

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 cm^{-1} 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 Nusinovi \acute{c} ,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

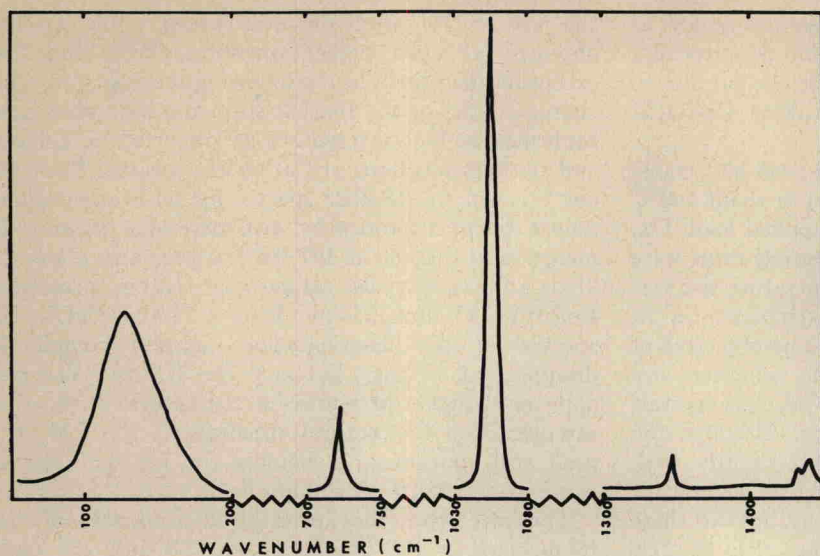


FIG. 5. Raman spectrum of KNO_3 III at 54°C and 3.2 kbar. The frequencies of the peaks of the spectrum are: 120, 716, 1057, 1352, 1434, and 1443 cm^{-1} .⁶

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

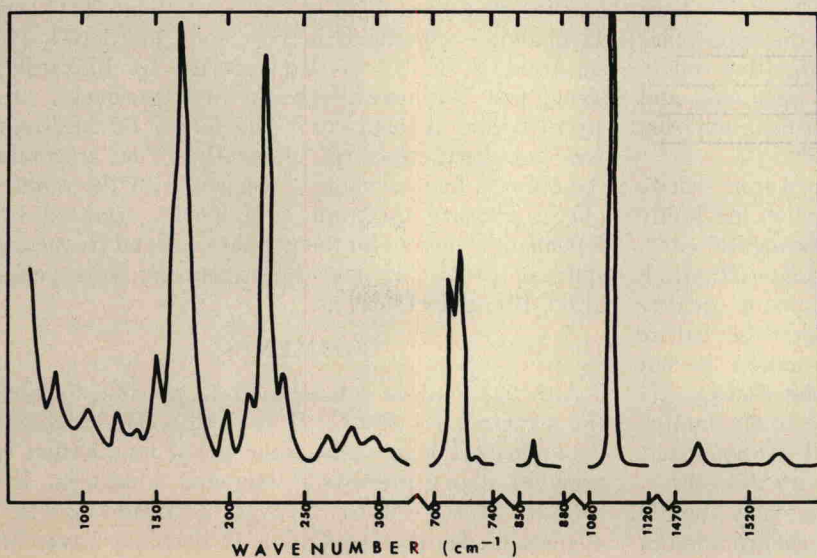
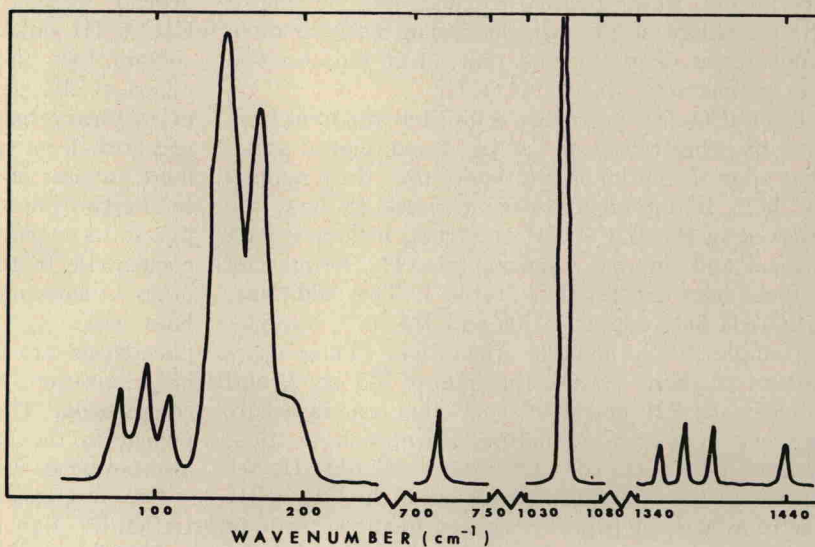


FIG. 7. Raman spectrum of a natural polycrystalline aragonite at 20°C and 18 kbar. The frequencies of the indicated peaks are: 86, 107, 127, 131, 154, 168, 201, 216, 230, 242, 265, 283, 298, 309, 716, 721, 864, 1103, 1484, and 1542 cm^{-1} .