

structure of the ferroelectric  $\text{KNO}_3$  III phase and that  $\text{CaCO}_3$  III does not have the  $\text{KNO}_3$  IV structure. Neither  $\text{CaCO}_3$  II nor  $\text{CaCO}_3$  III is aragonite. The  $\text{CaCO}_3$  II spectrum has both more and narrower lines than the spectrum of the high-temperature phase of  $\text{NaNO}_3$  reported by Chisler,<sup>18</sup> indicating that these phases have different structures.

The  $\text{CaCO}_3$  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  $\text{CaCO}_3$  II, except that at  $99\text{ cm}^{-1}$ , is not more than  $27\text{ cm}^{-1}$  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  $\text{CaCO}_3$  II spectrum at this time. Further study of possible similarities between  $\text{CaCO}_3$  II and  $\text{KNO}_3$  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  $\text{CaCO}_3$  III spectra provide fewer clues concerning its possible structures. The splittings of the  $\nu_1$  and  $\nu_3$  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  $\text{CaCO}_3$  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  $\text{CaCO}_3$  phases. In the internal phonon region, the relationship between the  $\text{CaCO}_3$  III and the aragonite spectra somewhat parallels that between  $\text{CaCO}_3$  II and calcite. This suggests the possibility that  $\text{CaCO}_3$  III is a disordered or differently ordered variant of aragonite, although the observation that  $\text{CaCO}_3$  II and calcite (but no aragonite) are obtained from  $\text{CaCO}_3$  III upon decompression

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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<sup>14</sup> Preliminary results of a study of the Raman spectrum of  $\text{CaCO}_3$  III at  $77^\circ\text{K}$ , obtained directly from a calcite crystal whose optic axis was oriented approximately perpendicular to the axis of the high-pressure cell by compression at  $77^\circ\text{K}$ , i.e., well below calcite:  $\text{CaCO}_3$  II:  $\text{CaCO}_3$  III triple point, confirms the behavior of the  $131\text{-cm}^{-1}$  line. Both the  $715\text{-}$  and  $723\text{-cm}^{-1}$  lines were absent from the  $77^\circ\text{K}$  spectra of  $\text{CaCO}_3$  III at 18 and 32 kbar. This suggests that these lines, and possibly the  $1099\text{-cm}^{-1}$  shoulder, are due to residual  $\text{CaCO}_3$  II.<sup>6</sup> The calcite:  $\text{CaCO}_3$  III transition pressure at  $77^\circ\text{K}$  is  $12 \pm 2$  kbar.

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