assume that the entropy and the components of strain of the material all depend on the temperature and the components of stress. Then the variation of entropy S will be given by

$$dS = \left(\frac{\partial S}{\partial T}\right)_\sigma dT + \left(\frac{\partial S}{\partial \sigma_{ij}}\right)_{\sigma \neq \sigma_{ij}, T} \cdot d\sigma_{ij} \quad \text{(B1)}$$

where the subscript σ means all components of stress are held constant, the subscript $\sigma \neq \sigma_{ij}$ means all stress components except the one particular σ_{ij} are held constant, and the summation convention is used, so the last term stands for nine terms. The transition temperature T_λ is a function of the components of stress, and it is useful to introduce in the manner of *Buckingham and Fairbank* [1961] an auxiliary variable $t \equiv T - T_\lambda$. If we divide both sides of equation B1 by $d\sigma_{kl}$, holding all the other components of stress and t constant, we find

$$(\partial S/\partial\sigma_{kl})_{\sigma\neq\sigma_{kl},t} = (\partial S/\partial T)_\sigma(\partial T/\partial\sigma_{kl})_{\sigma\neq\sigma_{kl},t}$$
$$+ (\partial S/\partial\sigma_{kl})_{\sigma\neq\sigma_{kl},T}$$

Applying the Maxwell relation [*Callen*, 1960, p. 225]

$$(\partial S/\partial\sigma_{kl})_{\sigma\neq\sigma_{kl},T} = V(\partial\epsilon_{kl}/\partial T)_\sigma$$

and rearranging, we obtain one of the generalized Pippard relations

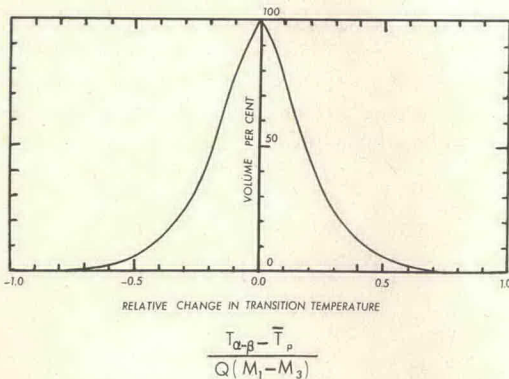$$\frac{T_{\alpha-\beta} - \overline{T}_P}{Q(M_1 - M_3)}$$

Fig. 10b. Amount of sample in volume per cent in which the transition temperature $T_{\alpha-\beta}$ varies symmetrically by a given amount about the mean transition temperature $\langle T_P \rangle$. Abscissa is plotted in relative units so that temperature variations can be computed for hollow cylinders of any dimensions subjected to any external pressure, using $Q = P (b^2/b^2 - a^2)$ and $(M_1 - M_3) = 5.6°C/kb$.

$$V\alpha_{kl} = M_{kl}(C_\sigma/T) + (\partial S/\partial\sigma_{kl})_{\sigma\neq\sigma_{kl},t} \quad \text{(B2)}$$

where

$$M_{kl} \equiv -\left(\frac{\partial T}{\partial\sigma_{kl}}\right)_{\sigma\neq\sigma_{kl},t} \equiv -\left(\frac{\partial T_\lambda}{\partial\sigma_{kl}}\right)_{\sigma\neq\sigma_{kl}}$$

$$C_\sigma \equiv T\left(\frac{\partial S}{\partial T}\right)_\sigma \quad \text{and} \quad \alpha_{kl} \equiv \left(\frac{\partial\epsilon_{kl}}{\partial T}\right)_\sigma$$

$-M_{kl}$ is the slope of the phase boundary in the $\sigma_{kl} - T$ plane at the point on the boundary determined by the state of stress, and C_σ, α_{kl}, and V are, respectively, the specific heat at constant stress, linear thermal expansion, and specific volume of the material in the same state of stress and at temperature T.

Similarly, if we consider the variation of a particular strain component ϵ_{ij} in the $\sigma_{kl} - T$ plane parallel to the transition boundary ($t = $ constant), we find the other generalized Pippard relations

$$s_{ijkl}{}^T = M_{kl}\alpha_{ij} + (\partial\epsilon_{ij}/\partial\sigma_{kl})_{\sigma\neq\sigma_{kl},t} \quad \text{(B3)}$$

where

$$s_{ijkl}{}^T \equiv (\partial\epsilon_{ij}/\partial\sigma_{kl})_{\sigma\neq\sigma_{kl},T}$$

is the isothermal compliance tensor.

The hydrostatic Pippard relations can be obtained from these equations. Setting $i = j$ in (B2) and summing yields

$$V\alpha = (\partial T/\partial P)_t (C_P/T) - (\partial S/\partial P)_t \quad \text{(B4)}$$

whereas summing (20) over all $i = j$ and all $k = l$ yields

$$\beta^T = (\partial T/\partial P)_t \alpha - (1/V)(\partial V/\partial P)_t \quad \text{(B5)}$$

In these equations α is the volumetric coefficient of thermal expansion and β^T the volumetric coefficient of isothermal compressibility.

The last term in equations (B2) and (B3) is the rate of change of entropy and strain, respectively, *parallel* to the phase boundary, and thus must be finite everywhere *on* the boundary (except perhaps at discrete points). Hence (B2) requires that the components of α_{kl} that are nonzero become infinite at the boundary (because C_σ becomes infinite for a λ transition and M_{kl} is finite) and that the components that are zero be matched by zero values for the corresponding components of M_{kl}. Likewise equation (B3) requires that $s_{ijkl}{}^T$ becomes infinite at the boundary for all values of i, j, k, l such that

both α_{ij} and M_{kl} are nonzero. For these cases in which α_{kl} and $s_{ijkl}{}^T$ become infinite on approaching the transition there will be some neighborhood about the boundary in which the first and second terms of (B2) and (B3) vary much more quickly than the third, so that M_{kl} will be given by the limiting slope of $V\alpha_{kl}$ plotted versus C_σ/T or $s_{ijkl}{}^T$ versus α_{ij}. We symbolize these asymptotic relations by the following notation:

$$V\alpha_{kl} \rightarrow M_{kl}(C_\sigma/T) \qquad \text{as} \quad T \rightarrow T_\lambda \qquad \text{(B6)}$$

$$s_{ijkl}{}^T \rightarrow M_{kl}\alpha_{ij} \qquad \text{as} \quad T \rightarrow T_\lambda \qquad \text{(B7)}$$

Another important relation that follows immediately from (B2) is

$$\alpha_{ij} \rightarrow (M_{ij}/M_{kl})\alpha_{kl} \qquad \text{as} \quad T \rightarrow T_\lambda \qquad \text{(B8)}$$

If we apply these asymptotic relations to a crystal with trigonal symmetry, choosing the reference axes for the tensors to coincide with the symmetry axes as shown in Figure 4, then (B6) yields

$$V\alpha_1 \rightarrow M_1(C_\sigma/T) \qquad \qquad \text{(B9)}$$
$$V\alpha_3 \rightarrow M_3(C_\sigma/T)$$
$$T \rightarrow T_\lambda$$

and (B7) yields

$$s_{1111}{}^T \equiv s_{11}{}^T \rightarrow M_1\alpha_1$$
$$s_{1122}{}^T \equiv s_{12}{}^T \rightarrow M_1\alpha_1$$
$$s_{1133}{}^T \equiv s_{13}{}^T \rightarrow M_3\alpha_1 \qquad \text{(B10)}$$
$$s_{3333}{}^T \equiv s_{33}{}^T \rightarrow M_3\alpha_3$$
$$s_{3311}{}^T \equiv s_{13}{}^T \rightarrow M_i\alpha_3 \qquad \text{as} \quad T \rightarrow T_\lambda$$

can be found in *Nye* [1957]. Single subscripts on second-rank symmetric tensors α_{kl} and M_{kl} denote principal values.) Equation B8 reduces to the important constraint

$$\alpha_1 \rightarrow (M_1/M_3)\alpha_3 \qquad \text{as} \quad T \rightarrow T_\lambda \qquad \text{(B11a)}$$

There are two nonzero compliance components in trigonal crystals that do not enter in the asymptotic relations above: $s_{1123}{}^T \equiv s_{14}{}^T$ and $s_{2323}{}^T \equiv s_{44}{}^T$. The fact that $M_{23} = 0$ means that the phase boundary is parallel to the σ_{23} axis, so that $dt = dT_\lambda = dT = 0$ for any $d\sigma_{23}$, and (B3) reduces to the definition of compliance. Thus, we would not expect $s_{14}{}^T$ and $s_{44}{}^T$ to be infinite at a λ transition in trigonal crystals.

Although it is quite uncertain whether the α-β transition in quartz rigorously satisfies the definition of a λ transition, there is no doubt that the behavior generally resembles a λ transition, and indeed it seems that $s_{14}{}^T$ and $s_{44}{}^T$ behave differently from the other compliance components of quartz near the transition. Thus, both *Mayer* [1960] and *Perrier and de Mandrot* [1923] report that s_{14} goes smoothly to zero as the transition is approached from the α-quartz side (of course, $s_{14} \equiv 0$ for β quartz because of its hexagonal symmetry), and s_{44} appears to increase less drastically near the transition than any of the other four components (Figure 3).

Hence, from equations B2 and B3 we conclude that the following asymptotic form should hold for the compliance matrix of a crystal when $T \rightarrow T_\lambda$ of a λ transition that involves inversion from trigonal (class 32) to hexagonal (class 62) symmetry:

$$s_{ij}{}^T \rightarrow s_{11}{}^T \cdot
\begin{bmatrix}
1 & 1 & M_3/M_1 & 0 & 0 & 0 \\
1 & 1 & M_3/M_1 & 0 & 0 & 0 \\
M_3/M_1 & M_3/M_1 & (M_3/M_1)^2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
\qquad \text{(B11b)}$$
$$\text{as} \quad T \rightarrow T_\lambda$$

(The condensed two-index matrix form of the compliance for crystals of all symmetry groups

This matrix, though still consistent with hexagonal symmetry, is much simpler than the