. The problem is one of calculating the quantum mechanical matrix elements of the direction cosines of the molecule-fixed axes to the space-fixed electric field axis. Induced polarization may generally be ignored as Golden and Wilson⁵ have shown. Fortunately, necessary direction-cosine matrix elements have been tabu-

² Strandberg, Wentink, and Kyhl, *Phys. Rev.* **75**, 270 (1949).

** The $J\tau$ notation will be used. J is the total angular momentum quantum number, and τ is a running index over the energy levels within the given J group.

³ C. H. Townes and F. R. Merritt, *Phys. Rev.* **70**, 558 (1946).

⁴ Strandberg *et al.*, *Phys. Rev.* **73**, 188 (1948).

⁵ S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.* **16**, 669 (1948).

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¹ King, Hainer, and Cross, *Phys. Rev.* **71**, 433 (1947).