

TABLE 3. Average Slope of Phase Boundary for Various Orientations of the Crystal to the Axis of Compression

Selection of Data	$\partial T_{\alpha-\beta}/\partial \sigma^*$, °C/kb			
	$\perp C$	$\parallel C$	o	r'
All	$10.3 \pm 0.7^\dagger$	5.0 ± 0.3	7.3 ± 0.1	9.1 ± 0.5
Excluding runs 580 & 590	10.6 ± 0.4	5.0 ± 0.3	7.3 ± 0.1	9.1 ± 0.5
$P = 3$ kb	10.6 ± 0.4	5.0 ± 0.4	7.3 ± 0.1	9.1 ± 0.5

* $\sigma > 0$ for compression in this table.

† The uncertainty listed after each slope is either the standard deviation of the mean calculated from the different slopes, $s.d. = (\sum_i [(\partial T/\partial \sigma)_i - \langle (\partial T/\partial \sigma) \rangle]^2 / (n-1))^{1/2}$ or the average standard deviation calculated from the individual standard deviations of the slopes, $s.d. = (\sum_i (s.d.)_i^2 / n)^{1/2}$, whichever is larger.

phiné twins. The standard deviation of the mean of the slopes for a given orientation, however, is not seriously large.

4. There is clear indication of a hysteresis in the α - β transition, for the $\beta \rightarrow \alpha$ boundary is systematically lower than the $\alpha \rightarrow \beta$ boundary for all orientations and conditions of stress. Giving more emphasis to lines that are more nearly parallel and more precisely determined by the experimental points, a weighted mean value for the hysteresis at zero compressive stress is estimated to be $1.6 \pm 0.9^\circ\text{C}$. This is consistent with the 1° - 2°C observed by *Keith and Tuttle* [1952] in homogeneous single quartz crystals at atmospheric pressure. (In estimating the mean intercepts in Table 2, $0.8 \pm 0.9^\circ\text{C}$ has therefore been added to $T_{\beta \rightarrow \alpha}^\circ$ for those few runs in which the $\alpha \rightarrow \beta$ phase boundary was not determined.)

By far the most interesting result of this study is that the slope of the phase boundary $\partial T_{\alpha-\beta}/\partial \sigma$ depends strongly on the orientation of the crystal with respect to the axes of compression (Table 3). Regardless of whether all the data at all pressures or selected data at $P = 3$ kb are averaged, the conclusion is essentially the same: the transition temperature is raised about 10.6°C for each kilobar of compressive stress perpendicular to the C axis and only $5.0^\circ\text{C}/\text{kb}$ parallel to the C axis.

When extrapolated to zero compressive stress, the results of these experiments are in good agreement with existing hydrostatic data. This is demonstrated in Figure 7, where the mean temperature intercept (last column of

Table 2) is plotted versus hydrostatic pressure (or mean pressure for hollow samples, as discussed later in the text). The least-squares slope and temperature intercept of the phase boundary in P - T space are $25.83 \pm 0.06^\circ\text{C}/\text{kb}$ and $573.6 \pm 1.0^\circ\text{C}$, which represents an amazingly good agreement with published values. (*Klement and Cohen* [1968] estimate $26^\circ\text{C}/\text{kb}$ and 574°C from their own work, that of *Cohen and Klement* [1967], and that of others; cf.

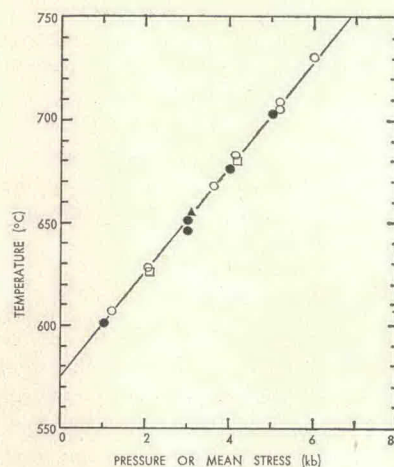


Fig. 7. Temperature intercepts $T_{\alpha-\beta}^\circ$ (obtained by extrapolating the α - β boundary to zero compressive stress) plotted versus pressure (solid samples) or mean pressure (hollow samples, see Table 2, Appendix A, and text). Open symbols are for hollow specimens, solid symbols are for solid specimens. Orientations are shown by circles ($\perp C$), squares ($\parallel C$), and triangles (o). Ten points are not shown because they are obscured by the other points.

also Keith and Tuttle [1952], $573 \pm 2^\circ\text{C}$; Yoder [1950], 29°C/kb ; and Gibson [1928], 21°C/kb .) If the six points determined with the 0.05-cm thermocouples are omitted as being less reliable, the values change, and the uncertainty decreases slightly to $25.82 \pm 0.05^\circ\text{C/kb}$ and $574.4 \pm 0.8^\circ\text{C}$. Taking into account the uncertainty in absolute calibration of the pressure and temperature, we feel that the best estimates from our measurements are $25.8 \pm 0.3^\circ\text{C/kb}$ and $574 \pm 2^\circ\text{C}$.

DISCUSSION

The results show that the change in transition temperature due to the addition of compressive stress depends on the orientation of the quartz crystal with respect to the compression axis as well as on the magnitude of the stress. In other words, the transition temperature $T_{\alpha-\beta}$ can be regarded as a function of the components of stress σ_{ij} so that

$$dT_{\alpha-\beta} = \left(\frac{\partial T_{\alpha-\beta}}{\partial \sigma_{ij}} \right)_{\sigma \neq \sigma_{ij}} \cdot d\sigma_{ij} \equiv -M_{ij} d\sigma_{ij} \quad (1)$$

$$M_{ij} \equiv - \left(\frac{\partial T_{\alpha-\beta}}{\partial \sigma_{ij}} \right)_{\sigma \neq \sigma_{ij}} \quad (2)$$

where the summation convention over repeated indices is implied ($i, j = 1, 2, 3$) and the sign of σ_{ij} is positive for tension. Because $T_{\alpha-\beta}$ is a scalar and σ_{ij} is a second rank symmetric tensor, M_{ij} is a second rank symmetric tensor as well [see Nye, 1957]. In the case of hydrostatic pressure, $d\sigma_{ij} = -dP$ for $i = j$ and $d\sigma_{ij} = 0$ for $i \neq j$, so (1) yields

$$dT_{\alpha-\beta}/dP = M_{11} + M_{22} + M_{33} \quad (3)$$

In applying general theory to the specific situation in quartz, we change the sign convention for convenience so that σ is positive in compression, choose the tensor reference axes x_1, x_2, x_3 to coincide with the symmetry axes as in Figure 4, and impose the symmetry conditions of α or β quartz. Equation 2 can then be written

$$M_1 = M_2 = (\partial T_{\alpha-\beta}/\partial \sigma)_{\perp C} \quad (4a)$$

$$M_3 = (\partial T_{\alpha-\beta}/\partial \sigma)_{\parallel C}$$

Single subscripts are used in (4a) to indicate that the diagonal components of M_{ij} are prin-

cipal values when the normal stresses are directed perpendicular and parallel to the C axis. Because only two of the three principal values are unique for quartz, (3) simplifies to

$$dT_{\alpha-\beta}/dP = 2M_1 + M_3 \quad (4b)$$

From our measured values $M_1 = 10.6 \pm 0.4^\circ\text{C/kb}$ and $M_3 = 5.0 \pm 0.4^\circ\text{C/kb}$ (Table 3) we obtain an estimate from (4b) of $dT_{\alpha-\beta}/dP = 26.2 \pm 0.7^\circ\text{C/kb}$, which agrees within experimental error with the value of $25.8 \pm 0.3^\circ\text{C/kb}$ that we determined directly on the same crystal by extrapolating the phase boundaries to conditions of hydrostatic pressure (zero uniaxial stress) for runs at various confining pressures (Figure 7).

Special Aspects of the Results

The effects of stress inhomogeneities. Non-uniformities of stress in the specimen would smear the transition, and, if the stress were not symmetrically distributed about the nominal stress calculated from the applied load, systematic error would result. In all specimens stress inhomogeneities could arise from end effects, but in the hollow specimens we might expect additional inhomogeneity not related to end effects, because these cores are subjected to the confining pressure over the outer cylindrical surface but to only one atmosphere over the internal surface.

The stress distribution in a hollow cylinder of homogeneous, anisotropic elastic material having hexagonal or trigonal symmetry arising from the application of unequal hydrostatic pressures to its inner and outer surfaces does not appear to have been explicitly calculated, but some of the characteristics of the distribution would be expected to be similar to the case for an isotropic material. In Appendix A we calculate the transition temperature at each point in such an isotropic, homogeneous specimen by summing the effects of the three principal stresses. We find that $T_{\alpha-\beta}$ would vary over the circular cross section of specimens of all orientations except $\parallel C$ (in which there would be no variation) in a symmetrical manner about a mean value that would be the transition temperature for a solid specimen of the same orientation subjected to a confining pressure equal to the mean stress in the hollow specimen. The magnitude of the predicted varia-