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 $CaCO_3$ II and $CaCO_3$ 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 $CaCO_3$ II and calcite spectra recovered upon decompression from $CaCO_3$ III and $CaCO_3$ 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 survey[6] of the Raman spectra of KNO_3 at comparable temperatures and pressures also are presented.

The room-temperature Raman spectra of $CaCO_3$ 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, $CaCO_3$ II, and $CaCO_3$ 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 $CaCO_3$ III at 38 kbar also are given in Table I to give a rough idea about how these frequencies change with pressure.

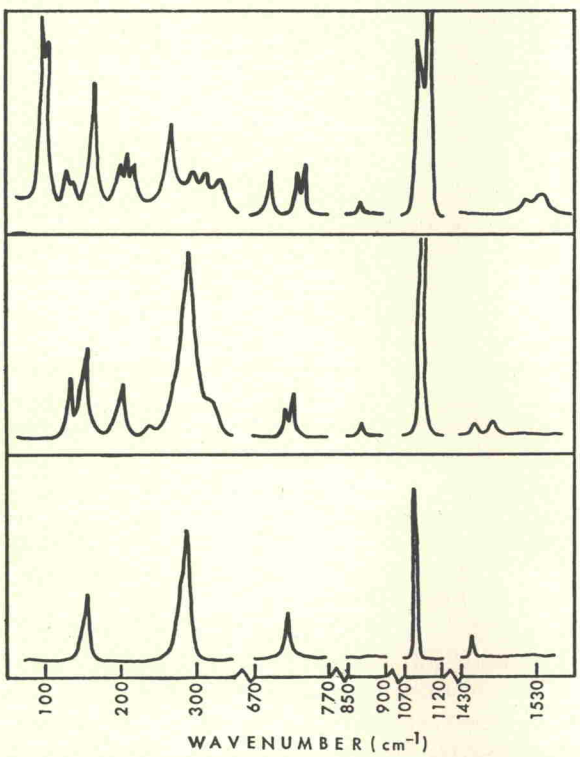

FIG. 3. Room-temperature Raman spectra of calcite (lower trace, 1 bar), $CaCO_3$ II (middle trace, 14 kbar), and $CaCO_3$ III (upper trace, 18 kbar) obtained upon compression of a calcite crystal of parallel orientation.

TABLE I. Frequencies of Raman-active phonons of calcite, $CaCO_3$ II, and $CaCO_3$ III.[a]

Phase	Calcite		$CaCO_3$ II	$CaCO_3$ III	
Pressure	1 bar	10 kbar	14 kbar	18 kbar	38 kbar
			99 (n)	99	99
				105	109
			133	131, 137	139
	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]	
ν_4	713	719			
			721	[721]	[723 (n)]
				733	739
				741	745
ν_2			866	870	870
				1087	1093
ν_1				[1099 (n)]	[1099 (n)]
	1082	1094	1096	1104	1108
ν_3	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 $CaCO_3$ III that are enclosed in brackets are thought to be due to residual $CaCO_3$ II. All frequencies are in cm^{-1}.

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 $CO_3^=$ 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 $CO_3^=$ 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,

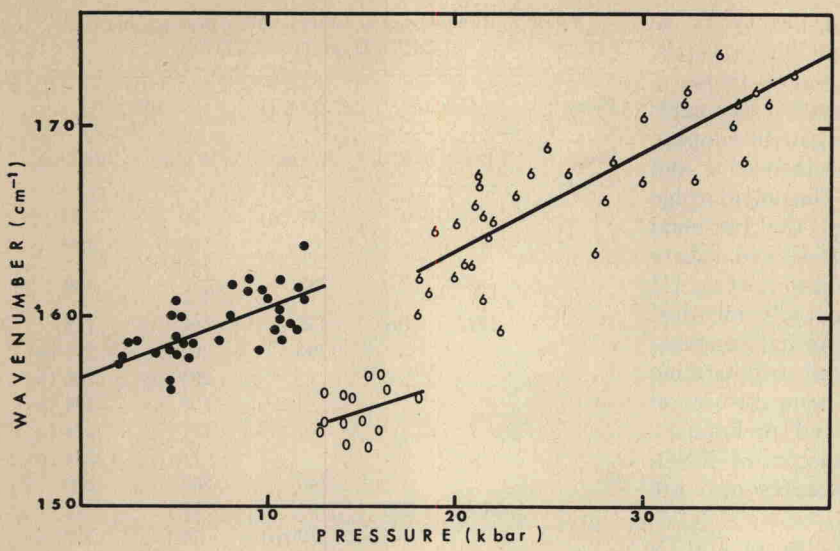

FIG. 4. A plot of the frequency of the Raman-active phonon in the 150–175-cm^{-1} range vs pressure. The solid points are from calcite spectra, the open circles are from $CaCO_3$ II spectra, and the sixes are from $CaCO_3$ III spectra. The solid lines represent least-squares fits to the three sets of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