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An anomaly in the crystal structure of Na_2CO_3.

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The structure of Na_2CO_3 at room temperature is not known. We found this phase to be of interest because it contains an unusual type of super-lattice, *viz.* an extra one-dimensional, perfect periodicity, *not* coinciding with any set of lattice planes of the main lattice. The present note describes the evidence for this anomaly as well as some investigations at high temperature.

In the course of routine investigations we tried to index the powder pattern of anhydrous sodium carbonate. This proved to be uncommonly difficult. A clue to the solution was eventually obtained through application of a computer method (de Wolff 1963). This led to a C-centered monoclinic unit cell (Table 1) which, however, did not explain all powder lines. A considerable number (roughly 20% of the total) of lines, mostly of weak intensity, withstood every attempt either to incorporate them on the basis of a multiple cell, or to eliminate them by different ways of chemical preparation.

We then succeeded in obtaining a small single crystal by slow cooling of the molten salt. This was mounted in a Weissenberg camera with what proved later to be the b axis parallel to the axis of rotation. Photographs were taken of the levels $k = 0$, 1, and 2. The results fully corroborated the unit cell derived from the powder pattern. The zero layer was completely normal. In the other photographs, however, extra spots were easily detectable as weak but perfectly sharp satellites of the 'main' spots. In reciprocal space, the extra spots form linear rows of 3–5 equidistant points, with the main spot as a centre. Writing these rows as $\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{p}^*$, ($m = 0$, ± 1, ± 2) where h, k, l, are the indices of the main spot ($m = 0$), the observed facts can be described as follows.

(1) $\mathbf{p}^*$ is a vector independent of h, k, and l.

(2) The intensity of the satellites, being zero for $k = 0$, increases with increasing k and seems to be roughly proportional to the main spot intensity, for a given k.

The outer satellites ($m = \pm 2$) are generally much weaker than the inner ones. In a few cases those for $m = 3$ are visible. The intensity sequence is often irregular.

All these facts were completely and quantitatively in accordance with the extra lines in the powder pattern, meaning that the extra lines and the satellite spots represent the same phenomenon. The powder diffraction angles provided the more accurate means for measuring $\mathbf{p}^*$, be it indirectly. They also made it possible to do the same at higher temperatures.

A Guinier camera as described by Lenné (1961) was used for the high-temperature work. In this camera the powder pattern is continuously recorded on a moving film while the temperature of the sample is raised. Three phases were discernible, in accordance with the differential thermal analysis results of Reisman (1959), whose data for the transition temperatures are used below:

(*a*) The C-centered monoclinic γ phase below 361 °C (with extra lines)

(*b*) The C-centered monoclinic β phase between 361 °C and 489 °C)

(*c*) The primitive hexagonal α phase above 489 °C, stable up to the melting point.

In the monoclinic γ phase the fractional coordinates of the vector $\mathbf{p}$ change continuously with temperature (Table 1). This proves that $\mathbf{p}$ is not conjugated to a set of lattice planes.

The transition to the β form is a gradual one. The β phase is characterized by the absence of extra lines and by large temperature coefficients of the unit-cell parameters. The transition to the α form is a sharp transition of the α–β quartz type.

The relation between β and α, as shown by the transition behaviour, is

$$(2\mathbf{a}+\mathbf{b})_\alpha = \mathbf{a}_\beta;\quad \mathbf{a}_\alpha = \mathbf{b}_\alpha = \mathbf{b}_\beta;\quad \mathbf{c}_\alpha = \mathbf{c}_\beta.$$

An investigation of the structures of these phases is in progress. The powder data of sodium carbonate at room temperature have been sent to the X-ray Powder Data File.

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Table 1. *Crystallographic data of* Na_2CO_3 *at various temperatures*

Phase	Temp. (°C)	a	b	c	β	$\mathbf{p}$	$1/p$	Z
γ	23	8·90 Å	5·24 Å	6·04 Å	101·2°	$0{\cdot}182\mathbf{a}^* + 0{\cdot}318\mathbf{c}^*$	16·3 Å	4
γ	330	8·96	5·24	6·20	99·7	$0{\cdot}154\mathbf{a}^* + 0{\cdot}286\mathbf{c}^*$	19·0	4
β	440	9·00	5·24	6·31	96·9	—	—	4
α	500	(9·01)*	5·20	6·50	90	—	—	2
α	790	(9·05)*	5·22	6·75	90	—	—	2

* Values of $(2\mathbf{a}+\mathbf{b})$ have been listed for the hexagonal γ phase.