

ment and experimental material for various sets of data in the literature). Thus, the smoothed compliances presented in Figure 3 are almost all dynamically measured adiabatic values rather than isothermal values, which are theoretically more useful.

A qualitative description of the α - β inversion on an atomic scale has been developed by Young [1962, 1964], based on his X-ray studies of single crystals. He concludes from measurements of the intensities of reflections from several planes as a function of temperature that there are actually two sorts of changes that reach a climax at nearly the same temperature: (1) a true first-order transition marked by an 'experimentally discontinuous' shift of the equilibrium positions of the atoms, a 50% increase in amplitude of vibration of the oxygen atoms perpendicular to the Si-O-Si planes, and an

abrupt increase in the Si-O-Si bond angle of about 2 degrees; and (2) a dramatic increase in the development of small-scale Dauphiné twins. The first-order transition is the culmination of a continuous change toward the β configuration, which is induced by increasing thermal vibrations as the critical transformation temperature is approached and does not vary significantly from crystal to crystal. The degree of development of Dauphiné twins, however, is different for different specimens; it may start anywhere from a few degrees to many tens of degrees C below the transition and may or may not achieve a maximum (50% twinning by volume) throughout the sample before the real transition.

The extensive formation of Dauphiné twins, whether they are fixed in space at a given temperature or whether they hop around in the

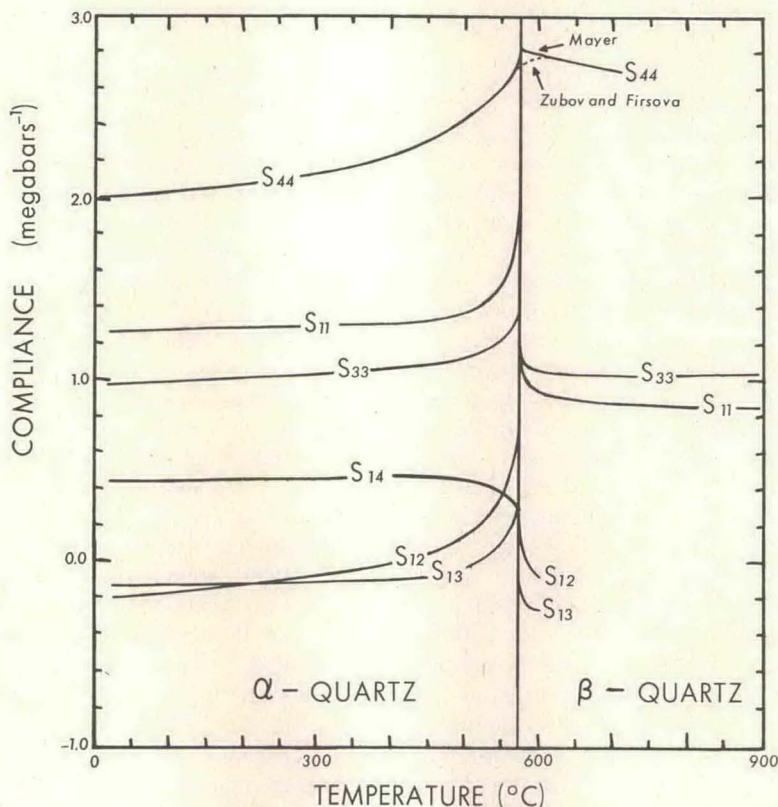


Fig. 3. Drawn from dynamically measured adiabatic compliances of quartz according to Mayer [1960] and Zubov and Firsova [1962]. (Except for s_{11} and s_{33} for $T > 600^\circ\text{C}$, which are statically measured isothermal values of Perrier and de Mandrot [1923]. The adiabatic correction for these values is negligible.) Agreement between the two sets of data is, in general, good.

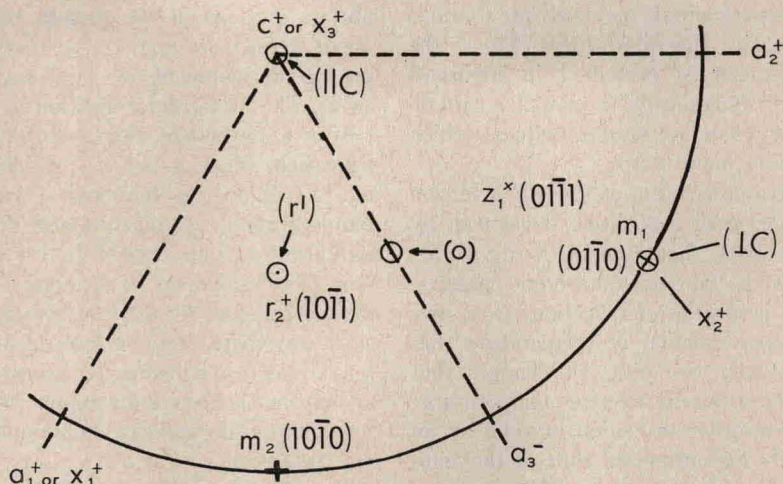


Fig. 4. Segment of upper hemisphere equal-area projection of α -quartz crystal showing crystal axes (a_1 , a_2 , a_3 , c) and Cartesian reference axes (x_1 , x_2 , x_3) as proposed in the *IRE Standards* [1949, p. 1384], rhombohedral faces (r_2 , z_1), prismatic faces (m_1 and m_2), and the orientations of the sample cores ($\perp C$, $\parallel C$, o and r').

crystal, seems to be capable of explaining many troubling phenomena connected with the transition and gives substance to the postulated micro-heterogeneities of *Semenchenko* [1957, 1965]. The difference between the structures on either side of a Dauphiné twin boundary can be described by a 180° rotation about the C axis, so that in the bounding wall some atoms must be vibrating about positions that correspond more nearly to those of hexagonal β quartz. An increase in the degree of twinning, which is to be expected as the transition to β quartz is approached, may possibly explain the reports of some workers [*Khlapova*, 1963; *Berger et al.*, 1966] that α - and β -quartz lattices coexist over ranges of temperatures as large as 10° to 30°C . In addition, the rapid increase in the scattering of light by quartz observed by *Yakovlev et al.* [1956] can be interpreted as arising from boundaries between microtwins (see also the more recent study by *Shapiro and Cummins* [1968]). Finally, as was pointed out by *Young* [1962], the variation in twinning from sample to sample may also help explain the variability in latent heat (or rate of increase of specific heat) reported in the literature and indicated by the variable shapes of the DTA peaks found by *Keith and Tuttle* [1952]. There is some question, however, whether the twin-boundary energy is large

enough close to the transition for this effect to be significant.

The question still remains whether or not there is a truly first-order component in the α - β transition. The measurements of volume and specific heat are not conclusive; all we can say is that they change very fast near the transition. *Young* [1962] shows that the abrupt changes in intensity of X-ray reflections from certain planes that are not affected by Dauphiné twinning are completed within a temperature range as small as 1°C . Anomalous increases in the rotation of plane-polarized light at the transition reported by *Mikheeva and Shustin* [1964] occur within an interval of about 0.3°C , and the thousandfold increase in the Rayleigh scattering observed by *Yakovlev et al.* [1956] occurs within about 0.1°C . The uncertainty of absolute temperature measurements and the variability of the properties of quartz used in the various investigations, however, prevent us from knowing whether these anomalous changes all take place at precisely the same point, and, if they do, whether this point corresponds exactly to the transition temperature (defined by the change in crystal symmetry).

In summary, there may well be a small first-order component in the α - β quartz inversion, but it certainly is not a typical first-order tran-