of M_1 and M_3 are influenced by this phenomenon.

5. The transition might actually be marked by a small first-order change in entropy, volume, and some of the components of strain, so that the derivatives of these quantities on approaching the transition might never get large enough to rigorously satisfy the asymptotic relations derived for a λ transition (see Figure 9). This hypothesis is supported by the existence of hysteresis in the transition, for if there were a continuous series of states in which quartz were stable as the phase boundary was traversed, it is difficult to see how there could be any hysteresis at all.

This hypothesis is further supported by the character of the DTA peaks observed when squeezing the specimens through the transition (see section on experimental procedure). If the α-β inversion were a λ transition, then the cause of the DTA peaks would be the sudden increase of heating due to compression as the transition was approached and crossed. The increase in temperature under adiabatic conditions owing to compression perpendicular or parallel to the C axis differs, however, so that the ratio of the two effects is given by

$$\left(\frac{\partial T}{\partial \sigma_1}\right)_{S,\sigma\neq\sigma_1} \bigg/ \left(\frac{\partial T}{\partial \sigma_3}\right)_{S,\sigma\neq\sigma_3} = \frac{TV\alpha_1}{C_\sigma} \bigg/ \frac{TV\alpha_3}{C_\sigma} = \frac{\alpha_1}{\alpha_3}$$

yet we could not distinguish any systematic

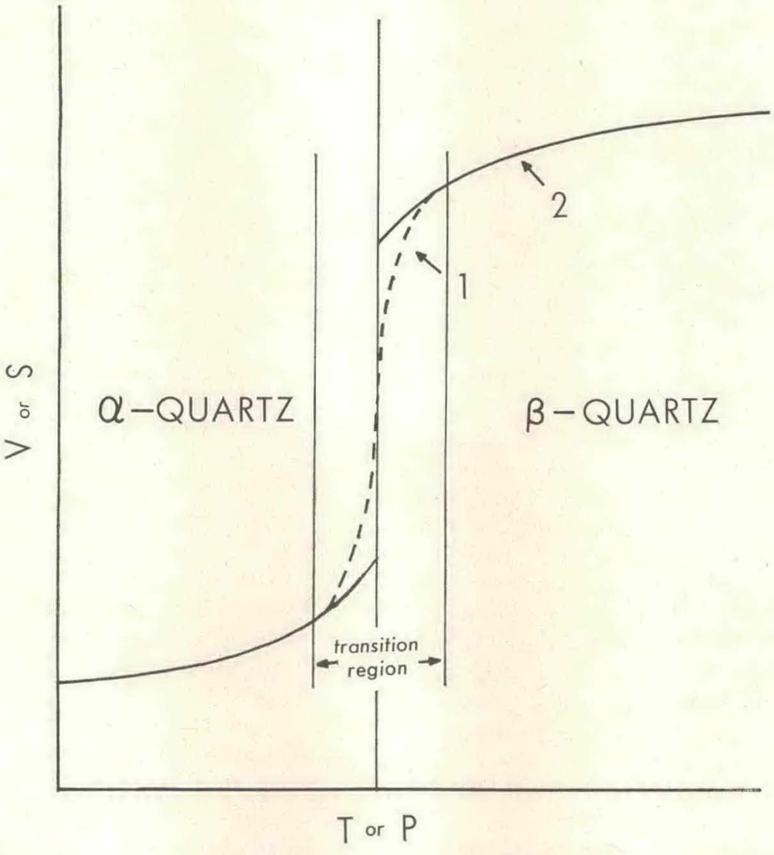

Fig. 9. Two models for the α-β inversion in quartz, which differ only in the behavior of the extensive parameters as a function of the intensive parameters near the transition: in (1), a λ transition, the variation is continuous and a vertical tangent occurs at the transition, whereas in (2), the model we prefer, a first-order discontinuity terminates the rapid rate of change of V and S at the transition before a vertical tangent is reached (case 5 in text).

difference in DTA peak height for the two orientations. It is unlikely that a compensating directional anomaly in the thermal conductivity of quartz, even if it existed, could obscure any significant directional difference in heat effect, because it is probable that heat generated in the specimen would be conducted away both radially and longitudinally under our experimental conditions. If the transition were first-order, however, then a latent heat would be released as the specimen was squeezed through the transition, and this heating would not depend particularly on the orientation of the crystal to the compression. Another pair of observations, that the height of the DTA peak was not affected by the fivefold range of squeezing rate used in these experiments, whereas the *position* of the peak lagged slightly behind the compliance maximum at the highest rate, might also be explained by assuming that the hysteresis holds up the first-order transition so that the latent heat is released more suddenly when it finally occurs.

In conclusion, we tend to favor the last of these possibilities, but to prove or disprove this and to resolve the many troubling conflicts touched upon earlier, higher quality measurements of α_{ij}, s_{ijkl}^{T} (by both static and dynamic means), C_P, and M_{kl} on the same crystal and very near the transition will probably be needed.

The α-β Inversion Treated as a Coherent First-Order Transition

We gave indirect reasons above that suggest to us that the α-β inversion may involve a small first-order component. Some workers actually claim to detect discontinuities in the volume and entropy at the transition, but these are difficult to establish on account of their small magnitudes and the rapid rate of change of these quantities in the neighborhood of the transition. Thus, *Majumdar et al.* [1964] give $\Delta v \simeq 0.11 \pm 0.015$ cm^3/mole and $\Delta s \simeq 0.10 \pm 0.02$ cal/mole °C, which, when substituted into the Clapeyron equation

$$dT_{\alpha-\beta}/dP = \Delta v/\Delta s \qquad (10)$$

yield an estimate for the slope of 26 ± 6°C/kb, whereas *Berger et al.* [1965, 1966] give $\Delta v \simeq 0.15 \pm 0.01$ cm^3/mole and $\Delta s \simeq 0.15 \pm 0.04$ cal/mole °C, which yield an estimate of 24 ± 6°C/kb. On the other hand, *Sinel'nikov*'s [1953] upper bound of 0.003 cal/mole °C for Δs would imply Δv no larger than 0.0033 cm^3/mole to yield the experimentally observed slope of 26°C/kb from (10). It is difficult to resolve this and other inconsistencies of the data in the literature.

We shall assume the transition is first-order, however, and that it is characterized by a reversible first-order discontinuity in the strain that we call the transformation strain. As pointed out in the Introduction, this latter feature is tied to the notion that the transition mechanism involves a coherent interface between the two phases, so that the displacement vector for the quartz as it undergoes the phase transformation is a continuous function of position. If the transformation strain $\Delta\epsilon_{kl}$ is small enough so that the approximations of infinitesimal strain theory are valid, the generalization of the Clapeyron equation applicable to the transition is (equation C6, Appendix C)

$$M_{kl} \equiv -(\partial T_{\alpha-\beta}/\partial \sigma_{kl})_{\sigma\neq\sigma_{kl}}$$

$$= v_0\, \Delta\epsilon_{kl}/\Delta s \qquad (11)$$

where v_0 is the molar volume in the reference state of strain and Δs is the entropy per mole associated with the transition.

As shown in Appendix C, (11) is in direct analogy to the formulas (7) and (8) for the slope of the boundary of a λ transition; moreover, it reduces to the conventional Clapeyron equation (10) for hydrostatic pressure. In the general case of nonhydrostatic stress, (11) shows that shear stresses will be important thermodynamic variables in determining the field of stability of a polymorph, if $\Delta\epsilon_{kl}$ includes significant shear strains. In fact, if the transformation strain involves a change in shape but not of volume, the transition temperature will be independent of pressure but not of the individual components of stress.

Applying (11) to quartz and choosing the coordinate axes as in Figure 4, we obtain expressions for the increase of transition temperature owing to compression perpendicular or parallel to the C axis, respectively, in terms of the relative discontinuity of the lattice parameters $\Delta a/a$ or $\Delta c/c$ in the same direction:

$$M_1 = v_0\, \Delta\epsilon_1/\Delta s = v_0(\Delta a/a)/\Delta s \qquad (12a)$$

$$M_3 = v_0\, \Delta\epsilon_3/\Delta s = v_0(\Delta c/c)/\Delta s \qquad (12b)$$