

stress. It is easy, however, to write down the nonhydrostatic Pippard relations for arbitrary axes by the method of *Buckingham and Fairbank* [1961], as set out in Appendix B. These lead to the following asymptotic relations:

$$V\alpha_{kl} \rightarrow M_{kl}(C_\sigma/T) \quad \text{as } T \rightarrow T_\lambda \quad (7)$$

$$s_{ijkl}^T \rightarrow M_{kl}\alpha_{ij} \quad \text{as } T \rightarrow T_\lambda \quad (8)$$

where $-M_{kl}$ is the slope of the phase boundary in the $\sigma_{kl} - T$ plane $(\partial T_\lambda / \partial \sigma_{kl})_{\sigma \neq \sigma_{kl}}$, the sign of σ_{kl} following from the usual convention that tensional stress is positive.

Garland, also using the thermal expansion and compliance measurements of *Mayer* [1960], found that (8) yielded a best average $M_1 \simeq 10^\circ\text{C/kb}$ and, less convincingly, $M_3 \simeq 6^\circ\text{C/kb}$ approximately 5°C/kb is obtained if the data nearest to the transition are retained). The difference between these estimates and our direct measurements of $M_1 = 10.6^\circ\text{C/kb}$ and $M_3 = 5.0^\circ\text{C/kb}$ may not be significant because of the differences in experimental material and the difficulty in matching the absolute temperatures accurately enough near the transition for the thermal expansion and compliance measurements. Another problem is that the conversion from the adiabatic compliances of Mayer to isothermal values involves the specific heat, which requires data from another investigator on yet a different specimen of quartz. Near the transition the difference between adiabatic and isothermal compliances becomes significant, so that compatibility of the data is a crucial requirement in evaluating the asymptotic limits. That the specific heat data of *Moser* [1936] and the thermal expansion data of *Mayer* [1960] are not compatible is shown by the fact that consistent values of M_1 , M_3 , and dT_λ/dP are not obtained in (7) [Garland, 1964] and (5) [Hughes and Lawson, 1962], respectively.

Both Garland's and our own values of M_1 and M_3 satisfy the constraint (4b) within experimental error. Garland showed, however, that if C_σ/T is eliminated from (7) another important constraint on the values of M_1 and M_3 is obtained asymptotically from α_1 and α_3 (B11a, Appendix B):

$$\alpha_1 \rightarrow (M_1/M_3)\alpha_3 \quad \text{as } T \rightarrow T_\lambda \quad (9)$$

The evaluation of this limit appears to be free of many of the difficulties discussed above, be-

cause the independent measurements of *Mayer* [1960], *Coenen* [1963], and *Berger et al.* [1966] on different specimens of quartz all convincingly agree that $\alpha_1/\alpha_3 = 1.68 \pm 0.04$ throughout the temperature range 100° to 570°C (Figure 8). Moreover, Coenen and Berger et al. used X-ray techniques in which α_1 and α_3 are determined simultaneously over the same portion of quartz, thus eliminating possible errors in α_1/α_3 due to differences of material within the same specimen and inconsistencies in temperature measurement. If this value of $\alpha_1/\alpha_3 = 1.68$ that holds between 100° and 570°C is the true limit at the transition ($T \simeq 574^\circ\text{C}$), then Garland's $M_1/M_3 \simeq 10/6 \simeq 1.7$ is consistent with equation 9 and our value of $M_1/M_3 = 2.1 \pm 0.2$ is not.

There are similar sorts of asymptotic constraints on M_1/M_3 that are imposed by pairs of components of the isothermal compliance tensor s_{ijkl}^T as the boundary of a λ transition is approached (B11b, Appendix B). *Klement and Cohen* [1968] showed that plotting the adiabatic compliance components for quartz one against the other should yield the same asymptotic limits as with the isothermal compliances as long as the relation $\alpha_1/\alpha_3 = 1.68$ held, which enables one to use the dynamic data directly without introducing the uncertainty of the specific heat by converting to isothermal values. Even so, however, a convincing estimate for M_1/M_3 is not obtainable from the asymptotic

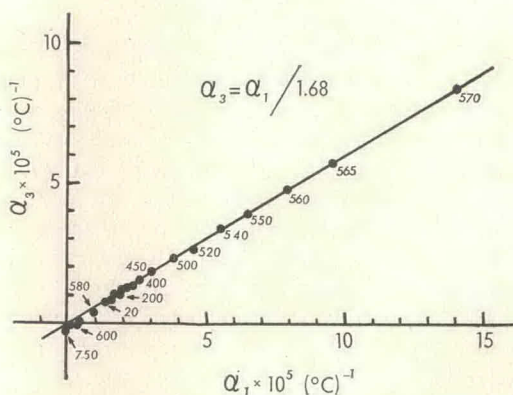


Fig. 8. Linear thermal expansion coefficients of quartz parallel (α_3) and perpendicular (α_1) to the C axis. Numbers beside the points are temperatures in degrees C. From 20°C to 570°C the data fits a straight line through the origin: $\alpha_3 = \alpha_1 / 1.68$. Data are from *Mayer* [1960].

behavior of the presently available dynamic compliance data. The linear asymptotes found by Klement and Cohen and others found by us agree a little better with a value of M_1/M_3 of 1.7 than 2.1, but the variation among the individual estimates is large. What is worse, although the 'straight' portions of the graphs start 20° to 50°C below the transition, the values within 4° or 5°C of the phase boundary often depart significantly from these lines.

A set of static determinations of s_{11}^T and s_{33}^T through the transition were made by *Perrier and de Mandrot* [1923] in a series of careful experiments involving the bending of quartz beams. These yield an asymptotic estimate of M_1/M_3 between 2.0 and 2.2 in (B11b) for the temperature interval from 545° to 574.5°C. Their static method has the virtue of producing isothermal values directly, but their compliances

$$\left(\frac{\partial \alpha_1}{\partial P}\right)_T \bigg/ \left(\frac{\partial \alpha_3}{\partial P}\right)_T = \left[\frac{\partial(s_{11}^T + s_{12}^T + s_{13}^T)}{\partial T} \right]_P \bigg/ \left[\frac{\partial(s_{33}^T + 2s_{13}^T)}{\partial T} \right]_P \approx 1.7$$

at temperatures near the transition are open to question because the inhomogeneous state of stress in the bent beams of quartz would cause the apparent compliance to exceed its true value. The overestimate would be greater for s_{11}^T than for s_{33}^T , resulting in an overestimate of M_1/M_3 from (B11b), but an approximate calculation shows that the magnitude of this increase would be less than 5% for all temperatures more than 3°C below the transition temperature. Thus the discrepancy between the asymptotic estimates of M_1/M_3 from dynamic and static compliances is not easy to explain away. *Cady* [1964] mentions small systematic differences between dynamically measured compliances of quartz corrected to isothermal values and statically determined compliances (both at room temperature). Perhaps such differences are real and arise from a mechanism that becomes much more significant near the transition.

Thus, considering the uncertainty of the thermodynamic data near the transition, we might regard our experimental values of M_1 and M_3 as sufficiently consistent with the asymptotically estimated values of *Garland* [1964] to provide support for the hypothesis that the α - β inversion is a λ transition, except for the fact that the ratio $M_1/M_3 = 1.7$ predicted by the same hypothesis from the much more accurately

known ratio of the thermal expansions is in significant conflict with our directly measured value of 2.1 ± 0.2 . There are several possible ways this discrepancy might be explained:

1. We might have overlooked a serious source of systematic error in our experiments. This seems unlikely because the errors in M_1 and M_3 would have had to be positive and negative, respectively, in just such a way that the constraint (4b) remained valid.

2. The difference might be due to the effect of pressure, because our measurements centered around 3-kb confining pressure whereas the data used to evaluate the asymptotic limits in (9) were for 1 atm. This seems unlikely for the same reason that is given immediately above and also because direct calculation shows that the ratio α_1/α_3 should not be very sensitive to pressure. That is,

as calculated from rates of change of the adiabatic compliances of *Mayer* [1960] at 1 atm and converted to isothermal values using $\alpha_1/\alpha_3 = 1.68$.

3. The data might be too far from the transition for the correct asymptotic limit to be defined. For example, equation 6 only begins to display the expected asymptotic behavior in liquid helium about 0.01°K from the λ transition at 2.2°K [*Buckingham and Fairbank*, 1961]. If, however, this is the root of the discrepancy, it means that the remarkably consistent linear relation $\alpha_1/\alpha_3 = 1.68$, which holds from 100° to 570°C, must cease to be valid somewhere between 570° and 574°C and a limiting value of 2.1 must be approached.

4. The asymptotic behavior on approaching the transition might vary from crystal to crystal. This is supported by the variability of the DTA signals reported by *Keith and Tuttle* [1952] and by the variability of the rate of increase of Dauphiné twins observed by *Young* [1962, 1964], but it is contradicted by the consensus of several independent studies that $\alpha_1/\alpha_3 = 1.68$ and by the relatively good agreement among the experimental determinations of $dT_{\alpha-\beta}/dP$. If the Dauphiné twinning reaches a maximum before the α - β transition proper, it is possible that the asymptotically derived values