

tion is significant, because for the specimen of run 610 (Table 3), in which the hole was 0.4 cm and the confining pressure was 5 kb, the total variation calculated is 67°C, and, even within the least affected 50% of the specimen,  $T_{\alpha-\beta}$  should vary by 13°C about the mean.

In the actual experiments, however, the transition in hollow specimens was just as sharp as in solid specimens and occurred precisely at the symmetric mean of the predicted range of transition temperatures. The explanation probably lies in a 'focusing' effect brought about by the dramatic increase of compliance in quartz as the transition is approached. This can be seen by assuming that the specimen is inhomogeneous in elastic properties near the transition, so that the above stress analysis is not valid. This is probable because the carbide endpieces at each end of the specimen are elastically much stiffer than the quartz, constraining each elementary column of the specimen parallel to the cylindrical axis to be of essentially the same length. As the specimen is squeezed toward the transition from the  $\beta$  field, those columns with highest  $T_{\alpha-\beta}$  become more compliant than the rest of the crystal. Hence they support less of the applied load and also deform in the cross-sectional plane such that the stress difference is reduced, thereby slowing their rate of approach toward the transition. The columns with the lowest  $T_{\alpha-\beta}$  support proportionally more of the load and a greater stress difference in the cross-sectional plane, so that their rate of approach toward the transition is increased. The two effects converge, and the transition finally occurs when the increasing load has raised the mean  $T_{\alpha-\beta}$  to the constant temperature of the specimen.

A similar 'focusing' effect will arise if the transition is approached from the  $\alpha$  field by decreasing the load or if it is approached from either field by changing the temperature while either the load or the length is held constant. An exact calculation has not been carried through because of its difficulty, but intuitively this explanation of the sharpness of the transition in the hollow specimens seems convincing because the increase in compliance in the neighborhood of the transition is in fact very large.

In both solid and hollow specimens, stress inhomogeneities will arise from frictional con-

straints at the ends (which tend to cause barrelling) and from eccentric loading and anisotropic response of the crystal (which tend to cause bending). The maximum stress difference in the specimen due to bending can be estimated to be 150 bars per kilobar of compressive stress applied, assuming all the bending to be absorbed by the specimen. In fact, the piston assembly is not rigid compared with the specimen; it will absorb about half the bending. Also, this estimate is the maximum variation over the whole specimen; in the central two-thirds of the specimen the variation is about one-third of the total. Finally, the 'focusing' effect discussed above with respect to hollow specimens would further reduce any smearing of the transition, because the stress inhomogeneities due to bending would approximately average to zero over the cross section of the specimen. On the other hand, the stress inhomogeneities due to the frictional constraints at the ends would not average to zero over the cross section, and, if a limited and variable amount of slipping between the quartz and the carbide endpiece is supposed, some of the scatter of results both within a run and between runs may be qualitatively accounted for. When the percentage of the whole specimen that might be affected by the frictional constraints is estimated, however, it would appear that the quantitative effect must be small. Thus we feel that it is unlikely that our results have been significantly biased by stress inhomogeneities in the specimens.

*Apparent anomaly in the  $o$  and  $r'$  specimens.* Because the two principal values of  $M_1$ , (equation 2) corresponding to the two principal directions perpendicular to the  $C$  axis are equal, it follows from the transformation properties of tensors [Nye, 1957, p. 11] and from our experimental results that the component  $M_{33}'$  along any direction at 45° to the  $C$  axis should be given by

$$\begin{aligned} M_{33}' &= \frac{1}{2}(M_1 + M_3) \\ &= \frac{1}{2}(10.6 \pm 0.4 + 5.0 \pm 0.4) \\ &= 7.8 \pm 0.3^\circ\text{C/kb} \end{aligned}$$

From Table 3, however, we see that the two different orientations at approximately 45° yielded different values:  $M_{33}'$  is  $7.3 \pm 0.1^\circ\text{C/kb}$

for the  $o$  orientation and  $9.1 \pm 0.5^\circ\text{C}/\text{kb}$  for the  $r'$  orientation. The average value is  $8.2 \pm 0.5^\circ\text{C}/\text{kb}$ , in better agreement with the value predicted from  $M_1$  and  $M_3$ .

An analogous inconsistency is exhibited by the  $\beta$ -quartz compliances  $s_{33}'$  measured for these orientations (Table 1), which differ by a comparable amount despite the fact that symmetry requires that they should be equal. The ratios of  $M_{33}'$  to  $s_{33}'$ , however, are more nearly equal for the two orientations, suggesting that perhaps both sorts of discrepancies arise from a common cause.

One possibility is that these inconsistencies may arise from the anisotropic response of the crystal to uniaxial loading in these directions. Both orientations have the property that the application of a uniaxial stress  $\sigma_{33}'$  results in shear strains that are resisted by the stiff carbide endpieces, so that other components of stress must be present. (This is not true in the case of the  $\parallel C$  orientation nor, in the  $\beta$  field, for the  $\perp C$  orientation.) The exact effect on the compliance and the slope of the transition measured in these orientations is not calculated because we do not have the detailed knowledge of the boundary conditions that is necessary.

Yet another possibility is that the Dauphiné twinning thought to occur near the transition might influence the results differently for different orientations. Experiments of *Thomas and Wooster* [1951] indicate that the effect of uniaxial stress on the  $r'$  cores would be to tend to untwin them, whereas there is no such effect for the cores of  $o$ ,  $\perp C$ , and  $\parallel C$  orientations. Maximum estimates of the energy that could possibly be required to form the twin boundaries, however, suggest that any associated effect on latent or specific heat is probably too small to account for the inconsistencies in the slopes of the specimens oriented at  $45^\circ$  to the  $C$  axis.

Thus, we cannot be sure of the source of these discrepancies, just as we cannot be sure why in a single run  $(\partial T/\partial\sigma)_{a \rightarrow \beta}$  is usually greater than  $(\partial T/\partial\sigma)_{\beta \rightarrow a}$  and why the mean slopes for a given orientation scatter as much as they do. It seems possible that some of these inconsistent features are related in origin, but more experimentation would be required to be sure. A promising experiment would be to cross the transition in extension (by lowering the

axial principal stress below the confining pressure), for the effects of some of the mechanisms that might be causing discrepancies would be expected to be of opposite sign in extension from those in compression. The study of these details would certainly be of interest, but we feel that our important *average* results are probably correct within the uncertainties estimated from the scatter.

#### *The $\alpha$ - $\beta$ Inversion Treated as a $\lambda$ Transition*

By a  $\lambda$  transition we shall mean one in which the volume  $V$  and entropy  $S$  vary continuously across the phase boundary while the pressure and temperature derivatives of  $V$  and  $S$  (compressibility  $\beta_T$ , thermal expansion  $\alpha$ , specific heat  $C_P$ ) become infinite there. *Pippard* [1956, 1957] derived two relations that, he showed, asymptotically define the slope of the phase boundary  $dT_\lambda/dP$  as the transition boundary is approached closely enough so that a 'cylindrical approximation' represents the actual variation of the entropy and volume:

$$V\alpha \rightarrow (dT_\lambda/dP)(C_P/T) \quad \text{as } T \rightarrow T_\lambda \quad (5)$$

$$\beta_T \rightarrow (dT_\lambda/dP)\alpha \quad \text{as } T \rightarrow T_\lambda \quad (6)$$

These relations have been obtained more simply and without reference to any geometrical picture by *Buckingham and Fairbank* [1961], with the advantage that the requirements sufficient to ensure the validity of the Pippard relations have become clearer [*Klement and Cohen*, 1968]. The application to quartz was first made by *Hughes and Lawson* [1962], who showed that measurements of thermal expansion and compressibility by *Mayer* [1960] yielded a  $dT_\lambda/dP$  consistent with experimental values in (6), whereas *Mayer's* data for thermal expansion and specific heat measurements by *Moser* [1936] did not yield a consistent value in (5).

If a  $\lambda$  transition occurs under nonhydrostatic stress, then the components of strain  $\epsilon_{ij}$  and the entropy vary continuously across the phase boundary while *some* of the derivatives with respect to the components of stress  $\sigma_{ki}$  and temperature  $T$ , (isothermal compliances  $s_{ijkl}^T$ , linear thermal expansion coefficients  $\alpha_{ij}$ , specific heat at constant stress  $C_\sigma$ ) become infinite at the boundary. *Garland* [1964] generalized the Pippard relations in terms of principal axes of