

## Raman Spectrum of Calcium Carbonate at High Pressures\*

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(Received 28 August 1970)

FONG-MY 71-0013

Raman spectra of calcite,  $\text{CaCO}_3$  II, and  $\text{CaCO}_3$  III have been studied at various pressures as high as 40 kbar. Thirteen lines have been observed in the previously unreported spectrum of  $\text{CaCO}_3$  II and 20 lines are reported for the  $\text{CaCO}_3$  III spectrum. These spectra are compared with Raman spectra of aragonite,  $\text{KNO}_3$  III, and  $\text{KNO}_3$  IV; and previous suggestions that  $\text{CaCO}_3$  II and  $\text{KNO}_3$  III may be isostructural and that  $\text{CaCO}_3$  III and  $\text{KNO}_3$  IV also may be isostructural are shown to be incorrect. Alternative structures for  $\text{CaCO}_3$  II and  $\text{CaCO}_3$  III are briefly considered.

Calcium carbonate occurs naturally in three structural forms: the rhombohedral calcite form, the orthorhombic aragonite, and the orthorhombic vaterite forms. Calcite is the stable phase of  $\text{CaCO}_3$  at atmospheric pressure, and aragonite is the stable phase at high pressures. At temperatures below  $100^\circ\text{C}$ , however, the calcite: aragonite transition proceeds so slowly, at least in the absence of mineralizers, that it can be ignored for all practical purposes. The stability field of vaterite is not well established. The structures of these phases of calcium carbonate are given by Wyckoff.<sup>1</sup>

Two other phases of calcium carbonate were discovered in 1939 by Bridgman using isothermal compression of ordinary calcite at room temperature.<sup>2</sup> These phases, commonly designated  $\text{CaCO}_3$  II and  $\text{CaCO}_3$  III, were detected by discontinuities of the isothermal compressibility: one at 14 kbar due to the calcite: $\text{CaCO}_3$  II transition, and one at 18 kbar due to the  $\text{CaCO}_3$  II: $\text{CaCO}_3$  III transition. Bridgman followed both transition lines between 300 and  $500^\circ\text{K}$ . The existence of  $\text{CaCO}_3$  II and  $\text{CaCO}_3$  III at room temperature has been confirmed by independent x-ray powder diffraction studies by Jamieson<sup>3</sup> and Davis,<sup>4</sup> although they draw divergent structural inferences from their data. Both the slope of the calcite: $\text{CaCO}_3$  II boundary and the x-ray data suggest that  $\text{CaCO}_3$  II is a disordered variant of calcite, but other details of the structures of  $\text{CaCO}_3$  II and  $\text{CaCO}_3$  III are unknown and have been subjects of dispute. Several speculations have been based upon analogies to phase diagrams of other alkaline earth carbonates and the alkali nitrates. Prominent among these suggestions are that  $\text{CaCO}_3$  II is isostructural with the high-temperature, anion-disordered phase of  $\text{NaNO}_3$ <sup>3</sup> or with the ferroelectric potassium nitrate phase  $\text{KNO}_3$  III,<sup>4,5</sup> and that  $\text{CaCO}_3$  III is isostructural with the high-pressure  $\text{KNO}_3$  IV phase of potassium nitrate.<sup>4,5</sup> In contrast to these effects of compression for calcite, no transitions are observed when aragonite is compressed isothermally at room temperature.

The investigation of the Raman spectrum of calcium carbonate under high pressures described herein was undertaken to obtain additional detailed information about possible structures of  $\text{CaCO}_3$  II and  $\text{CaCO}_3$  III. Raman spectra of calcite, aragonite,  $\text{CaCO}_3$  II, and

$\text{CaCO}_3$  III were obtained at various pressures up to 40 kbar at several temperatures between about 300 and  $450^\circ\text{K}$ . The vaterite phase was not studied. The emphasis of this work was to obtain as complete and detailed Raman spectra of the  $\text{CaCO}_3$  II and  $\text{CaCO}_3$  III phases as possible.

It is usually difficult to determine complex structures unambiguously from Raman spectra alone, and this is the case here. However, such spectra provide at least some structural information, e.g., an estimate of the number of formula units in the primitive cell. These spectra can also be compared with Raman spectra of related materials, ideally of known structures, to determine whether the materials have similar structures. Thus, in this case, the Raman spectra of the  $\text{CaCO}_3$  II and  $\text{CaCO}_3$  III phases can be compared with spectra of the various  $\text{KNO}_3$  phases, for example, to test the suggested structural identifications of the phases mentioned above. For this purpose, a separate investigation of the Raman spectra of four phases of  $\text{KNO}_3$  was undertaken in this laboratory by Ellenson. The results of that study will be described in detail elsewhere,<sup>6</sup> but some relevant preliminary results of his work of immediate interest to the  $\text{CaCO}_3$  problem will be described later in this paper.

## EXPERIMENTAL

The high-pressure spectroscopic techniques used for this study have been described previously,<sup>7,8</sup> except for the external heating of the high-pressure optical cell used to obtain spectra at temperatures up to  $160^\circ\text{C}$ . This is approximately the upper temperature limit at which this optical cell can be used with unsupported windows. During these experiments, the temperature of the sample was measured with a copper-constantan thermocouple mounted on the cylinder wall of the high-pressure cell about 3–5 mm from the sample.

The pressure within the cell was determined from the load applied to the pistons, and a recent calibration of the pressure scale for the cell in terms of several known phase transitions shown in Fig. 1.<sup>9</sup> This shows the approximately linear relationship between the pressure within the cell and the applied load at pressures



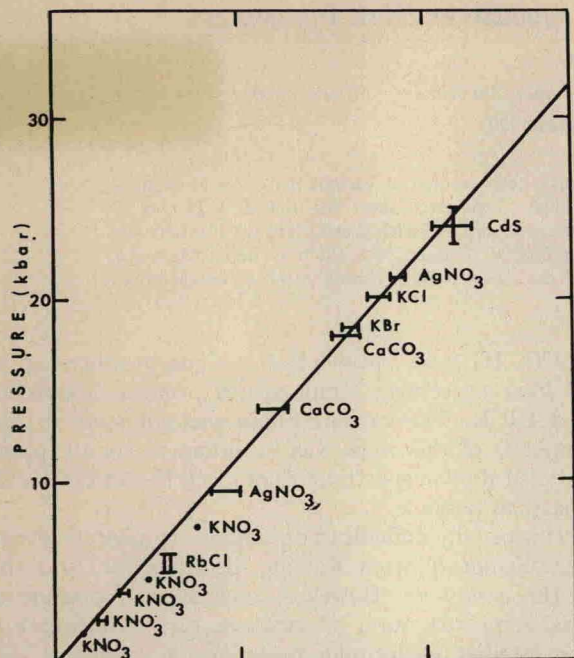


FIG. 1. A plot of the pressures at which several known phase transitions occur vs the load applied to this high-pressure cell (the units of linear axis of abscissas are arbitrary) at which these transitions were observed, representing the near linearity of the pressure vs load relationship for this cell. Note that some of the data for  $\text{KNO}_3$  are for transitions at elevated temperature; all other transitions were observed at room temperature.

up to 25 kbar. This calibration was used at all temperatures.

The samples of calcite used in this work generally had the dimension  $1.5 \times 1.5 \times 2.4$  mm and were cleaved or were cut from larger single crystals with a Be-Cu wire saw. The calcite came from two sources. Small natural cleavages of excellent quality were used for the preliminary experiments, while large (about 1 in. in dimension) natural cleavages were obtained from Ward's Natural Science Company for later experiments including those involving oriented samples. No differences were detected between the Raman spectra of the two types of natural cleavage crystals.

The calcite crystal to be studied was mounted in the high-pressure cell with its long axis parallel to the axis of compression. It was surrounded by pieces of sodium chloride that had been cleaved to fit the sample from a 3.18-mm-diam  $\times$  4-mm-length-cylinder of machined single-crystal salt. The salt serves to maintain an approximately constant orientation of the sample relative to the cell and to transmit pressure to the sample. Two thin pieces of this salt cylinder, each about 0.8 mm long, cover the top and bottom sides of the sample so that the sample is not in direct contact with the steel pistons. The whole assembly is then inserted into the high-pressure cell, with the sample faces approximately normal to the axes of the optical windows.

Two distinct orientations of calcite crystals were

used in these experiments; throughout this report, these orientations are called (1) natural and (2) parallel orientations. Natural orientation refers to cleaved crystals that were oriented with the direction of compression (the axis of the cylindrical high-pressure cell) normal to one of the natural cleavage planes and at an angle of  $38^\circ$  to the  $z$  axis of the crystal. Parallel orientation designates crystals that were cut and oriented with the  $z$  axis parallel to the axis of the high-pressure cell. The unique, optic ( $z$ ) axis of the calcite crystal passes through two vertices of the natural cleavages and can usually be identified with ease. Therefore, sample orientations were selected only visually in a rough manner before cutting or cleaving. Examinations of the oriented samples with a polarized microscope confirmed that this method was satisfactory. More than ten samples of each orientation were studied.

The significance of the orientation is due to use of solid NaCl as the pressure-transmitting medium. This means that the stress on the sample may be axially anisotropic. The unique axes of the stress and crystal are parallel for the parallel orientation of the sample.

## RESULTS

In the experiments described here, Raman spectra of several calcite crystals of each orientation were

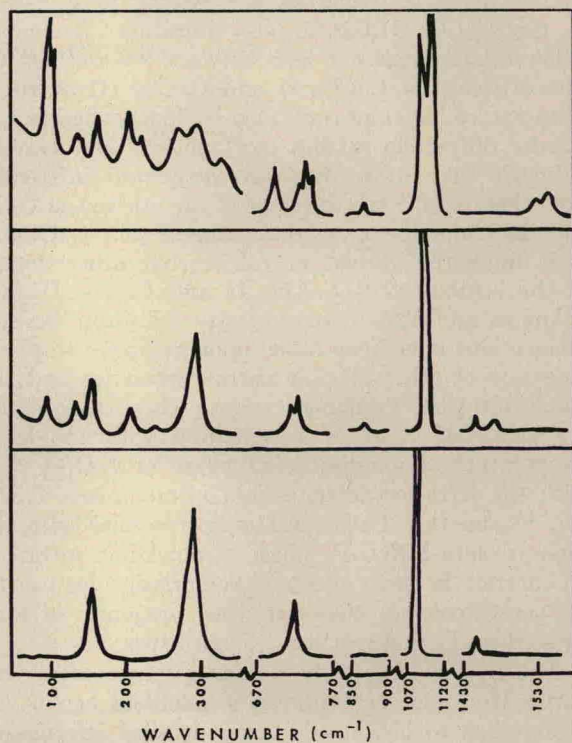


FIG. 2. Room-temperature Raman spectra of calcite (lower trace, 1 bar),  $\text{CaCO}_3$  II (middle trace, 14 kbar), and  $\text{CaCO}_3$  III (upper trace, 18 kbar) obtained upon compression of a calcite crystal of natural orientation.