Just as in the hydrostatic case, the scatter in the experimental data makes the testing of (12a) and (12b) unsatisfactory. Using values of $\Delta a/a \simeq 0.0027 \pm 0.003$, $\Delta c/c \simeq 0.0012 \pm 0.001$, and $\Delta s \simeq 0.15 \pm 0.04$ cal/mole °C of *Berger et al.* [1965, 1966] leads to $M_1 \simeq 9.7 \pm 2.7$°C/kb and $M_3 \simeq 4.4 \pm 1.2$°C/kb, which are very roughly the same as our experimental values, but the uncertainty is great and becomes even greater if attempts are made to combine the data of other workers.

In a manner completely analogous to the discussion of the α-β inversion as a λ transition, we can avoid the large uncertainties in the value of Δs by eliminating it between (12a) and (12b), yielding

$$M_1/M_3 = \Delta\epsilon_1/\Delta\epsilon_3 = \Delta a/a/\Delta c/c \qquad (13)$$

The X-ray data of Berger et al. yield $M_1/M_3 \simeq 2.2 \pm 0.3$, which is in decent agreement with our directly measured value of 2.1 ± 0.2, but the dilatometric studies of *Mayer* [1960] yield $M_1/M_3 \simeq 1.7$. There is no way to decide without further experiments whether this discrepancy arises from experimental errors or real differences in the material studied.

Summary

The change of the temperature of the α-β inversion in quartz with hydrostatic pressure or with general stress that we measured directly in our experiments can be interpreted equally well by assuming the inversion to be a λ transition or a coherent first-order transition. For reasons discussed above, we favor the first-order interpretation and suggest further that the asymptotic limits required by the λ transition hypothesis may not be rigorously attained (Figure 9).

GENERAL COMMENTS

The class of phase transitions that has been described by *Buerger* [1951] as displacive is certainly coherent in the sense used in this paper. These are generally characterized by being rapid, reversible, and involving relatively minor structural reorganization at the atomic level. Another example for which an interpretation similar to that for the quartz inversion is suggested is the α-β transition in $AlPO_4$, which, according to *Troccaz et al.* [1967], is completely analogous to the α-β transition in quartz. Assuming this transition is a coherent first-order one, and using their values for $\Delta a/a$ and $\Delta c/c$ in (13), we find $M_1/M_3 \simeq 8.2$. If we apply the λ transition formula (9), however, and use the slopes of the steepest parts of the thermal expansion curves for a and c which they measured just before the supposed first-order discontinuity from the α to the β phase, we find $M_1/M_3 \simeq 2$. This significant discrepancy can be explained by assuming the asymptotic limit required in (9) is never reached. If their measurement of Δs is valid, then the first-order theory further predicts $M_1 \simeq 16.5$°C/kb and $M_3 = 2.0$°C/kb from (12a) and (12b) and $dT_{\alpha\text{-}\beta}/dP = 35$°C/kb from (4$b$). We do not know of any direct measurement of these quantities for $AlPO_4$.

Besides the displacive, martensitic, and twinning type of crystallographic transformations, it is interesting to speculate whether other more sluggish transformations may also occur coherently. This mode of transformation requires that diffusion be suppressed and thus is more likely the more rapidly it can occur. Under dry conditions at sufficiently low temperatures, however, a slow coherent mechanism may possibly be favored over a reconstructive one that requires significant diffusion. As long as the phase change is characterized by a reversible transformation strain that involves a significant change of shape as well as of volume—no matter whether it is rapid or sluggish—the stability fields of the polymorphs must depend on the shear stresses as well as on the hydrostatic pressure. This is a thermodynamic effect, different from any catalytic effects of shear stress on reaction rates and may throw light on the issue of stress-sensitive minerals which has appeared intermittently in the geological literature for many years.

APPENDIX A

Temperature smearing in homogeneous, isotropic, hollow specimens. If we choose cylindrical coordinates with z axis along the core axis, it can be shown [*Timoshenko and Goodier,* 1951, p. 59] that when the specimen is subjected to a hydrostatic pressure P on its outer surface ($r = b$), zero pressure on its inner surface ($r = a$), and an extra uniaxial compression $\sigma > 0$ along the axis, the resultant nonzero components of stress are

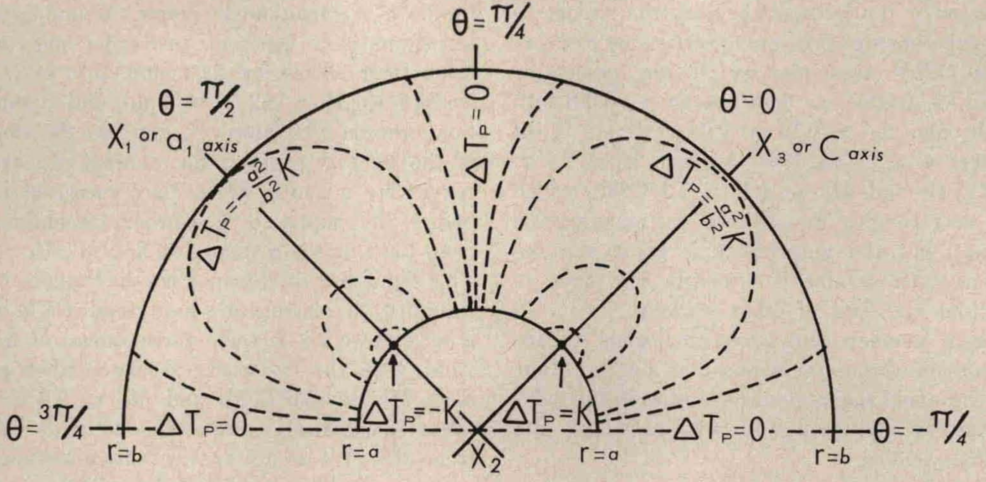

Fig. 10a. Lines of equal $\Delta T_P \equiv T_{\alpha\text{-}\beta}\ (r, \theta) - \langle T_P \rangle$ plotted on the cross section of a hollow specimen oriented $\perp C$ (equations A3 and A4, Appendix A). ΔT_P is the increase in transition temperature (above the mean transition temperature $\langle T_P \rangle$), owing to the stresses caused by the external pressure P.

$$\sigma_{rr} = -Q(1 - a^2/r^2)$$
$$\sigma_{\theta\theta} = -Q(1 + a^2/r^2) \qquad \text{(A1)}$$
$$\sigma_{zz} = -Q - \sigma$$

Where Q is the equivalent hydrostatic pressure

$$Q \equiv P(b^2/b^2 - a^2) \qquad \text{(A2)}$$

(A1) shows that although the stress depends on r in the $r - \theta$ plane, the mean pressure arising from P is constant at each point in the crystal and equal to the equivalent hydrostatic pressure Q: $\langle P \rangle = (-\sigma_{rr} - \sigma_{\theta\theta} - \sigma_{zz})/3 = Q$.

Transforming (A1) for a specimen cored $\perp C$ to rectangular axes in which X_2 lies along the core axis and assuming hexagonal or trigonal symmetry ($M_1 = M_2$) so that (4a) $T_{\alpha\text{-}\beta} \simeq T_0 - M_1(\sigma_{11} + \sigma_{22}) - M_3\sigma_{33}$, we find (Figure 10$a$) that the transition temperature that results from the external pressure alone varies with r and θ and is given by

$$T_{\alpha\text{-}\beta}(r, \theta)$$
$$\simeq \langle T_P \rangle + Q(M_1 - M_3)(a^2/r^2) \cos 2\theta \qquad \text{(A3)}$$

where

$$\langle T_P \rangle - T_0 = Q(2M_1 - M_3) \qquad \text{(A4)}$$

is the mean increase of transition temperature above the value at zero P and σ ($T_0 \simeq 574$°C). A hollow specimen with axis $||C$, however, would have a constant transition temperature $T_{\alpha\text{-}\beta} = \langle T_P \rangle$, given by (A4), because the component of M_{kl} along any direction in the $r - \theta$ plane is constant ($M_1 = M_2$).

Integration of (A3) over the specimen (Figure 10a) shows that the proportion of the specimen that is significantly affected depends on the size of the hole as well as on the external pressure. The results are expressed in Figure 10b, which shows that for most of the hollow specimens (in which $a \simeq 0.175$ cm and $b \simeq 1.0$ cm and $P \simeq 3$ kb) $|T_{\alpha\text{-}\beta} - \langle T_P \rangle| < 3.3$ °C for 50% of the volume. For the sample of run 610 (Table 2, $a \simeq 0.4$ cm, $b \simeq 1.0$ cm, $P = 5$ kb) the effect is larger: within the least affected half of the sample $T_{\alpha\text{-}\beta}$ varies by 12.8°C about the mean $\langle T_P \rangle$.

As discussed in the text, the absence of this predicted smearing of the transition temperature is the basis for our believing that stress inhomogeneities that average to zero over the cross section of the specimen are effectively removed as the transition is approached by a 'focusing' mechanism arising from the large increase in the compliance of quartz.

APPENDIX B

Slope of phase boundary for λ transitions under conditions of nonhydrostatic stress. We