

from calcite to  $\text{CaCO}_3$  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:  $\text{CaCO}_3$  II transition.

Several samples of each orientation that had transformed to  $\text{CaCO}_3$  II were slowly heated to about  $160^\circ\text{C}$  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  $\text{CaCO}_3$  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  $\text{CaCO}_3$  II.

The  $\text{CaCO}_3$  III spectra are completely different from those of either calcite or  $\text{CaCO}_3$  II and depend somewhat upon the initial orientation of the calcite sample. For both initial orientations, at least 18 lines are observed in the  $\text{CaCO}_3$  III spectrum, including both external and internal fundamentals. The frequencies of these lines are listed in Table I. Two additional  $\text{CaCO}_3$  III lines appear at 208 and  $314\text{ cm}^{-1}$ , but only for samples in the parallel orientation. (Three other features of these  $\text{CaCO}_3$ , the line at  $715\text{ cm}^{-1}$ , and shoulders at 721 and  $1099\text{ cm}^{-1}$  that are especially apparent in spectra of natural orientation samples, seem to be associated with residual  $\text{CaCO}_3$  II, see below.) In the internal mode region of the  $\text{CaCO}_3$  III spectrum, at least two lines related to the  $\nu_1$  mode of the carbonate ion, one related to  $\nu_2$ , two related to  $\nu_3$ , and three related to  $\nu_4$  can be resolved for both orientations. Thus number of lines and the appearance of a  $\nu_2$  component suggests that the primitive cell of the  $\text{CaCO}_3$  III structure contains at least two, and probably four, formula units and lacks inversion symmetry.

$\text{CaCO}_3$  III spectra of crystals obtained from calcite samples mounted in the natural orientation inevitably have a strong continuous background below  $500\text{ cm}^{-1}$ . This is attributed to relatively intense Rayleigh scattering by  $\text{CaCO}_3$  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  $\text{CaCO}_3$  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  $\text{CaCO}_3$  III at 18 kbar may contain contributions from residual  $\text{CaCO}_3$  II, confirmation of

the  $\text{CaCO}_3$  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  $\text{CaCO}_3$  III spectra. The  $131\text{-cm}^{-1}$  line in the 18-kbar spectra for both orientations moves to higher frequencies with increasing pressure. It merges into the line at  $137\text{ cm}^{-1}$  at pressures above 22 kbar and cannot be resolved at higher pressures. Both the  $715\text{-}$  and  $723\text{-cm}^{-1}$  lines of 18-kbar  $\text{CaCO}_3$  III spectra of parallel-orientation samples completely disappear at 38 kbar, but only the  $715\text{-cm}^{-1}$  line disappears at higher pressures for the natural-orientation samples. For the natural orientation, the  $723\text{-cm}^{-1}$  peak still appears as a shoulder the  $739\text{-cm}^{-1}$  line of some spectra taken at 40 kbar.<sup>14</sup>

The intensities and pressure dependences of the frequencies of the lines between 200 and  $235\text{ cm}^{-1}$  depend significantly on pressure. The spectra of  $\text{CaCO}_3$  III obtained from natural-orientation calcite contain two lines of comparable intensities in this region at 204 and  $221\text{ cm}^{-1}$ . Both of these lines shift in frequency by about  $0.1\text{ cm}^{-1}\cdot\text{kbar}^{-1}$ . For  $\text{CaCO}_3$  prepared from parallel-orientation calcite, a third, more intense line appears at  $208\text{ cm}^{-1}$ , in addition to the two lines at 202 and  $221\text{ cm}^{-1}$ . The  $202\text{-cm}^{-1}$  line shifts in frequency by  $0.1\text{ cm}^{-1}\cdot\text{kbar}^{-1}$ , which is comparable to the shift of the  $204\text{-cm}^{-1}$  line for the other orientation; but both the  $208\text{-}$  and  $221\text{-cm}^{-1}$  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  $314\text{-cm}^{-1}$  component in the spectrum for the parallel orientation also can be attributed to these effects.

For comparison with the spectra of  $\text{CaCO}_3$  II and  $\text{CaCO}_3$  III, Raman spectra of  $\text{KNO}_3$  III at about  $54^\circ\text{C}$  and 3.2 kbar,  $\text{KNO}_3$  IV at about  $52^\circ\text{C}$  and 8.0 kbar, and the aragonite phase of  $\text{CaCO}_3$  at about  $20^\circ\text{C}$  and 18 kbar are reproduced in Figs. 5-7. The  $\text{KNO}_3$  III spectrum is similar to that reported by Balkanski, Teng, and Nusinovič,<sup>15</sup> except for a previously unreported line at  $1443\text{ cm}^{-1}$ ; the  $\text{KNO}_3$  IV spectrum has not been reported previously. The aragonite spectrum is in reasonable agreement with the atmospheric pressure spectrum of aragonite reported by Krishnan,<sup>16,17</sup> except for the pressure-induced frequency shifts of  $10\text{--}25\text{ cm}^{-1}$  and the presence of weak peaks at 86, 107, and  $113\text{ cm}^{-1}$ .

#### COMMENTS

Although it does not seem to be possible to infer the structures of  $\text{CaCO}_3$  II or  $\text{CaCO}_3$  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  $\text{CaCO}_3$  II does not have the

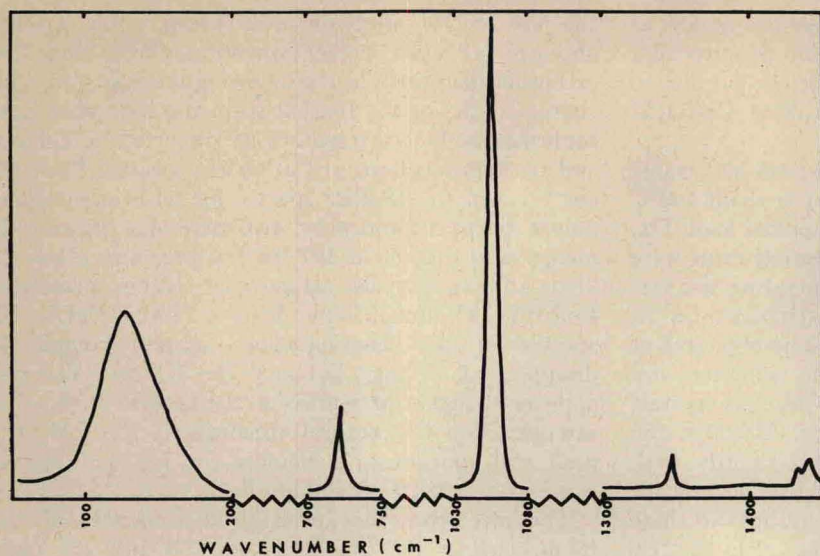


FIG. 5. Raman spectrum of  $\text{KNO}_3$  III at  $54^\circ\text{C}$  and 3.2 kbar. The frequencies of the peaks of the spectrum are: 120, 716, 1057, 1352, 1434, and  $1443\text{ cm}^{-1}$ .<sup>6</sup>

FIG. 6. Raman spectrum of  $\text{KNO}_3$  IV at  $52^\circ\text{C}$  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  $1427\text{ cm}^{-1}$ .<sup>6</sup>

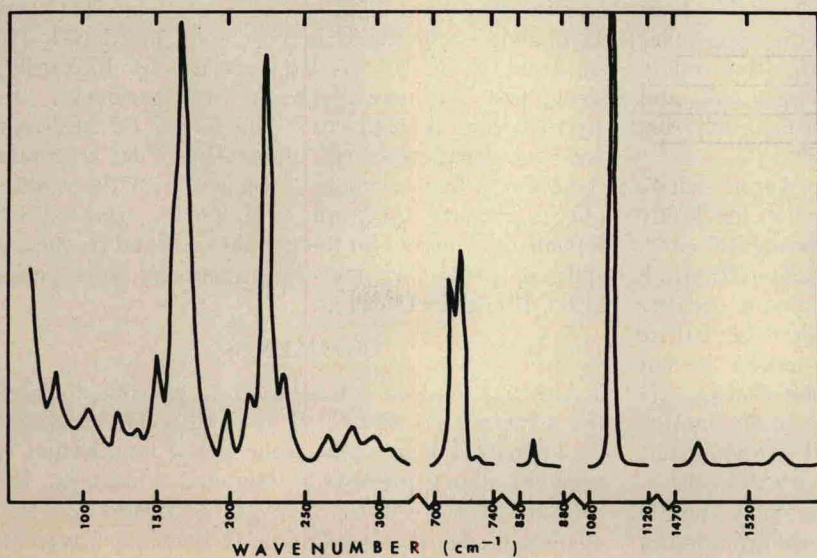
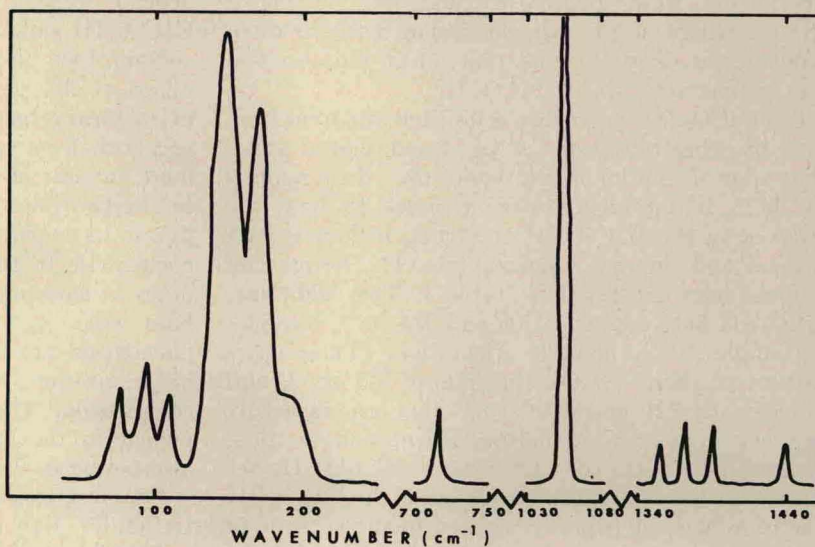


FIG. 7. Raman spectrum of a natural polycrystalline aragonite at  $20^\circ\text{C}$  and 18 kbar. The frequencies of the indicated peaks are: 86, 107, 127, 131, 154, 168, 201, 216, 230, 242, 265, 283, 298, 309, 716, 721, 864, 1103, 1484, and  $1542\text{ cm}^{-1}$ .