

Raman Spectrum of Calcium Carbonate at High Pressures*

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Raman spectra of calcite, CaCO_3 II, and 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 CaCO_3 II and 20 lines are reported for the CaCO_3 III spectrum. These spectra are compared with Raman spectra of aragonite, KNO_3 III, and KNO_3 IV; and previous suggestions that CaCO_3 II and KNO_3 III may be isostructural and that CaCO_3 III and KNO_3 IV also may be isostructural are shown to be incorrect. Alternative structures for CaCO_3 II and 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 CaCO_3 at atmospheric pressure, and aragonite is the stable phase at high pressures. At temperatures below 100°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.¹

Two other phases of calcium carbonate were discovered in 1939 by Bridgman using isothermal compression of ordinary calcite at room temperature.² These phases, commonly designated CaCO_3 II and CaCO_3 III, were detected by discontinuities of the isothermal compressibility: one at 14 kbar due to the calcite: CaCO_3 II transition, and one at 18 kbar due to the CaCO_3 II: CaCO_3 III transition. Bridgman followed both transition lines between 300 and 500°K . The existence of CaCO_3 II and CaCO_3 III at room temperature has been confirmed by independent x-ray powder diffraction studies by Jamieson³ and Davis,⁴ although they draw divergent structural inferences from their data. Both the slope of the calcite: CaCO_3 II boundary and the x-ray data suggest that CaCO_3 II is a disordered variant of calcite, but other details of the structures of CaCO_3 II and 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 CaCO_3 II is isostructural with the high-temperature, anion-disordered phase of NaNO_3 ³ or with the ferroelectric potassium nitrate phase KNO_3 III,^{4,5} and that CaCO_3 III is isostructural with the high-pressure KNO_3 IV phase of potassium nitrate.^{4,5} 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 CaCO_3 II and CaCO_3 III. Raman spectra of calcite, aragonite, CaCO_3 II, and

CaCO_3 III were obtained at various pressures up to 40 kbar at several temperatures between about 300 and 450°K . The vaterite phase was not studied. The emphasis of this work was to obtain as complete and detailed Raman spectra of the CaCO_3 II and 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 CaCO_3 II and CaCO_3 III phases can be compared with spectra of the various 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 KNO_3 was undertaken in this laboratory by Ellenson. The results of that study will be described in detail elsewhere,⁶ but some relevant preliminary results of his work of immediate interest to the CaCO_3 problem will be described later in this paper.

EXPERIMENTAL

The high-pressure spectroscopic techniques used for this study have been described previously,^{7,8} except for the external heating of the high-pressure optical cell used to obtain spectra at temperatures up to 160°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. 1.⁹ This shows the approximately linear relationship between the pressure within the cell and the applied load at pressures

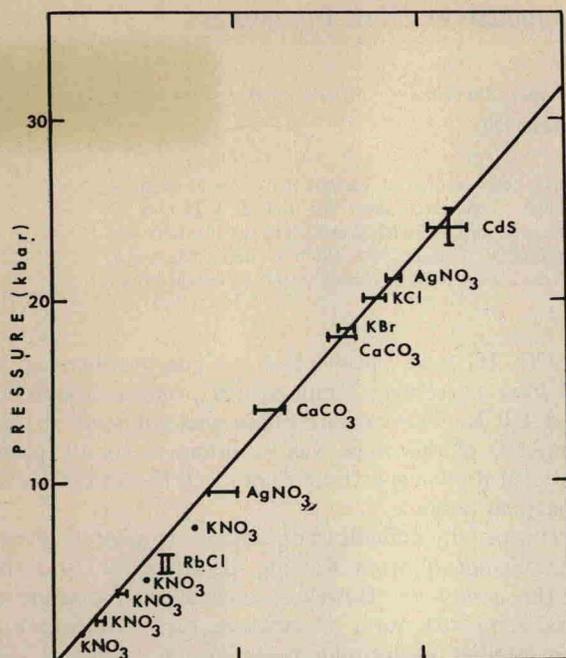


FIG. 1. A plot of the pressures at which several known phase transitions occur vs the load applied to this high-pressure cell (the units of linear axis of abscissas are arbitrary) at which these transitions were observed, representing the near linearity of the pressure vs load relationship for this cell. Note that some of the data for 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° 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

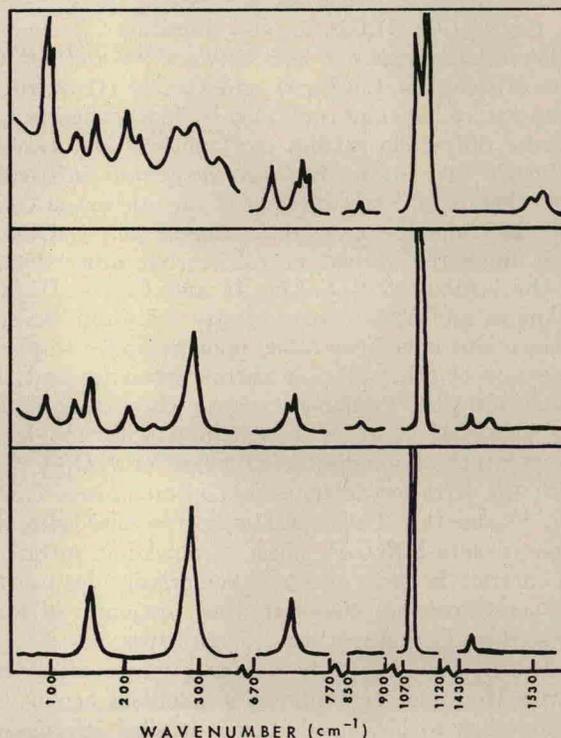


FIG. 2. Room-temperature Raman spectra of calcite (lower trace, 1 bar), CaCO_3 II (middle trace, 14 kbar), and CaCO_3 III (upper trace, 18 kbar) obtained upon compression of a calcite crystal of natural orientation.

obtained at various pressures from 1 bar up to 40 kbar at room temperature. For some of these crystals, Raman spectra also were obtained at several temperatures between 20 and 160°C along isobars in the fields of CaCO₃ II and CaCO₃ III. For some calcite samples, Raman spectra were taken upon both increasing and decreasing the pressure on the sample. The polymorphic transitions were reversible except for the frictional hysteresis of the cell, and the CaCO₃ II and calcite spectra recovered upon decompression from CaCO₃ III and CaCO₃ II, respectively were essentially identical with the spectra obtained during the initial compression. A few experiments were performed to determine the effects of compression at room temperature on the Raman spectrum of aragonite, and preliminary results of a survey⁶ of the Raman spectra of KNO₃ at comparable temperatures and pressures also are presented.

The room-temperature Raman spectra of CaCO₃ at 1 bar, 14 kbar, and 18 kbar, obtained by compression of natural- and parallel-orientation calcite crystals, are represented in Figs. 2 and 3. Several differences are apparent between the spectra taken at different pressures which correspond to the three polymorphs, calcite, CaCO₃ II, and CaCO₃ III. The frequencies of the observed Raman-active phonons, determined from these spectra, are summarized in Table I. The frequencies of calcite at 10 kbar, and of CaCO₃ III at

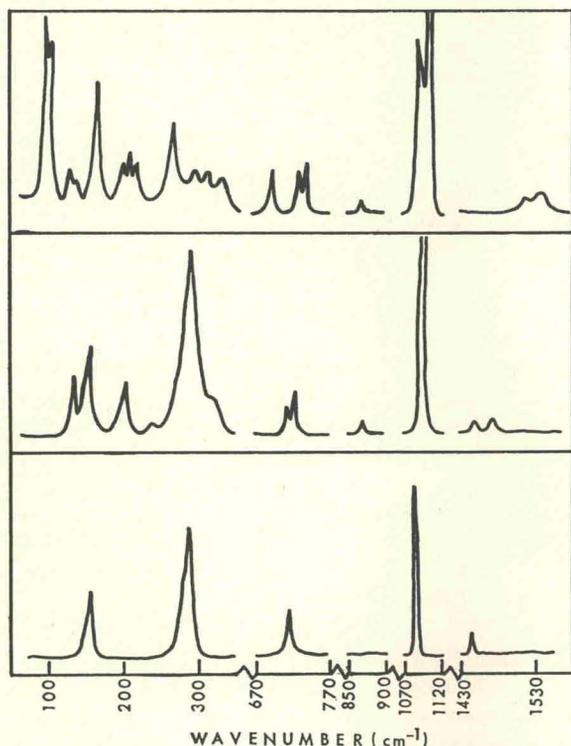


FIG. 3. Room-temperature Raman spectra of calcite (lower trace, 1 bar), CaCO₃ II (middle trace, 14 kbar), and CaCO₃ III (upper trace, 18 kbar) obtained upon compression of a calcite crystal of parallel orientation.

TABLE I. Frequencies of Raman-active phonons of calcite, CaCO₃ II, and CaCO₃ III.^a

Phase	Calcite		CaCO ₃ II	CaCO ₃ III	
	1 bar	10 kbar	14 kbar	18 kbar	38 kbar
			99 (n)	99	99
				105	109
			133	131	139
				137	
	151	161	155	161	173
			204	202 (p), 204 (n)	205 (p), 206 (n)
				208 (p)	224 (p)
				221	224 (n)
					234 (p)
			240	269	270
	287	290	292	299	312
			319 (p)	314 (p)	318 (p)
				333	351
				695	695
			715	[715]	
	713	719	721	[721]	[723 (n)]
				733	739
				741	745
			866	870	870
				1087	1093
				[1099 (n)]	[1099 (n)]
	1082	1094	1096	1104	1108
	1440	1444	1445	1515	1520
			1471	1540	1540

^a Except when indicated by the letters p (parallel) or n (natural), the frequencies are the same for both initial orientations of the calcite crystal. Frequencies for CaCO₃ III that are enclosed in brackets are thought to be due to residual CaCO₃ II. All frequencies are in cm⁻¹.

38 kbar also are given in Table I to give a rough idea about how these frequencies change with pressure.

The Raman spectrum of calcite at room temperature and atmospheric pressure has been well known for a long time; the assignment of the calcite spectrum has recently been reviewed by Porto *et al.*¹⁰ The five-line spectrum is attributed to two sets of doubly degenerate external or lattice modes belonging to the E_g representation of D_{3d} , two sets of doubly degenerate internal E_g modes of the CO₃²⁻ ion and a nondegenerate A_{1g} internal mode. The external modes at 151 cm⁻¹ and 287 cm⁻¹ are associated with translations of the two CO₃²⁻ ions of the primitive cell normal to the C_3 axis, and librations of these ions around axes normal to the C_3 axis, respectively. The internal E_g modes at 714 cm⁻¹ and 1440 cm⁻¹ are associated with the ν_4 bond-bending and ν_3 bond-stretching modes, while the A_{1g} mode is associated with ν_1 , the symmetric stretch. Modes associated with ν_2 , the out-of-plane bending mode, are Raman inactive in calcite due to the inversion symmetry of the crystal structure. Except for understandable minor variations in the relative intensities of the lines of the calcite spectrum,

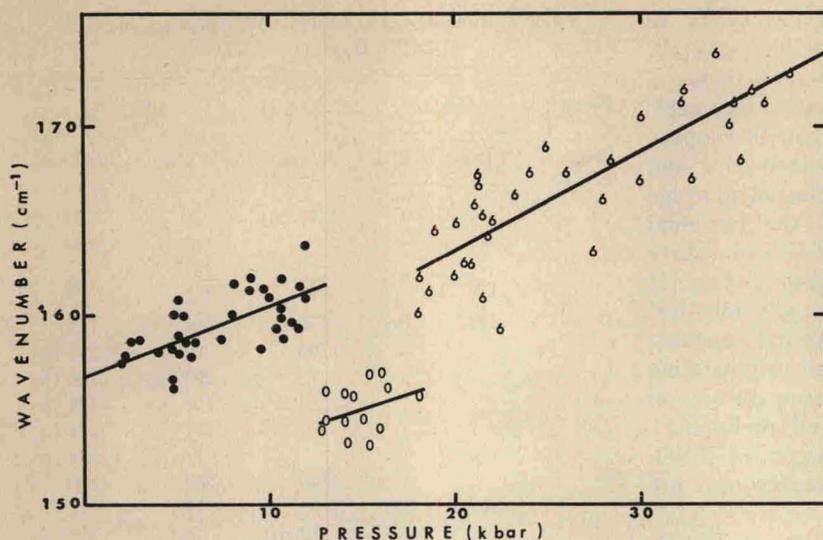


FIG. 4. A plot of the frequency of the Raman-active phonon in the 150–175- cm^{-1} range vs pressure. The solid points are from calcite spectra, the open circles are from CaCO_3 II spectra, and the sixes are from CaCO_3 III spectra. The solid lines represent least-squares fits to the three sets of data.

the Raman spectra obtained for the calcite phase were independent of orientation.

As the data in Table I indicates, the frequencies of all of the lines of the Raman spectrum of calcite increase with pressure. The average rate of increase over 10 kbar ranges from 0.3 to 1.2 $\text{cm}^{-1}\cdot\text{kbar}^{-1}$. These rates are typical of other ionic crystals studied in this laboratory. The 12- cm^{-1} shift of ν_1 from 1 bar to 10 kbar, however, is somewhat larger than the shift of ν_1 determined in infrared absorption studies by Wier *et al.*¹¹ and by Schock and Katz.¹² A possible explanation of this discrepancy attributes the appearance of ν_1 in the infrared spectra (as well as the appearance of the 865- cm^{-1} band and the splitting of ν_4)¹² to formation of CaCO_3 II in the diamond cell used for the infrared studies. The increase of the Raman frequencies with pressure is presumably due to a narrowing of the corresponding vibrational potential wells as the atoms are compressed together, but these shifts have not been analyzed in quantitative detail.

The Raman spectrum of CaCO_3 II is characterized by splitting of the ν_4 internal mode into a pair of lines at 715 and 721 cm^{-1} ; by the appearance of new lattice phonon lines at 133, 204, and 240 cm^{-1} as well as at 99 or 319 cm^{-1} , for certain sample orientations discussed below; and by the appearance of a weak line attributed to ν_2 at 866 cm^{-1} . The frequency of the translational lattice mode (at 155 cm^{-1} in the atmospheric pressure spectrum) also shifts discontinuously when the system transform from calcite to CaCO_3 II.

In calcite, this frequency increases approximately linearly with increasing pressure at about 1.0 $\text{cm}^{-1}\cdot\text{kbar}^{-1}$, but it abruptly disappears around 14 kbar, and a new peak of comparable intensity appears at about 7 cm^{-1} below the expected frequency of this phonon as extrapolated from lower pressures. This pressure dependence is represented in Fig. 4.

The appearance of the weak ν_2 line in the Raman spectrum of CaCO_3 II is consistent with the appearance of ν_1 in the infrared spectrum of CaCO_3 at comparable pressures.¹² The Raman frequency for ν_2 agrees with the infrared data. Although the possibility that the ν_2 line is induced by nonhydrostatic stresses cannot be excluded, these lines suggests that the CaCO_3 II structure lacks inversion symmetry. This is consistent with the suggestions that the anion orientations are disordered in CaCO_3 II.

The 99- cm^{-1} line is observed only for cleaved, natural-orientation samples; and the 319- cm^{-1} shoulder of the 292- cm^{-1} line is found only in spectra of parallel-orientation samples. The 99- cm^{-1} line also is unusual because its frequency is independent of pressure over the (small) stability range of CaCO_3 II, unlike the other lines of the calcite, CaCO_3 I[†] and CaCO_3 III spectra, but the frequencies of some Raman lines of other materials^{7,13} are similarly insensitive to pressure. Comparison of spectra taken with 5145- and 4880- \AA excitation, either with or without narrow-bandpass filters on the excitation, suggest that the 99- cm^{-1} line is neither an argon emission or a grating ghost. Although these effects are not completely understood, it seems likely that they result from a combination of polarization and preferred orientation effects. The intensity of the 99- cm^{-1} line appears to be inversely related to the intensities of the 133- and 319- cm^{-1} lines when all three are normalized by the intensity of the 154- cm^{-1} line.

Except for the 99- and 319- cm^{-1} features, the frequencies of all of the lines of the CaCO_3 II spectra are observed to be independent of sample orientation, within experimental error of ± 3 cm^{-1} . However, calcite crystals mounted in the parallel orientation are found to transform into CaCO_3 II with greater difficulty than samples in the natural orientation; often "parallel" samples appear to transform directly

from calcite to CaCO_3 III even at pressures as low as 15 kbar. The reason for this behavior is uncertain, but it may indicate that a uniaxial stress parallel to the optic axis of calcite suppresses the calcite: CaCO_3 II transition.

Several samples of each orientation that had transformed to CaCO_3 II were slowly heated to about 160°C while under approximately constant applied load, i.e., approximately isobaric conditions. Heating rates were about $10\text{--}20^\circ\text{C}$ per hour, and the temperature rise was interrupted at a few intermediate temperatures at which Raman spectra were recorded. The objective of these experiments was to determine whether any features of the Raman spectra of these CaCO_3 II crystals were sensitive to such crude annealing. Although the frequencies of the Raman lines shifted slightly with the temperature change as expected, no significant changes in the relative intensities of any lines of these spectra were observed either on heating or, in the few experiments when thermal cycling was completed without failure of the cell, on cooling back to room temperatures. This suggests that all of the observed lines are characteristic of CaCO_3 II.

The CaCO_3 III spectra are completely different from those of either calcite or CaCO_3 II and depend somewhat upon the initial orientation of the calcite sample. For both initial orientations, at least 18 lines are observed in the CaCO_3 III spectrum, including both external and internal fundamentals. The frequencies of these lines are listed in Table I. Two additional CaCO_3 III lines appear at 208 and 314 cm^{-1} , but only for samples in the parallel orientation. (Three other features of these CaCO_3 , the line at 715 cm^{-1} , and shoulders at 721 and 1099 cm^{-1} that are especially apparent in spectra of natural orientation samples, seem to be associated with residual CaCO_3 II, see below.) In the internal mode region of the CaCO_3 III spectrum, at least two lines related to the ν_1 mode of the carbonate ion, one related to ν_2 , two related to ν_3 , and three related to ν_4 can be resolved for both orientations. Thus number of lines and the appearance of a ν_2 component suggests that the primitive cell of the CaCO_3 III structure contains at least two, and probably four, formula units and lacks inversion symmetry.

CaCO_3 III spectra of crystals obtained from calcite samples mounted in the natural orientation inevitably have a strong continuous background below 500 cm^{-1} . This is attributed to relatively intense Rayleigh scattering by CaCO_3 III crystals of poorer quality than those crystals formed by compressing calcite in the parallel orientation. This situation is not significantly improved by heating the CaCO_3 III crystals over several days, perhaps due to the limited temperature range available below the II-III boundary, even at the highest pressures possible with this cell.

Since spectra of CaCO_3 III at 18 kbar may contain contributions from residual CaCO_3 II, confirmation of

the CaCO_3 III spectrum was based upon spectra obtained at even higher pressures. With the few exceptions described in the following remarks, only the characteristics of the 18-kbar spectrum that were thus confirmed at higher pressures are reported in Table I and the reproductions of CaCO_3 III spectra. The 131-cm^{-1} line in the 18-kbar spectra for both orientations moves to higher frequencies with increasing pressure. It merges into the line at 137 cm^{-1} at pressures above 22 kbar and cannot be resolved at higher pressures. Both the 715- and 723-cm^{-1} lines of 18-kbar CaCO_3 III spectra of parallel-orientation samples completely disappear at 38 kbar, but only the 715-cm^{-1} line disappears at higher pressures for the natural-orientation samples. For the natural orientation, the 723-cm^{-1} peak still appears as a shoulder the 739-cm^{-1} line of some spectra taken at 40 kbar.¹⁴

The intensities and pressure dependences of the frequencies of the lines between 200 and 235 cm^{-1} depend significantly on pressure. The spectra of CaCO_3 III obtained from natural-orientation calcite contain two lines of comparable intensities in this region at 204 and 221 cm^{-1} . Both of these lines shift in frequency by about $0.1\text{ cm}^{-1}\cdot\text{kbar}^{-1}$. For CaCO_3 prepared from parallel-orientation calcite, a third, more intense line appears at 208 cm^{-1} , in addition to the two lines at 202 and 221 cm^{-1} . The 202-cm^{-1} line shifts in frequency by $0.1\text{ cm}^{-1}\cdot\text{kbar}^{-1}$, which is comparable to the shift of the 204-cm^{-1} line for the other orientation; but both the 208- and 221-cm^{-1} lines shift by about $0.7\text{--}0.8\text{ cm}^{-1}\cdot\text{kbar}^{-1}$. These phenomena are presumably due to combined effects of polarization, preferred orientation, and anisotropic compression. The appearance of the 314-cm^{-1} component in the spectrum for the parallel orientation also can be attributed to these effects.

For comparison with the spectra of CaCO_3 II and CaCO_3 III, Raman spectra of KNO_3 III at about 54°C and 3.2 kbar, KNO_3 IV at about 52°C and 8.0 kbar, and the aragonite phase of CaCO_3 at about 20°C and 18 kbar are reproduced in Figs. 5-7. The KNO_3 III spectrum is similar to that reported by Balkanski, Teng, and Nusinovič,¹⁵ except for a previously unreported line at 1443 cm^{-1} ; the KNO_3 IV spectrum has not been reported previously. The aragonite spectrum is in reasonable agreement with the atmospheric pressure spectrum of aragonite reported by Krishnan,^{16,17} except for the pressure-induced frequency shifts of $10\text{--}25\text{ cm}^{-1}$ and the presence of weak peaks at 86, 107, and 113 cm^{-1} .

COMMENTS

Although it does not seem to be possible to infer the structures of CaCO_3 II or CaCO_3 III from the data reported here alone, some useful information is provided about previously suggested structures. Inspection of the spectra in Figs. 2, 3, and 5-7 immediately suggest that CaCO_3 II does not have the

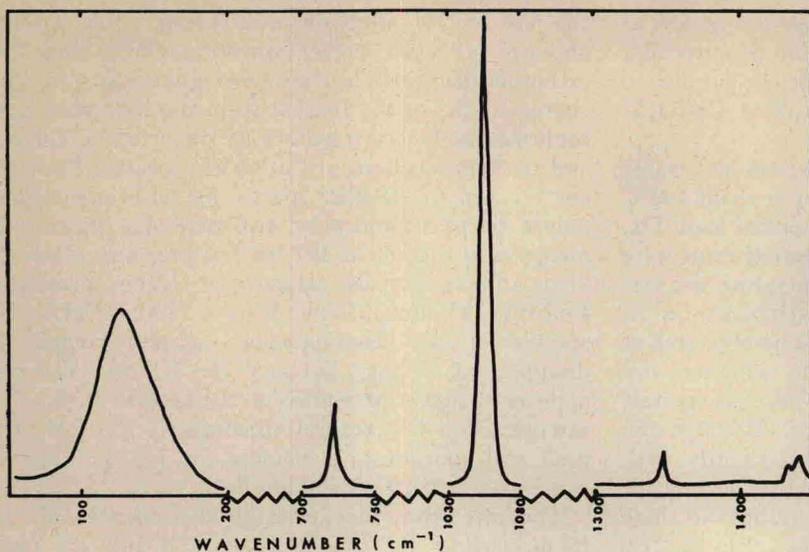


FIG. 5. Raman spectrum of KNO_3 III at 54°C and 3.2 kbar. The frequencies of the peaks of the spectrum are: 120, 716, 1057, 1352, 1434, and 1443 cm^{-1} .⁶

FIG. 6. Raman spectrum of KNO_3 IV at 52°C and 8.0 kbar. The frequencies of the peaks of the spectrum are: 78, 99, 111, 144, 161, 180, 718, 1059, 1362, 1372, 1389, and 1427 cm^{-1} .⁶

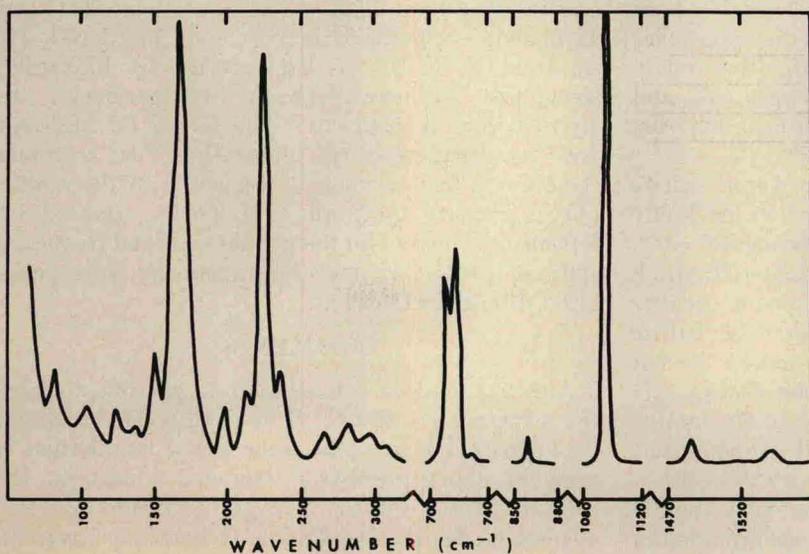
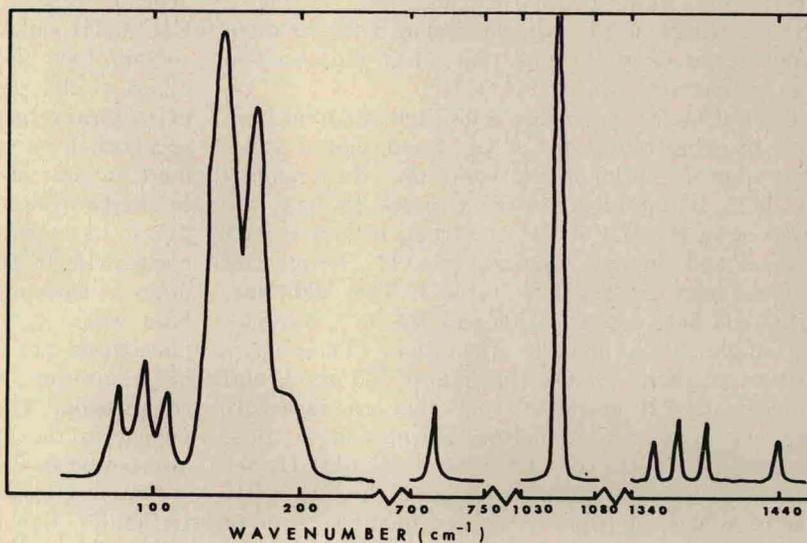


FIG. 7. Raman spectrum of a natural polycrystalline aragonite at 20°C and 18 kbar. The frequencies of the indicated peaks are: 86, 107, 127, 131, 154, 168, 201, 216, 230, 242, 265, 283, 298, 309, 716, 721, 864, 1103, 1484, and 1542 cm^{-1} .

structure of the ferroelectric KNO_3 III phase and that CaCO_3 III does not have the KNO_3 IV structure. Neither CaCO_3 II nor CaCO_3 III is aragonite. The CaCO_3 II spectrum has both more and narrower lines than the spectrum of the high-temperature phase of NaNO_3 reported by Chisler,¹⁸ indicating that these phases have different structures.

The CaCO_3 II spectrum would be consistent with a structure with a trigonal lattice and a primitive cell containing one formula unit suggested by x-ray powder patterns if anion orientational disorder or crystal field splitting of otherwise degenerate modes into transversely and longitudinally polarized modes combined with lower than D_{3d} factor group symmetry to make essentially all Raman modes allowed. In this regard, it may be noteworthy that each of the lattice phonon lines in the Raman spectrum of CaCO_3 II, except that at 99 cm^{-1} , is not more than 27 cm^{-1} higher in frequency than a strong infrared or Raman-active phonon of calcite at atmospheric pressure. Such differences in frequency can be attributed to pressure-dependent frequency shifts. The assignment of the lattice phonons of calcite, however, is still incomplete, and it would be premature to make more definite statements about this possible assignment of the CaCO_3 II spectrum at this time. Further study of possible similarities between CaCO_3 II and KNO_3 IV are also suggested by several qualitative similarities of their Raman spectra; and, of course, several other structures not discussed here for lack of data and other reasons also must be considered.

The CaCO_3 III spectra provide fewer clues concerning its possible structures. The splittings of the ν_1 and ν_3 bands suggests that the primitive cell contains at least two and possibly four formula units; available x-ray data are inconclusive in this regard. Although the spectra clearly indicate that CaCO_3 III and aragonite are distinct species, some similarities between their spectra suggest that they may be closely related. The distribution of lattice phonon frequencies, although not the Raman intensities of these polycrystalline and probably preferentially oriented samples, are comparable for these two CaCO_3 phases. In the internal phonon region, the relationship between the CaCO_3 III and the aragonite spectra somewhat parallels that between CaCO_3 II and calcite. This suggests the possibility that CaCO_3 III is a disordered or differently ordered variant of aragonite, although the observation that CaCO_3 II and calcite (but no aragonite) are obtained from CaCO_3 III upon decompos-

ition argues against this. It would be interesting to compare these spectra with the Raman spectrum of vaterite and, of course, to have more detailed x-ray information about these materials. Without more precise structural information about these materials than is available, it is beyond the scope of this work to comment in greater detail about the origins and magnitudes of the frequency shifts of these phonon modes.

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† Contribution No. 2704.

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¹⁴ Preliminary results of a study of the Raman spectrum of CaCO_3 III at 77°K , obtained directly from a calcite crystal whose optic axis was oriented approximately perpendicular to the axis of the high-pressure cell by compression at 77°K , i.e., well below calcite: CaCO_3 II: CaCO_3 III triple point, confirms the behavior of the 131-cm^{-1} line. Both the 715- and 723-cm^{-1} lines were absent from the 77°K spectra of CaCO_3 III at 18 and 32 kbar. This suggests that these lines, and possibly the 1099-cm^{-1} shoulder, are due to residual CaCO_3 II.⁶ The calcite: CaCO_3 III transition pressure at 77°K is 12 ± 2 kbar.

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