

increase in entropy of phase II' with respect to II, due to disorder in the stacking sequence.

By analogy with ZnS, mechanism (a) can be eliminated because of the known greater compressibility of wurtzite (Bridgman, 1940, p. 41). Mechanism (b), however, has possibilities when considering the possible number of stacking sequences for hexagonal close-packed layers. Smith (1955) has shown that several stacking polytypes are probable for ZnS structures, a conclusion verified in part by the low-angle coherent scatter occurring between the normal diffraction spectra of AB and ABC close-packed repeat units. This disorder in stacking can be treated as a mixing of AB and ABC layers, as well as other polytypes (such as ABABB . . .), that would contribute to the total entropy of the phase and would create the necessary drop in free energy of phase II'. The latter should then be more properly called a disordered sphalerite-type phase because of the presence of other than ABC stacking, and the free energy of this disordered phase would be represented by the dashed line of figure 14. As the temperature of this material is raised two different, but perhaps intimately related, processes should occur: (a) the elimination of intermediate stacking polytypes (other than AB or ABC) with the energy requirement for this process indicated by the vertical arrow of figure 14, and (b) the transformation of ABC stacking to AB stacking which is equivalent to the II'→II transformation. The abscissa label "displacement" refers to the distance through which the "C" layer of the ABC sphalerite-type stacking must shift to become another "A" layer. A specific mechanism for this shift has been proposed by Burley (1964).

The II'⇌III transformation may be dilatational, but because it involves a change from tetrahedral to octahedral coordination (primary) would not be an exceedingly rapid one.

It is obvious that the most rapid transformations involve phase I. This may be mostly due to the temperature effect, but it may also be related to the relative mobility of the Ag<sup>+</sup> ion.

A most interesting feature of these experiments is the formation of phase II' rather than II in transformations from halite-type and body-centered phases. Higher temperatures do favor the formation of a greater percentage of the wurtzite-type phase, as expected, but in general the phenomenon appears to follow the so-called Ostwald rule which states that the sequence from unstable to stable may include the appearance of metastable phases.

*CaCO<sub>3</sub>-I⇌III*: Figure 15 shows the transformation rate between calcite (*CaCO<sub>3</sub>-I*) which is hexagonal and the high-pressure orthorhombic polymorph *CaCO<sub>3</sub>-III*. The transformation was followed by oscillating about the high-pressure 030 peak at a scanning rate of 1 deg/min. The break in the record shown represents a short period of a few minutes during which the pressure was raised to about 25 kb which resulted in no further increase in the rate of transformation. The insets in the figure give the integrated intensities of the calcite 104 peak (also indexed as the high-pressure 220 peak) and the unique high-pressure 030 peak. The rate curve serves to show both the reversibility and the speed of the I-III transition. An estimate of 75 percent transformation was the maximum attained in this experiment.

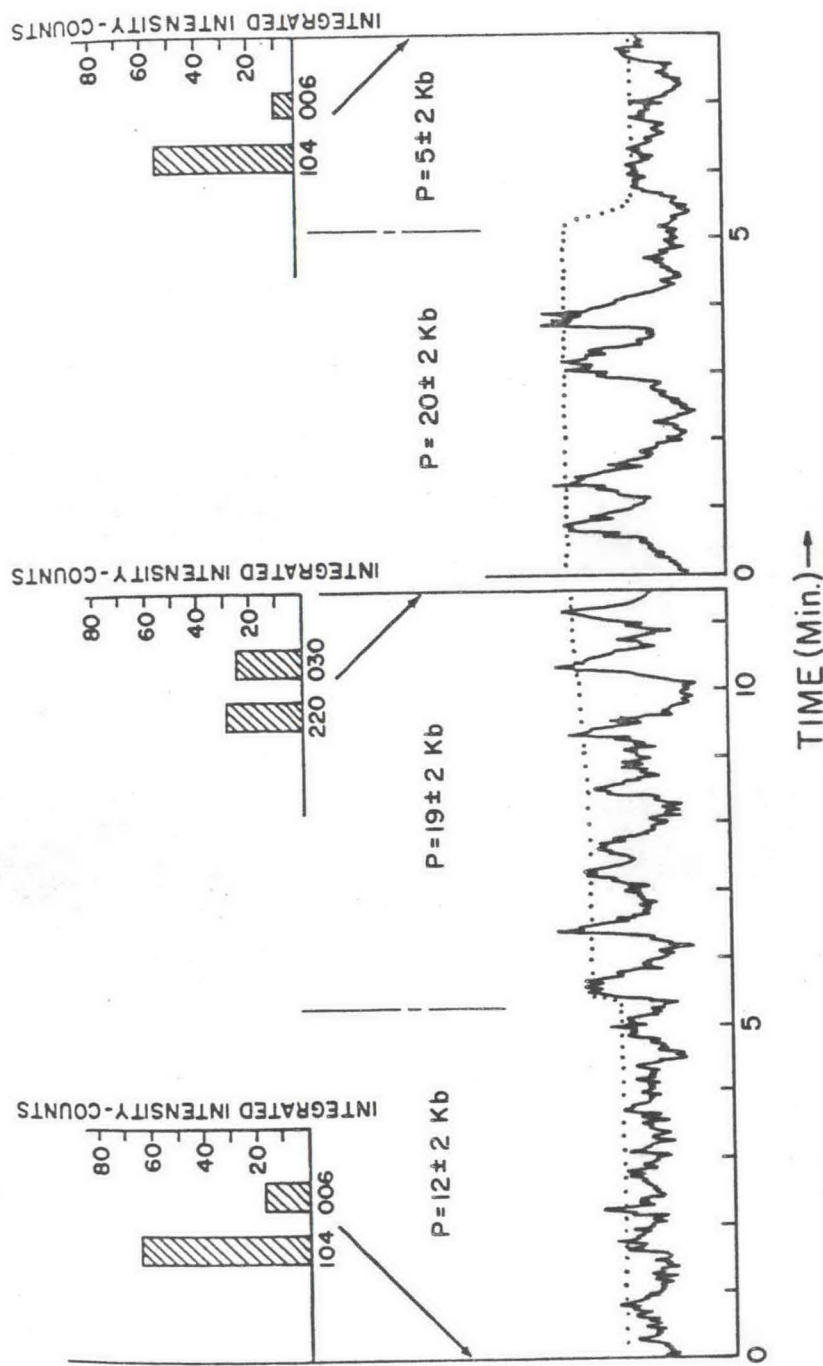


Fig. 15. Transformation rate of  $\text{CaCO}_3\text{-I} \rightleftharpoons \text{CaCO}_3\text{-III}$  based on the growth of 030 peak of phase III. See text for further explanation.