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## FEB 11 1970 The $\alpha$ - $\beta$ Inversion in Quartz: A Coherent Phase Transition under Nonhydrostatic Stress

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Experiments on oriented cores from a single crystal of quartz show that the temperature of the  $\alpha$ - $\beta$  transition is raised 10.6  $\pm$  0.4°C/kb and 5.0  $\pm$  0.4°C/kb by uniaxial compression perpendicular and parallel, respectively, to the optic axis at a confining pressure of 3 kb. Approximately the same results are indicated for confining pressures ranging from 1 to 5 kb. There is no detectable curvature of the phase boundary for uniaxial stresses  $\sigma$  between 0 and 10 kb:  $|(d^2T_{a-\beta}/d\sigma^2)| < 0.05^{\circ}$ C/kb<sup>3</sup>. The increase of transition temperature with hydrostatic pressure of 25.8  $\pm$  0.3°C/kb between 1 and 5 kb also determined in these experiments is consistent with previous determinations. These results and others for quartz are analyzed assuming the  $\alpha$ - $\beta$  inversion is either a  $\lambda$  transition or a first-order transition characterized by a small reversible transformation strain. Although both hypotheses are roughly consistent with most of the results, the hysteresis in the transition suggests that the second may be preferable, and a theory is developed that describes the effect of general nonhydrostatic stress on such transitions.

#### INTRODUCTION

The effect of nonhydrostatic stress in the solid earth on the thermodynamic stability of minerals may yet prove important to geology. The problem has attracted considerable interest over the past 75 years, and various aspects of the thermodynamics of nonhydrostatically stressed solids have been treated by scientists of many backgrounds.

In his classic 1878 paper, Gibbs [1906] considered a solid in a state of homogeneous, nonhydrostatic stress in equilibrium with a fluid (either the pure melt or a solution of the solid). By applying the basic thermodynamic prescription for equilibrium—that the internal energy be minimum with respect to all virtual infinitesimal changes of the system that maintain the entropy S and volume V constant-he derived the familiar thermal and mechanical conditions for equilibrium as well as the novel condition that the chemical potential of the solid in the adjacent liquid varies with the orientation of the interface. The magnitude of this variation he showed to depend chiefly on the degree to

which the stress departs from hydrostatic pressure; crystalline anisotropy (if any) enters only as a second-order effect. The sense of this variation is always such that the solubility of the solid is greatest at the interface that is subjected to the greatest compressive stress. Thus, if selfdiffusion were to take place at a noticeable rate, material would diffuse from the faces with maximum compressive stress to those with least compressive stress until hydrostatic pressure was restored. This result shows that true thermodynamic equilibrium requires hydrostatic pressure; the nonhydrostatically stressed state is a metastable one. If it is assumed, however, that self-diffusion is exceedingly slow compared to other processes such as melting or dissolving, then a pseudo-equilibrium state can be defined in which the stress need not be hydrostatic and the melting point or solubility of the solid at various interfaces can be determined.

Gibbs' conclusions retain their validity today, but there has been considerable further work. His ideas have been applied recently by Kamb [1959, 1961a] and Ida [1969] to the problem of preferred orientations of minerals developed by recrystallization in nonhydrostatically stressed polycrystalline materials. Bridgman [1916] generalized the case treated by Gibbs to include any two phases of a pure substance in differ-

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ent arbitrary states of stress in equilibrium across a permeable membrane that supports the stress differences. (A special case of this was considered by Riecke [1895].) In particular, he concluded for the case of two crystalline polymorphs in identical states of stress that a change of orientation of the crystal axes with respect to a given stress system and interface has only a second-order effect on the change of temperature of the transition due to the stress. Mac-Donald [1957] applied Gibbs' theory to polymorphic transitions in solids under conditions that amount to a special case of Bridgman's treatment and, likewise, concluded that crystalline anisotropy produces a negligible effect on the slope of the phase boundary of most firstorder transitions. He pointed out, however, that, when  $\Delta S$  and  $\Delta V$  of a first-order transition are very small, the terms involving elastic anisotropy become significant, and he therefore predicted that the  $\alpha$ - $\beta$  quartz transition would be greatly influenced by nonhydrostatic stress. Although he was certainly correct in this prediction, the experimental results we present in this paper are not consistent with his theory. Finally, McLellan [1966, 1968] generalized Gibbs' treatment to include the question of equilibrium of any number of components between any number of phases and showed that, except for a few very special sorts of configurations, true thermodynamic equilibrium can only occur if the stress is hydrostatic (even if selfdiffusion could not take place). There are many other works dealing with aspects of the problem; these include Goranson [1940a, b] Verhoogen [1951], MacDonald [1960], Kumazawa [1963], and Ito [1966], some of which are discussed below.

There is considerable disagreement among many of these papers. (See Kamb [1961a] for a discussion of some of these discrepancies and the ensuing discussions by Hoffer [1961], Mac-Donald [1961], Kumazawa [1961], and Kamb [1961b].) One of the difficulties has been the lack of quantitative experimental studies to provide tests for the theories. As an approach to the problem we chose to investigate the effects of nonhydrostatic stress on the  $\alpha$ - $\beta$  transition in quartz because this transition is fast and reversible and because quartz can withstand large stress differences without breaking. Moreover, quartz is a relatively simple material of general interest, about which much is known, and is of great importance in geology, especially in structural and metamorphic studies. Finally, our investigation is relevant to other work on quartz, in particular to recrystallization experiments under nonhydrostatic conditions near the  $\alpha$ - $\beta$  phase boundary, where it sometimes may not have been certain in which field recrystallization took place [Carter et al., 1964; Green, 1967].

In this paper we demonstrate that the temperature of the  $\alpha$ - $\beta$  transition in a single crystal of quartz subjected to a given nonhydrostatic stress depends strongly on the orientation of the crystal with respect to the principal axes of stress. The results are not consistent with any of the works cited above but are roughly consistent with predictions made by Garland [1964], which assume that the transition is a  $\lambda$ transition, that is, a second-order phase transition in which the volume V and entropy S are continuous across the boundary but the derivatives of V and S with respect to temperature Tand pressure P approach plus or minus infinity. (See Klement and Cohen [1968] for a careful examination of this assumption.)

A case can be made, however, that the inversion in quartz is actually a first-order transition that retains much of the character of a  $\lambda$  transition. The essential similarity is that the transition is characterized by a small reversible transformation strain which, for noncubic crystals, generally involves a change in shape as well as a change in volume. Thus, as the quartz crystal passes from the  $\alpha$  to the  $\beta$  phase, it remains intact, the optic axis remains the same, the relative elongation parallel to the optic axis is less than that perpendicular to it, and the original dimensions are recovered on passing back through the transition if the stress difference is not so large as to cause plastic flow. The difference from a  $\lambda$  transition is that the strain  $\epsilon_{kl}$  is assumed to undergo a first-order change, i.e., there as a nonzero  $\Delta \epsilon_{kl}$  at the transition.

3

We show that, for this type of transition, equilibrium depends on the orientation of the crystal with respect to the stresses but not on the orientation of the interface between the two phases. A chemical potential that reduces to the usual expression for hydrostatic pressure can be defined. This potential is the same

throughout a homogeneously stressed crystal at constant temperature and from it there follows a generalization of the Clapeyron equation that describes the slope of the phase boundary with respect to each stress component, in direct analogy to the formulas derived by *Garland* [1964] for  $\lambda$  transitions. Thus, the fact that our experimental results fit the first-order formula as well as the  $\lambda$ -transition formula is to be expected.

A transition between two crystalline phases that is characterized by a reversible transformation strain will be coherent. *McLellan* [1968] recognized this type of transition, but he seems not to have allowed for transformation strains that are not purely dilatational, and *Verhoogen*'s [1951] results suggest the same inherent limitation (see Appendix C). *Kumazawa* [1963], on the other hand, included shape as a thermodynamic parameter but did not consider the possibility of coherent first-order polymorphic transitions, except for twinning (see Appendix C).

All the other works referred to in the second and third paragraphs of the Introduction assume implicitly or explicitly that the transformation from one phase to the other involves an incoherent intermediate state, such as occurs in solid-liquid transitions and in solid-solid transitions that proceed via a liquid phase or involve diffusion along grain boundaries or within the crystal for distances large compared to the atomic spacing. These transitions are not characterized by a well-defined change in shape but only by a change in specific volume. Consequently, it is assumed that the transformation between the two phases at a given interface causes work to be done only by the component of stress normal to that interface, not by the tangential stresses. Because the difference in specific volume only changes with orientation in a nonhydrostatic stress field by the small amount due to the difference in elastic distortion of the two solid phases, equilibrium for this mode of transformation would not be sensitive to the crystallographic orientation unless the specific volumes were very nearly equal.

It may seem strange that the phase that is at equilibrium under nonhydrostatic stress may be different depending on whether the mode of transformation involves a coherent or an incoherent intermediate form, because either mechanism is capable of producing the same mineral in the same state of stress. The resolution of this apparent paradox lies in the realization that the equilibrium achieved in either case is metastable (unless the stress is hydrostatic) and that the change in shape involved in the transformation between the metastable forms differs for the two mechanisms.

In this paper we first discuss the nature of the  $\alpha$ - $\beta$  transition, then describe the experimental procedure, present the data, and discuss the results wih respect to the theories of both second- and first-order phase transitions. Finally, we conclude by briefly indicating other situations to which the theory may be applicable.

#### NATURE OF THE $\alpha$ - $\beta$ QUARTZ TRANSITION

When low or  $\alpha$  quartz (trigonal class 32) is heated at atmospheric pressure, it transforms to high or  $\beta$  quartz (hexagonal class 62) at about 574°C. (The temperature of the transition can be significantly affected by the presence of certain impurities, but in a careful study of many different natural quartz specimens *Keith* and *Tuttle* [1952] found that 95% of them had inversion temperatures within 2.5° of 573.2°C.) On cooling the quartz transforms back to the  $\alpha$  phase, usually 1° or 2°C below the temperature at which it transformed on heating [*Keith* and *Tuttle*, 1952].

The transition is heralded well in advance by accelerating rates of change of volume Vand entropy S. Because the expansion is isotropic in the plane perpendicular to the Caxis (from symmetry [Nye, 1957, p. 23]), the change of V with temperature T can be inferred from the relative changes in length par-



Fig. 1. Relative elongations of quartz parallel (||C) and perpendicular  $(\perp C)$  to the C axis as a function of absolute temperature [after Mayer, 1960].

COE AND PATERSON



Fig. 2. Specific heat of quartz according to Moser [1936] and Sinel'nikov [1953].

allel and perpendicular to the C axis (Figure 1). Agreement is good between these and other measurements except within a few degrees of the transition, where there is disagreement over whether or not a discontinuity exists.

The entropy is known even less well as a function of temperature than is the volume. Moreover, the detailed behavior of the specific heat,  $C_P = T (\partial S/\partial T)_P$ , in the region of the transition appears to be sensitive to the state of subdivision of the sample [Berger et al., 1965] and to the presence of impurities that hardly change the transition temperature at all [Coenen, 1963]. Thus, it is not surprising that the determinations of  $C_P$  vary from worker to worker and sample to sample (see two examples in Figure 2) and that there is disagreement about whether or not the entropy is continuous across the transition (absence of latent heat).

Measurements of the complete set of compliances for quartz as a function of temperature through the transition have only been obtained by dynamic means and, hence, are presumably adiabatic values. Ordinarily, the difference between the isothermal and adiabatic compliances is of the order of a per cent, and conversion, if necessary, is straightforward [Nye, 1957, p. 178]. Near the transition, however, the specific heat and thermal expansion become large, so that the difference is both significant (10 to 20% at 570°C) and quite uncertain (because of variations in absolute temperature measurement 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  $\alpha$ - $\beta$  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  $\beta$  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  $s_{85}$  for  $T > 600^{\circ}$ 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.

4926

COE AND PATERSON



Fig. 4. Segment of upper hemisphere equal-area projection of  $\alpha$ -quartz crystal showing crystal axes  $(a_1 \ a_2, \ a_5, \ c)$  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  $(\perp C, \mid \mid C, \ o \ and \ r')$ .

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  $180^{\circ}$  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  $\beta$ quartz. An increase in the degree of twinning, which is to be expected as the transition to  $\beta$ quartz is approached, may possibly explain the reports of some workers [Khlapova, 1963; Berger et al., 1966] that  $\alpha$ - and  $\beta$ -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  $\alpha$ - $\beta$  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 firstorder component in the  $\alpha$ - $\beta$  quartz inversion, but it certainly is not a typical first-order transition. Because a finite discontinuity in any physical quantity is difficult to distinguish from an extremely rapid continuous variation, it may seem futile to try to decide whether the transition is first or second order; the theoretical treatment should be capable of handling either possibility. Later, however, experimental details will be discussed that make us suspect that the transition is a first-order transition that closely resembles a  $\lambda$  transition but that does not rigorously satisfy the definition given in the Introduction for a  $\lambda$  transition.

#### SPECIMENS

Cores about 1 cm in diameter by 2 cm in length were drilled from a single clear lefthanded quartz crystal of unknown origin. Figure 4 shows the four orientations of the core axes that were determined from crystal morphology within an uncertainty of about 2°.

The ends of the cores were ground parallel within  $10^{-3}$  cm. Some were more highly finished—optically flat, parallel, and polished to better than  $0.5 \times 10^{-4}$  cm and ground smoother and truer on the cylindrical walls as well. One of these samples was silver plated on the ends. These refinements appeared to have little effect on the experiments, except possibly to raise the fracture strength.

In addition, hollow samples were tested for all orientations except r' (Figure 4). All but one of these were made by ultrasonically drilling a small hole of roughly circular cross section (diameter about 0.175 cm) along the axis of a solid sample. One hollow sample with a larger hole (0.4 cm) was made with a diamond core drill. Although the inner holes differed in degree of ellipticity, taper, and eccentricity by as much as about 10%, the effects of these variations could not be detected in our experiments.

#### APPARATUS

The experiments were done in an apparatus designed for rock deformation studies at pressures to 10 kb and temperatures to 1000°C (M. S. Paterson, unpublished data, 1969) [cf. *Raleigh and Paterson*, 1965]. It consists of an argon-filled pressure chamber with internal furnace into which a piston is introduced to apply an additional axial load to the specimen and has facilities for measuring the load exerted by the piston and its displacement as well as the temperature and the hydrostatic confining pressure.

Pressure was measured with an accuracy of  $\pm 1\%$  by the change in resistance of a manganin coil and was controlled within  $\pm 10$  bars. Temperature was measured with a commercial chromel-alumel thermocouple, sealed within a stainless steel sheath and insulated with magnesium oxide. In general, the sheath was 0.1 cm in outside diameter, but in some of the work a set of three 0.05-cm diameter thermocouples was used. The thermocouple was introduced along a small axial hole in the piston to make contact with the end of the specimen or to enter the specimen if it was hollow, the specimen being sheathed and sealed to the piston by use of a soft copper jacket of 0.025-cm wall thickness. Thus, the thermocouple was always at atmospheric pressure, eliminating any need for correcting for the effect of pressure. Sensitivity of temperature measurement was  $\pm 0.5$ to 1°C, and the overall accuracy was probably  $\pm 2^{\circ}$ C, except for some of the runs with 0.05cm thermocouples, when local shorting near the junction introduced error and possibly reduced this to  $\pm 4^{\circ}$ C.

The additional axial load was measured with about 5-kg sensitivity by a load cell inside the pressure chamber, thereby eliminating uncertainties due to piston friction. The load cell consisted of a hollow steel cylinder, to which electric resistance strain gages were attached, and was calibrated against an external load cell of known calibration, giving an accuracy of load measurement of about  $\pm 3\%$ . (There is possibly a somewhat greater error in runs 580 and 590, Table 2, owing to erratic behavior of an earlier load cell.)

Piston displacement could be measured with a sensitivity of about  $2 \times 10^{-4}$  cm. However, an apparatus distortion correction of about  $(7.0 \pm 0.5) \times 10^{-6}$  cm/kg load is needed for obtaining the actual strain, leading to an uncertainty of about  $0.25 \times 10^{-6}$  bar<sup>-1</sup> in determining compliances in the specimen.

#### EXPERIMENTAL PROCEDURE

The experiments were always conducted with a hydrostatic confining pressure of 1 kb or more in order to extend the range of the uniaxial stress that could be applied without fracturing





Fig. 5a. Tracing of load-displacement record for the 29th  $(\beta \rightarrow \alpha)$  and 30th  $(\alpha \rightarrow \beta)$  passage through the transition of run 602 (Table 2) at 3-kb confining pressure. Numbers along the load trace are sample temperatures in degrees C. The load pen led the displacement pen by the equivalent of 7-8 sec. The transition is marked by softening of the sample and can usually be seen in both the load and the displacement curves.

the sample. The technique was to hold the temperature and pressure fixed at values such that the sample was in the  $\beta$  field when the axial load was zero. The load was then smoothly increased to the point at which inversion to

the  $\alpha$  phase occurred and well beyond, then decreased until the  $\beta$  phase was regained (Figure 5a). The point on the load and displacement curves that corresponded to the greatest compliance was taken as the transition bound-



Fig. 5b. Stress-strain curve constructed from record of Figure 5a shows more clearly the softening that marks the transition as well as the hysteresis. The straightish section in the  $\beta$  field does not extrapolate to the origin because about 1-kb stress is needed to seat the various surfaces in the load column before the value  $7 \times 10^{-6}$  cm/kg taken for apparatus distortion is valid. The lack of coincidence below the transition stress of the curves of increasing and decreasing stress is unusually large in this example, and we have no ready explanation for it.

ary. In general, there was some hysteresis between points determined with increasing and decreasing load (Figure 5b), but the point of maximum compliance was not affected by rate of increase of stress within the range used (0.004 to 0.020 kb/sec). Table 1 shows how the magnitude of the observed compliance varied through the transition for different orientations of specimen.

The transition point given by the compliance maximum is essentially the same as that revealed by a differential temperature peak determined analogously to the usual DTA method. This was shown in a few runs with hollow samples (595, 596, and 601, Table 2), in which the difference in emf of a pair of 0.05-cm thermocouples-one 0.5 cm inside the sample and the other 1 cm above in the piston-was monitored. In 49 out of 54 times that the phase boundary was crossed, a peak of 0.5° to 1.5°C occurred at or just after the maximum in compliance, and the sign of the anomalous temperature difference was in every case consistent with the direction of crossing. (The sample cooled with respect to its immediate surroundings when going from  $\alpha$  to  $\beta$  and heated when going from  $\beta$  to  $\alpha$ .) The position of the peak was influenced by the rate of increase of stress: at the slowest rates it coincided with the compliance maximum, whereas at the fastest rate it lagged slightly behind.

The experimental difficulties were mainly associated with temperature variations in the specimen. If the temperature gradient along the specimen exceeded 1°C/cm, the transition became too smeared out to be reliably detected. The gradient was controlled by proportioning the current in the furnace between an upper and a lower winding, more current being required in the lower one in order to counteract the effects of intense vertical convection in the compressed argon along the furnace axis. In hollow samples the temperature gradient was observed directly, whereas in solid samples it was controlled by appropriately adjusting the gradient in the hollow piston immediately above. The temperature changed with time, sometimes erratically, but as long as the drift was less than 1°C/min the gradients in the sample remained negligible, the transition was sharp, and useful measurements could be made.

The transition did not appear to be signifi-

cantly smeared by nonuniformities of stress in the specimen. This will be discussed more fully later.

#### EXPERIMENTAL RESULTS

When the temperatures of transition at several values of uniaxial stress  $\sigma$  and constant hydrostatic pressure *P* are plotted versus stress for a given sample, the points fall remarkably close to a straight line. Figure 6 shows two such straight lines obtained in two runs on samples of different orientations at 3-kb confining pressure. Several interesting features are well illustrated: (1) the slope of the transition is quite different for the two orientations; (2) there is no identifiable curvature (less than 0.05°C/ kb<sup>2</sup> for  $0 < \sigma < 10$  kb) in either line; (3)

TABLE 1. Experimental Estimates of the Compliance of Quartz for Pressures between 1 kb and 5 kb

	Compliance, units $(10^6 \times bars)^{-1}$							
Orientation	$\alpha$ Field	β Field	Transition Point					
$\perp C$ (along $x_2$ )	$1.7 \pm 0.2$	$0.8 \pm 0.2$	$7.5 \pm 3.0$					
$  C \text{ (along } x_3) $	$1.2 \pm 0.2$	$1.0 \pm 0.2$	$3.0 \pm 1.0$					
$o$ (45° to $x_3$ )	$1.2 \pm 0.2$	$0.7 \pm 0.1$	$3.3 \pm 0.5$					
$r'$ (43° to $x_3$ )	$1.8 \pm 0.1$	$1.0 \pm 0.1$	$4.0 \pm 1.0$					

Notes.

Uncertainties listed are standard deviations, assuming the value used for apparatus distortion is correct, and thus represent the precision of the measurements. An additional uncertainty of  $\pm 0.25 \times 10^{-6} \text{ bars}^{-1}$  arises from uncertainty of apparatus distortion.

 $\alpha$  and  $\beta$  field compliances are averages for the region outside the obvious transition (0.5 - 1.0 kb uniaxial stress away from the point of maximum compliance) region.

The transition point compliance is the 'average maximum' compliance measured in the transition region and must be regarded as intermediate between isothermal and adiabatic.

Compliances for orientations  $\perp C$ , ||C, and o are for both solid and hollow specimens; r' for solid only.

Data are roughly in accord with dynamically measured compliances at atmospheric pressure. Greatest inconsistency is that all values calculated for o and r' orientations are considerably greater than those in Table 1. Also the values for o and r'(and all other orientations ~45° to  $x_3$ ) should be equal in the  $\beta$  field because of the hexagonal symmetry [Nye, 1957] but are obviously not in Table 1. COE AND PATERSON



Fig. 6. Temperature of the  $\alpha$ - $\beta$  transition at a constant confining pressure of 3 kb as a function of compressive stress  $\perp C$  (run 602) and  $\mid\mid C$  (run 603). The transition  $\beta \rightarrow \alpha$  (increasing stress) is denoted by triangles, whereas  $\alpha \rightarrow \beta$  (decreasing stress) is denoted by circles. See Table 2 for least-squares values of slope and intercept for these runs.

extrapolation of the lines to zero compressive stress yields essentially the same temperature intercept; (4) there is hysteresis in the transition even at zero compressive stress; and (5) the slope of the line determined from transitions from the  $\beta$  to the  $\alpha$  phase,  $(\partial T/\partial \sigma)_{\beta\to\alpha}$ , is slightly less than  $(\partial T/\partial \sigma)_{\alpha\to\beta}$ .

All the pertinent experimental data are collected in Table 2, including those graphically presented in Figure 6. The slopes, intercepts, and the standard deviations of both are those for the best-fitting straight line according to the method of least squares. (These singleregression standard deviations are not statistically rigorous because errors may occur in both  $T_{a-\beta}$  and  $\sigma_{a-\beta}$ , but they are useful indicators of relative scatter.)

Several points of interest in interpreting the results emerge from Table 2:

1. Solid and hollow samples behave the same under comparable conditions, as shown by runs 602 and 601, 607 and 606, and 603 and 595–596. There may be a slightly greater slope of the  $\alpha$ - $\beta$  boundary for hollow samples, but the scatter makes the reality of this distinction questionable.

2. A slight dependence of  $\partial T_{a,\beta}/\partial\sigma$  on pressure is observed for the  $\perp C$  orientation—about  $+0.2^{\circ}$ C/kb per kilobar of hydrostatic pressure in the range 1 to 5 kb. There are not enough data to be sure if this is a real variation, and the case for other orientations is even more doubtful.

3. From an analysis of the standard deviations there is a suggestion that  $(\partial T/\partial \sigma)_{a\to \theta}$  is slightly greater than  $(\partial T/\partial \sigma)_{\beta\to a}$  in the same experimental run by 0.25 ± 0.25°C/kb. A regular dependence of this difference on pressure or specimen orientation is not evident. (Therefore, in calculating the mean slope in Table 2 for those few runs in which only  $(\partial T/\partial \sigma)_{\beta\to\alpha}$ was determined,  $0.12 \pm 0.25$  °C/kb was added to this measured value.) It is also observed that the standard deviation of the mean slope of a line is generally significantly less than the scatter of slopes among different experimental runs under ostensibly the same conditions. Both these details of the results may be caused by additional variable components of stress, which could arise either from the difference in lateral changes of dimension between the quartz and the adjacent carbide endpieces or even possibly from differences in the development of Dau-

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S Com		Samp	Sample		(D) +	Min.	Max.	No. of Points‡		$\partial T_{\alpha-\beta}/\partial\sigma$ Slope, °C/kb			$T^{\circ}_{\alpha-\beta}$ Intercept, °C					
No.	Axis	Type	Final Condition	kb	kb	kb	kb	σĮ, kb	σĮ, kb	$\beta \rightarrow \alpha$	$\alpha \rightarrow \beta$	$\beta \rightarrow \alpha$	$\alpha \rightarrow \beta$	Mean§	$\beta \rightarrow \alpha$	$\alpha \rightarrow \beta$	Mean§	
580ª	$\perp C$	Solid		3.00	3.00	1.0	3.0	3	0	10.28 + 0.83		$10.40 \pm 0.87$	$650.1 \\ \pm 3.1$		$650.9 \\ \pm 3.2$			
				4.00	4.00	0.1	.2.7	16	0	10.80 + 0.09		10.92 + 0.27	675.5 + 0.5		676.3 + 1.0			
				5.00	5.00	0.2	0.9	3	0	11.50 +1.24		11.62 + 1.27	702.4 +1.3		703.2 +1.6	TUL		
602 <sup>b</sup>	TC	Solide	Intact: A few fractures	3.01	3.01	1.5	10.0	16	16	10.21 +0.03	10.41 + 0.03	10.31 +0.14	646.8 + 0.8	648.6 + 0.7	647.7 +1.3	2 a-p		
590ª	TC	Hollow	Intact: No fractures	1.01	1.04	0.4	3.8	5	3	9.18 + 0.10	9.71 + 0.06	9.44 + 0.37	600.9 +0.5	601.6 + 0.3	601.2 + 0.5	TIN		
			And the ob	2.01	2.07	0.3	3.8	7	4	8.93	9.53 + 0.44	9.23 + 0.43	627.3 + 0.6	628.5 +21	627.9 + 1.5	V PIR		
				3.02	3.11	0.7	5.3	14	8	9.60 + 0.04	9.48	9.54 + 0.09	654.2 + 0.4	657.3 +0.8	655.7 +2.2	TOTO		
				4.01	4.13	0.4	5.3	7	0	9.23 + 0.06	70100	9.35 + 0.26	682.1 + 0.5	±0.0	682.9 + 1.0	NT		
				5.02	5.17	1.1	4.8	5	0	9.12 + 0.18		9.24 + 0.31	708.0 +1.2		708.8 + 1.3	NOP		
601	$\bot C$	Hollow <sup>d</sup>	Intact: Fractures at both ends	3.01	3.01	2.2	6.1	7	7	10.31 + 0.12	10.51 + 0.11	10.45 + 0.14	648.6 +1.4	650.3 + 1.3	649.4 +1.4	AUT		
604- 605	TC	Hollow	Intact, but densely filled with fractures	1.00	1.03	0.5	6.2	8	6	10.01 + 0.06	9.86 + 0.11	$9.94 \\ \pm 0.10$	599.4 + 0.6	601.7 + 1.0	600.5 + 1.6	6		
			throughout entire length	3.00	3.09	0.6	6.6	7	4	10.48 + 0.03	11.42 + 0.06	$10.95 \pm 0.66$	652.9 + 0.3	650.0 + 0.5	651.4 + 2.0			
				5.01	5.16	2.2	5.7	4	0	10.94 + 0.10		$11.06 \pm 0.27$	704.8 + 0.8		705.6 +1.2			
610	$\perp C$	Hollow	Intact: No fractures	1.01	1.21	0.5	8.4	7	6	10.03 + 0.09	10.28 + 0.06	10.16 + 0.18	605.8 + 1.2	606.9 + 0.7	606.3			
				3.00	3.60	0.4	8.5	12	8	10.51 + 0.04	10.90 + 0.08	10.70 + 0.28	668.4 + 0.7	668.2 + 1.2	668.3 +1.0			
				5.00	6.00	0.9	6.1	6	5	10.51 +0.04	11.04 + 0.09	10.88 + 0.37	731.0	730.0	730.5 +0.7			

TABLE 2

21-	TABLE 2 (continued)																	
Sample				Min.	Max.	No. of Points‡		$\partial T_{\alpha-\beta}/\partial\sigma$ Slope °C/kb			$T^{\circ}_{\alpha-\beta}$ Intercept, °C							
Run No.	Core Axis	Type	Final Condition	$\begin{array}{ccc} P^*, & \langle P \rangle \dagger, \\ \mathrm{kb} & \mathrm{kb} \end{array}$	$\begin{array}{ll} P^*, & \langle P \rangle \dagger, \\ \mathrm{kb} & \mathrm{kb} \end{array}$	$\langle P  angle \dagger, \  m kb$	$\langle P \rangle \dagger, \ \mathrm{kb}$	σ‡, kb	σ‡, kb	$\beta \rightarrow \alpha$	$\alpha \rightarrow \beta$	$\beta \rightarrow \alpha$	$\alpha \rightarrow \beta$	Mean§	$\beta \rightarrow \alpha$	$\alpha \rightarrow \beta$	Mean§	
603*	<i>C</i>	Solid <sup>e</sup>	Divided in two by horizontal break, fractures at top and bottom	3.00	3.00	0.3	11.0	11 .	9	$4.72 \pm 0.02$	$\begin{array}{c} 4.90 \\ \pm 0.02 \end{array}$	$4.81 \pm 0.13$	$648.7 \pm 0.4$	$650.8 \pm 0.8$	$649.7 \\ \pm 1.5$			
595- 596 <sup>b</sup>	C	Hollow	Intact: Fractures	2.00	2.08	0.6	9.2	14	12	$4.68 \pm 0.02$	$4.92 \\ \pm 0.02$	$4.80 \pm 0.17$	$625.6 \pm 0.4$	$627.0 \pm 0.2$	$626.3 \pm 1.0$			
				3.01	3.13	1.1	6.8	6	4	$4.90 \pm 0.07$	$5.49 \pm 0.02$	$5.20 \pm 0.42$	$651.5 \pm 0.7$	$651.2 \\ \pm 0.2$	$651.3 \pm 0.5$			
				4.00	4.16	0.3	1.6	4	0	$5.07 \pm 0.33$		$5.19 \pm 0.41$	$678.9 \pm 0.7$		$   \begin{array}{r}     679.7 \\     \pm 1.1   \end{array} $	0		
607	0	Solid	Intact: No fractures	1.01	1.01	0.8	7.7	11	11	$7.02 \pm 0.04$	$7.37 \pm 0.06$	$7.20 \pm 0.25$	$599.8 \pm 0.7$	$   \begin{array}{r}     601.8 \\     \pm 0.8   \end{array} $	$   \begin{array}{r}     600.8 \\     \pm 1.4   \end{array} $	OE		
				3.00	3.00	0.4	8.9	10	9	7.30 + 0.03	7.35 + 0.04	7.32 + 0.04	653.4 + 0.5	655.9 + 0.7	$654.5 \\ \pm 1.8$	ANL		
606	0	Hollow	Intact: No fractures	1.00	1.04	0.5	7.1	8	8	7.30 + 0.04	7.32 + 0.02	7.31 + 0.03	601.0 + 0.4	602.4 + 0.3	601.7 + 1.0	) PA		
				3.00	3.12	0.4	7.3	8	7	7.41 + 0.04	7.33 + 0.04	7.37 + 0.06	655.0 + 0.5	656.9 + 0.4	655.9 + 1.3	TER		
598 <sup>b</sup>	r'	Solid	Intact: Bottom densely fractured (initially one natural fracture)	3.01	3.01	0.7	6.5	14	7	$8.73 \pm 0.07$	9.45 ±0.21	$9.09 \pm 0.51$	649.5 ±1.0	646.2 ±2.7	647.8 ±2.8	SON		

Notes.

\* Hydrostatic confining pressure exerted within bomb by compressed argon.

C.

† Calculated mean pressure in sample. For solid samples  $\langle P \rangle = P$ , but for hollow samples  $\langle P \rangle \approx P(b^2/b^2 - a^2)$ , where 2b and 2a are the outer and inner diameters of the bounding cylinders (see Appendix A).

<sup>‡</sup> The minimum and maximum compressive stresses applied above the hydrostatic pressure and the number of passages made through the transition in determining the line dividing the  $\alpha$ - and  $\beta$ -quartz fields. In this table,  $\sigma > 0$  for compression.

§ Mean slope and intercept are found by averaging the results obtained by passing from  $\beta \rightarrow \alpha$  and from  $\alpha \rightarrow \beta$ . Uncertainty listed is either the standard deviation of the mean or the combined standard deviation of the individual determinations, whichever is larger. For those runs in which data were gathered only for the  $\beta \rightarrow \alpha$  passage, the 'mean' slope and intercept were estimated by a method described in the text.

<sup>a</sup> Earlier model of load cell.

<sup>b</sup> Triplet of 0.05-cm thermocouples.

• Better finished sample.

<sup>d</sup> Same core as 590 but ground shorter to 1.6 cm.

#### THE $\alpha$ - $\beta$ INVERSION IN QUARTZ

	$\partial T_{lpha-eta}/\partial\sigma^*,\ ^{ m o}{ m C}/{ m kb}$							
Selection of Data	$\perp C$	C	0	r'				
All	$10.3 \pm 0.7^{+}$	$5.0 \pm 0.3$	$7.3 \pm 0.1$	$9.1 \pm 0.5$				
Excluding runs 580 & 590	$10.6 \pm 0.4$	$5.0 \pm 0.3$	$7.3 \pm 0.1$	$9.1 \pm 0.5$				
P = 3  kb	$10.6 \pm 0.4$	$5.0 \pm 0.4$	$7.3 \pm 0.1$	$9.1 \pm 0.5$				

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

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

<sup>†</sup> 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  $\alpha$ - $\beta$  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  $1.6 \pm 0.9^{\circ}$ 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°C has therefore been added to  $T_{\beta\to\alpha}$ ° 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  $\partial T_{a-\theta}/\partial \sigma$  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°C/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  $25.83 \pm 0.06$  °C/kb and  $573.6 \pm 1.0$  °C, which represents an amazingly good agreement with published values. (*Klement and Cohen* [1968] estimate 26 °C/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  $\alpha$ - $\beta$  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 ( $||C\rangle$ , and triangles (o). Ten points are not shown because they are obscured by the other points.

also Keith and Tuttle [1952],  $573 \pm 2^{\circ}$ 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  $25.82 \pm 0.05^{\circ}$ C/kb and  $574.4 \pm 0.8^{\circ}$ C. Taking into account the uncertainty in absolute calibration of the pressure and temperature, we feel that the best estimates from our measurements are  $25.8 \pm$  $0.3^{\circ}$ C/kb and  $574 \pm 2^{\circ}$ 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  $T_{a-\beta}$  can be regarded as a function of the components of stress  $\sigma_{ij}$  so that

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

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

where the summation convention over repeated indices is implied (i, j = 1, 2, 3) and the sign of  $\sigma_{ij}$  is positive for tension. Because  $T_{a-\beta}$  is a scalar and  $\sigma_{ij}$  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

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

In applying general theory to the specific situation in quartz, we change the sign convention for convenience so that  $\sigma$  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  $\alpha$  or  $\beta$  quartz. Equation 2 can then be written

$$M_{1} = M_{2} = (\partial T_{\alpha-\beta}/\partial\sigma)_{\perp C}$$

$$M_{3} = (\partial T_{\alpha-\beta}/\partial\sigma)_{\parallel C}$$
(4a)

Single subscripts are used in (4a) to indicate that the diagonal components of  $M_{kl}$  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

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

From our measured values  $M_1 = 10.6 \pm 0.4^{\circ}$ C/kb and  $M_a = 5.0 \pm 0.4^{\circ}$ C/kb (Table 3) we obtain an estimate from (4b) of  $dT_{a-\beta}/dP = 26.2 \pm 0.7^{\circ}$ C/kb, which agrees within experimental error with the value of  $25.8 \pm 0.3^{\circ}$ 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. Nonuniformities 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  $T_{a-\beta}$  would vary over the circular cross section of specimens of all orientations except ||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 variation 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,  $T_{a-\beta}$  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  $T_{a-\beta}$  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  $T_{a-\beta}$  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  $T_{a-\beta}$  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 twothirds 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 biassed by stress inhomogeneities in the specimens.

Apparent anomaly in the o and r' specimens. Because the two principal values of  $M_{ij}$  (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  $M_{ss'}$ along any direction at 45° to the C axis should be given by

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

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

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

An analogous inconsistency is exhibited by the  $\beta$ -quartz compliances  $s_{ss}$  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  $M_{ss}$  to  $s_{ss}$ , 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 ||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 ||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° 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  $(\partial T/\partial \sigma)_{a\to\beta}$  is usually greater than  $(\partial T/\partial \sigma)_{\beta\to a}$  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  $\beta_r$ , 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:

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

$$\beta_T \to (dT_{\lambda}/dP)\alpha$$
 as  $T \to T_{\lambda}$  (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).

8

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 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:

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

$$s_{ijkl} \xrightarrow{T} \to M_{kl} \alpha_{ij} \quad \text{as} \quad T \to T_{\lambda}$$

$$\tag{8}$$

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  $\sigma_{kl}$  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°C/kb and, less convincingly,  $M_{\rm s} \simeq 6^{\circ}$ 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  $M_1 = 10.6^{\circ}$ C/kb and  $M_3 =$ 5.0°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  $dT_{\lambda}/dP$ 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  $C_{\sigma}/T$  is eliminated from (7) another important constraint on the values of  $M_1$  and  $M_3$  is obtained asymptotically from  $\alpha_1$  and  $\alpha_3$  (B11*a*, Appendix B):

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

The evaluation of this limit appears to be free of many of the difficulties discussed above, because 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  $\alpha_1$  and  $\alpha_3$  are determined simultaneously over the same portion of quartz, thus eliminating possible errors in  $\alpha_1/\alpha_3$  due to differences of material within the same specimen and inconsistences 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 ( $T \simeq 574^{\circ}$ 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  $M_1/M_s$  that are imposed by pairs of components of the isothermal compliance tensor  $s_{ijkl}$  as the boundary of a  $\lambda$  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  $\alpha_1/\alpha_s = 1.68$  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  $M_1/M_s$  is not obtainable from the asymptotic



Fig. 8. Linear thermal expansion coefficients of quartz parallel ( $\alpha_3$ ) and perpendicular ( $\alpha_1$ ) 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  $s_{n}^{T}$  and  $s_{as}^{T}$  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  $M_1/M_s$  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

known ratio of the thermal expansions is in significant conflict with our directly measured value of  $2.1 \pm 0.2$ . 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  $\alpha_3/\alpha_3$  should not be very sensitive to pressure. That is,

$$\left(\frac{\partial \alpha_1}{\partial P}\right)_T \Big/ \left(\frac{\partial \alpha_3}{\partial P}\right)_T = \left[\frac{\partial (s_{11}^T + s_{12}^T + s_{13}^T)}{\partial T}\right]_P \Big/ \left[\frac{\partial (s_{33}^T + 2s_{13}^T)}{\partial T}\right]_P \approx 1.5$$

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  $\alpha$ - $\beta$  inversion is a  $\lambda$  transition, except for the fact that the ratio  $M_1/M_3 = 1.7$  predicted by the same hypothesis from the much more accurately 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  $\lambda$  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  $\alpha_1/\alpha_s = 1.68$  and by the relatively good agreement among the experimental determinations of  $dT_{\alpha_{-\beta}}/dP$ . If the Dauphiné twinning reaches a maximum before the  $\alpha$ - $\beta$  transition proper, it is possible that the asymptotically derived values of  $M_1$  and  $M_3$  are influenced by this phenomenon.

5. The transition might actually be marked by a small first-order change in entropy, volume, and some of the components of strain, so that the derivatives of these quantities on approaching the transition might never get large enough to rigorously satisfy the asymptotic relations derived for a  $\lambda$  transition (see Figure 9). This hypothesis is supported by the existence of hysteresis in the transition, for if there were a continuous series of states in which quartz were stable as the phase boundary was traversed, it is difficult to see how there could be any hysteresis at all.

This hypothesis is further supported by the character of the DTA peaks observed when squeezing the specimens through the transition (see section on experimental procedure). If the  $\alpha$ - $\beta$  inversion were a  $\lambda$  transition, then the cause of the DTA peaks would be the sudden increase of heating due to compression as the transition was approached and crossed. The increase in temperature under adiabatic conditions owing to compression perpendicular or parallel to the *C* axis differs, however, so that the ratio of the two effects is given by

$$\left(\frac{\partial T}{\partial \sigma_1}\right)_{S,\sigma\neq\sigma_1} / \left(\frac{\partial T}{\partial \sigma_3}\right)_{S,\sigma\neq\sigma_3} = \frac{T V \alpha_1}{C_\sigma} / \frac{T V \alpha_3}{C_\sigma} = \frac{\alpha_1}{\alpha_3}$$

yet we could not distinguish any systematic



Fig. 9. Two models for the  $\alpha$ - $\beta$  inversion in quartz, which differ only in the behavior of the extensive parameters as a function of the intensive parameters near the transition: in (1), a  $\lambda$  transition, the variation is continuous and a vertical tangent occurs at the transition, whereas in (2), the model we prefer, a first-order discontinuity terminates the rapid rate of change of V and S at the transition before a vertical tangent is reached (case 5 in text).

#### 4940

difference in DTA peak height for the two orientations. It is unlikely that a compensating directional anomaly in the thermal conductivity of quartz, even if it existed, could obscure any significant directional difference in heat effect, because it is probable that heat generated in the specimen would be conducted away both radially and longitudinally under our experimental conditions. If the transition were firstorder, however, then a latent heat would be released as the specimen was squeezed through the transition, and this heating would not depend particularly on the orientation of the crystal to the compression. Another pair of observations, that the height of the DTA peak was not affected by the fivefold range of squeezing rate used in these experiments, whereas the position of the peak lagged slightly behind the compliance maximum at the highest rate, might also be explained by assuming that the hysteresis holds up the first-order transition so that the latent heat is released more suddenly when it finally occurs.

In conclusion, we tend to favor the last of these possibilities, but to prove or disprove this and to resolve the many troubling conflicts touched upon earlier, higher quality measurements of  $\alpha_{ij}$ ,  $s_{ijkl}^{T}$  (by both static and dynamic means),  $C_P$ , and  $M_{kl}$  on the same crystal and very near the transition will probably be needed.

### The $\alpha$ - $\beta$ Inversion Treated as a Coherent First-Order Transition

We gave indirect reasons above that suggest to us that the  $\alpha$ - $\beta$  inversion may involve a small first-order component. Some workers actually claim to detect discontinuities in the volume and entropy at the transition, but these are difficult to establish on account of their small magnitudes and the rapid rate of change of these quantities in the neighborhood of the transition. Thus, *Majumdar et al.* [1964] give  $\Delta v \simeq 0.11 \pm 0.015$  cm<sup>3</sup>/mole and  $\Delta s \simeq 0.10 \pm$ 0.02 cal/mole °C, which, when substituted into the Clapeyron equation

$$dT_{\alpha-\beta}/dP = \Delta v/\Delta s \tag{10}$$

yield an estimate for the slope of  $26 \pm 6^{\circ}$ C/kb, whereas *Berger et al.* [1965, 1966] give  $\Delta v \simeq$  $0.15 \pm 0.01$  cm<sup>3</sup>/mole and  $\Delta s \simeq 0.15 \pm 0.04$ cal/mole °C, which yield an estimate of  $24 \pm$  $6^{\circ}$ C/kb. On the other hand, *Sinel'nikov*'s [1953] upper bound of 0.003 cal/mole °C for  $\Delta s$  would imply  $\Delta v$  no larger than 0.0033 cm<sup>3</sup>/mole to yield the experimentally observed slope of 26°C/kb from (10). It is difficult to resolve this and other inconsistencies of the data in the literature.

We shall assume the transition is first-order, however, and that it is characterized by a reversible first-order discontinuity in the strain that we call the transformation strain. As pointed out in the Introduction, this latter feature is tied to the notion that the transition mechanism involves a coherent interface between the two phases, so that the displacement vector for the quartz as it undergoes the phase transformation is a continuous function of position. If the transformation strain  $\Delta \epsilon_{kl}$  is small enough so that the approximations of infinitesimal strain theory are valid, the generalization of the Clapeyron equation applicable to the transition is (equation C6, Appendix C)

$$M_{kl} \equiv -(\partial T_{\alpha-\beta}/\partial \sigma_{kl})_{\sigma \neq \sigma_{kl}}$$
$$= v_0 \ \Delta \epsilon_{kl}/\Delta s \qquad (11)$$

where  $v_o$  is the molar volume in the reference state of strain and  $\Delta s$  is the entropy per mole associated with the transition.

As shown in Appendix C, (11) is in direct analogy to the formulas (7) and (8) for the slope of the boundary of a  $\lambda$  transition; moreover, it reduces to the conventional Clapeyron equation (10) for hydrostatic pressure. In the general case of nonhydrostatic stress, (11) shows that shear stresses will be important thermodynamic variables in determining the field of stability of a polymorph, if  $\Delta \epsilon_{kl}$  includes significant shear strains. In fact, if the transformation strain involves a change in shape but not of volume, the transition temperature will be independent of pressure but not of the individual components of stress.

Applying (11) to quartz and choosing the coordinate axes as in Figure 4, we obtain expressions for the increase of transition temperature owing to compression perpendicular or parallel to the C axis, respectively, in terms of the relative discontinuity of the lattice parameters  $\Delta a/a$  or  $\Delta c/c$  in the same direction:

$$M_1 = v_0 \ \Delta \epsilon_1 / \Delta s = v_0 (\Delta a/a) / \Delta s \qquad (12a)$$

$$M_3 = v_0 \ \Delta \epsilon_3 / \Delta s = v_0 (\Delta c/c) / \Delta s \qquad (12b)$$

Just as in the hydrostatic case, the scatter in the experimental data makes the testing of (12a) and (12b) unsatisfactory. Using values of  $\Delta a/a \simeq 0.0027 \pm 0.003$ ,  $\Delta c/c \simeq 0.0012 \pm$ 0.001, and  $\Delta s \simeq 0.15 \pm 0.04$  cal/mole °C of Berger et al. [1965, 1966] leads to  $M_1 \simeq 9.7 \pm$ 2.7°C/kb and  $M_s \simeq 4.4 \pm 1.2$ °C/kb, which are very roughly the same as our experimental values, but the uncertainty is great and becomes even greater if attempts are made to combine the data of other workers.

In a manner completely analogous to the discussion of the  $\alpha$ - $\beta$  inversion as a  $\lambda$  transition, we can avoid the large uncertainties in the value of  $\Delta s$  by eliminating it between (12*a*) and (12*b*), yielding

$$M_1/M_3 = \Delta \epsilon_1 / \Delta \epsilon_3 = \Delta a / a / \Delta c / c$$
 (13)

The X-ray data of Berger et al. yield  $M_1/M_3 \simeq 2.2 \pm 0.3$ , which is in decent agreement with our directly measured value of  $2.1 \pm 0.2$ , but the dilatometric studies of *Mayer* [1960] yield  $M_1/M_3 \simeq 1.7$ . There is no way to decide without further experiments whether this discrepancy arises from experimental errors or real differences in the material studied.

#### Summary

The change of the temperature of the  $\alpha$ - $\beta$ inversion in quartz with hydrostatic pressure or with general stress that we measured directly in our experiments can be interpreted equally well by assuming the inversion to be a  $\lambda$  transition or a coherent first-order transition. For reasons discussed above, we favor the first-order interpretation and suggest further that the asymptotic limits required by the  $\lambda$  transition hypothesis may not be rigorously attained (Figure 9).

#### GENERAL COMMENTS

The class of phase transitions that has been described by *Buerger* [1951] as displacive is certainly coherent in the sense used in this paper. These are generally characterized by being rapid, reversible, and involving relatively minor structural reorganization at the atomic level. Another example for which an interpretation similar to that for the quartz inversion is suggested is the  $\alpha$ - $\beta$  transition in AIPO<sub>4</sub>, which, according to *Troccaz et al.* [1967], is completely analogous to the  $\alpha$ - $\beta$  transition in quartz. Assuming this transition is a coherent first-order one, and using their values for  $\Delta a/a$  and  $\Delta c/c$  in (13), we find  $M_1/M_3 \simeq 8.2$ . If we apply the  $\lambda$  transition formula (9), however, and use the slopes of the steepest parts of the thermal expansion curves for a and c which they measured just before the supposed first-order discontinuity from the  $\alpha$  to the  $\beta$  phase, we find  $M_1/M_3 \simeq 2$ . This significant discrepancy can be explained by assuming the asymptotic limit required in (9) is never reached. If their measurement of  $\Delta s$  is valid, then the first-order theory further predicts  $M_1 \simeq 16.5^{\circ}$ C/kb and  $M_s = 2.0^{\circ}$ C/kb from (12a) and (12b) and  $dT_{a-\beta}/dP = 35^{\circ}\text{C/kb}$ from (4b). We do not know of any direct measurement of these quantities for AlPO4.

Besides the displacive, martensitic, and twinning type of crystallographic transformations, it is interesting to speculate whether other more sluggish transformations may also occur coherently. This mode of transformation requires that diffusion be suppressed and thus is more likely the more rapidly it can occur. Under dry conditions at sufficiently low temperatures, however, a slow coherent mechanism may possibly be favored over a reconstructive one that requires significant diffusion. As long as the phase change is characterized by a reversible transformation strain that involves a significant change of shape as well as of volume-no matter whether it is rapid or sluggish—the stability fields of the polymorphs must depend on the shear stresses as well as on the hydrostatic pressure. This is a thermodynamic effect, different from any catalytic effects of shear stress on reaction rates and may throw light on the issue of stress-sensitive minerals which has appeared intermittently in the geological literature for many years.

#### APPENDIX A

Temperature smearing in homogeneous, isotropic, hollow specimens. If we choose cylindrical coordinates with z axis along the core axis, it can be shown [Timoshenko and Goodier, 1951, p. 59] that when the specimen is subjected to a hydrostatic pressure P on its outer surface (r = b), zero pressure on its inner surface (r = a), and an extra uniaxial compression  $\sigma > 0$  along the axis, the resultant nonzero components of stress are COE AND PATERSON



Fig. 10a. Lines of equal  $\Delta T_P \equiv T_{a-\beta}$   $(r, \theta) - \langle T_P \rangle$  plotted on the cross section of a hollow specimen oriented  $\perp C$  (equations A3 and A4, Appendix A).  $\Delta T_P$  is the increase in transition temperature (above the mean transition temperature  $\langle T_P \rangle$ ), owing to the stresses caused by the external pressure P.

$$\sigma_{rr} = -Q(1 - a^2/r^2)$$
  

$$\sigma_{\theta\theta} = -Q(1 + a^2/r^2) \qquad (A1)$$
  

$$\sigma_{ss} = -Q - \sigma$$

Where Q is the equivalent hydrostatic pressure

$$Q \equiv P(b^2/b^2 - a^2) \tag{A2}$$

(A1) shows that although the stress depends on r in the  $r - \theta$  plane, the mean pressure arising from P is constant at each point in the crystal and equal to the equivalent hydrostatic pressure Q:  $\langle P \rangle = (-\sigma_{rr} - \sigma_{\theta\theta} - \sigma_{zz})/3 = Q$ .

Transforming (A1) for a specimen cored  $\perp C$ to rectangular axes in which  $X_z$  lies along the core axis and assuming hexagonal or trigonal symmetry  $(M_1 = M_z)$  so that (4a)  $T_{a-\beta} \simeq$  $T_o - M_1(\sigma_{11} + \sigma_{22}) - M_z\sigma_{33}$ , we find (Figure 10a) that the transition temperature that results from the external pressure alone varies with r and  $\theta$  and is given by

 $T_{\alpha - \beta}(r, \theta)$   $\simeq \langle T_P \rangle + Q(M_1 - M_3)(a^2/r^2) \cos 2\theta$  (A3) where

$$\langle T_P \rangle - T_0 = Q(2M_1 - M_3)$$
 (A4)

is the mean increase of transition temperature above the value at zero P and  $\sigma$  ( $T_{\circ} \simeq 574^{\circ}$ C).

A hollow specimen with axis ||C, however, would have a constant transition temperature  $T_{\alpha-\beta} = \langle T_P \rangle$ , given by (A4), because the component of  $M_{\mathbb{R}^1}$  along any direction in the  $r - \theta$  plane is constant  $(M_1 = M_2)$ .

Integration of (A3) over the specimen (Figure 10*a*) shows that the proportion of the specimen that is significantly affected depends on the size of the hole as well as on the external pressure. The results are expressed in Figure 10b, which shows that for most of the hollow specimens (in which  $a \simeq 0.175$  cm and  $b \simeq 1.0$ cm and  $P \simeq 3$  kb)  $|T_{a-\beta} - \langle T_P \rangle| < 3.3$  °C for 50% of the volume. For the sample of run 610 (Table 2,  $a \simeq 0.4$  cm,  $b \simeq 1.0$  cm, P = 5 kb) the effect is larger: within the least affected half of the sample  $T_{a-\beta}$  varies by 12.8°C about the mean  $\langle T_P \rangle$ .

As discussed in the text, the absence of this predicted smearing of the transition temperature is the basis for our believing that stress inhomogeneities that average to zero over the cross section of the specimen are effectively removed as the transition is approached by a 'focusing' mechanism arising from the large increase in the compliance of quartz.

#### APPENDIX B

Slope of phase boundary for  $\lambda$  transitions under conditions of nonhydrostatic stress. We

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

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

where the subscript  $\sigma$  means all components of stress are held constant, the subscript  $\sigma \neq \sigma_{ij}$ means all stress components except the one particular  $\sigma_{ij}$  are held constant, and the summation convention is used, so the last term stands for nine terms. The transition temperature  $T_{\lambda}$  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  $d\sigma_{ki}$ , 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



Fig. 10b. Amount of sample in volume per cent in which the transition temperature  $T_{a-\beta}$  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  $(M_1 - M_3) = 5.6^{\circ}$ C/kb.

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

$$M_{kl} \equiv -\left(\frac{\partial T}{\partial \sigma_{kl}}\right)_{\sigma \neq \sigma_{kl,l}} \equiv -\left(\frac{\partial T_{\lambda}}{\partial \sigma_{kl}}\right)_{\sigma \neq \sigma_{kl}}$$
$$C_{\sigma} \equiv T\left(\frac{\partial S}{\partial T}\right)_{\sigma} \text{ and } \alpha_{kl} \equiv \left(\frac{\partial \epsilon_{kl}}{\partial T}\right)_{\sigma}$$

 $-M_{kl}$  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  $C_{\sigma}$ ,  $\alpha_{kl}$ , 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  $\epsilon_{ij}$  in the  $\sigma_{ki} - T$  plane parallel to the transition boundary (t = constant), we find the other generalized Pippard relations

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

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

is the isothermal compliance tensor.

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

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

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

$$\beta^{T} = (\partial T/\partial P)_{\iota} \alpha - (1/V)(\partial V/\partial P)_{\iota}$$
(B5)

In these equations  $\alpha$  is the volumetric coefficient of thermal expansion and  $\beta^{T}$  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  $\alpha_{kl}$  that are nonzero become infinite at the boundary (because  $C_{\sigma}$  becomes infinite for a  $\lambda$  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  $\alpha_{ij}$  and  $M_{kl}$  are nonzero. For these cases in which  $\alpha_{kl}$  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  $C_{\sigma}/T$  or  $s_{ijkl}^{T}$  versus  $\alpha_{ij}$ . We symbolize these asymptotic relations by the following notation:

 $V\alpha_{kl} \to M_{kl}(C_{\sigma}/T)$  as  $T \to T_{\lambda}$  (B6)

$$s_{ijkl} \xrightarrow{T} \to M_{kl} \alpha_{ij}$$
 as  $T \to T_{\lambda}$  (B7)

Another important relation that follows immediately from (B2) is

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

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

$$W\alpha_1 \to M_1(C_\sigma/T)$$
 (B9)

$$V\alpha_3 \to M_3(C_\sigma/T) \qquad T \to T$$

and (B7) yields

 $s_{1111}^{T} \equiv s_{11}^{T} \rightarrow M_{1}\alpha_{1}$   $s_{1122}^{T} \equiv s_{12}^{T} \rightarrow M_{1}\alpha_{1}$   $s_{1133}^{T} \equiv s_{13}^{T} \rightarrow M_{3}\alpha_{1} \qquad (B10)$   $s_{3333}^{T} \equiv s_{33}^{T} \rightarrow M_{3}\alpha_{3}$   $s_{3311}^{T} \equiv s_{13}^{T} \rightarrow M_{4}\alpha_{3} \qquad \text{as} \quad T \rightarrow T_{\lambda}$ 

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

$$\alpha_1 \to (M_1/M_3)\alpha_3$$
 as  $T \to T_\lambda$  (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  $s_{222}^{T} \equiv s_{44}^{T}$ . The fact that  $M_{23} = 0$  means that the phase boundary is parallel to the  $\sigma_{23}$ 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  $\lambda$  transition in trigonal crystals.

Although it is quite uncertain whether the  $\alpha$ - $\beta$  transition in quartz rigorously satisfies the definition of a  $\lambda$  transition, there is no doubt that the behavior generally resembles a  $\lambda$  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  $\alpha$ -quartz side (of course,  $s_{14} \equiv 0$  for  $\beta$  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  $\lambda$  transition that involves inversion from trigonal (class 32) to hexagonal (class 62) symmetry:

	1	1	$M_{3}/M_{1}$	0	0	0	
	1	1	$M_{3}/M_{1}$	0	0	0	
$8 \cdots^T \rightarrow 8 \cdots^T$	$M_{3}/M_{1}$	$M_3/M_1$	$(M_3/M_1)^2$	0	0	0	(B115)
off , off	0	0	0	0	0	0	as $T \to T_{\lambda}$
	0	0	0	0	0	0	
A. S. Sala	0	0	0	0	0	0	

(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

#### THE $\alpha$ - $\beta$ INVERSION IN QUARTZ

usual compliance matrix for crystals of either symmetry class 32 or 62.

#### APPENDIX C

Slope of phase boundary for coherent firstorder transitions (assuming infinitesimal transformation strains) under conditions of nonhydrostatic stress. Let us assume that the solid-solid transition is characterized by a small reversible transformation strain  $\Delta \epsilon_{ij}$ , so that infinitesimal strain theory may be used. In this case the volume V never differs much from the volume  $V_0$  in the reference state of stress and strain, so that the elastic work done by the applied stresses when the body undergoes a small virtual deformation  $d\epsilon_{ij}$  is [Nye, 1957]

$$dW = V_0 \sigma_{ij} d\epsilon_{ij} \tag{C1}$$

where summation over repeated indices is understood.

We now define a thermodynamic potential function, which we shall prove has useful extremum properties at equilibrium under conditions of constant temperature and stress

$$G = U - TS - V_0 \sigma_{ij} \epsilon_{ij} + V_0 \langle P \rangle \qquad (C2)$$

where the mean pressure  $\langle P \rangle \equiv (-\sigma_{11} - \sigma_{22} - \sigma_{33})/3$ . There are, in fact, many such functions that would serve our purpose, but (C2) has the virtue of reducing in the case of hydrostatic pressure to the conventional Gibbs free energy G = U - TS + PV.

The first and second laws of thermodynamics and (C1) can be combined to yield

$$dU \le T \ dS + V_0 \sigma_{ij} \ d\epsilon_{ij} \tag{C3}$$

for any small spontaneous change in the entropy and state of strain of the elastic body, where the equality holds only when the body is in equilibrium. Differentiating (C2) and substituting (C3), we see

$$dG \leq -S \ dT - V_0 \epsilon_{ij} \ d\sigma_{ij} + V_0 \ d\langle P \rangle \quad (C4)$$

where the equality again implies equilibrium. Thus, at constant temperature and stress, G is a minimum at equilibrium, because any spontaneous change from a nonequilibrium state entails a decrease in G. Similarly, the chain of reasoning can be reversed to show that the first and second laws also imply the converse: whenever G is a minimum at constant temperature and stress, the body is in elastic and thermal equilibrium.

Consider now a situation where  $n^{\alpha}$  moles of the  $\alpha$  phase are in equilibrium with  $n^{\beta}$  moles of the  $\beta$  phase. This can occur only if G of the composite system is unchanged by a transformation of an infinitesimal number of moles of material  $dn^{\beta}$  from the  $\alpha$  to the  $\beta$  phase. That is,  $dG = g^{\alpha} dn^{\alpha} + g^{\beta} dn^{\beta} = (g^{\beta} - g^{\alpha}) dn^{\beta} = 0$ , which requires that G per mole of  $\alpha$  and  $\beta$  be equal:  $g^{\alpha} = g^{\beta}$ . At a nearby point on the boundary at equilibrium  $g^{\alpha} + dg^{\alpha} = g^{\beta} + dg^{\beta}$ , which requires that  $dg^{\alpha} = dg^{\beta}$ . Differentiation of (C2) yields

$$dg^{\alpha} = -s^{\alpha} dT - v_{0}\epsilon_{ij}^{\alpha} d\sigma_{ij} + v_{0} d\langle P \rangle$$
  
=  $-s^{\beta} dT - v_{0}\epsilon_{ij}^{\beta} d\sigma_{ij} + v_{0} d\langle P \rangle = dg^{\beta}$   
(C5)

where  $s^{\alpha}$  and  $s^{\beta}$  are the entropies per mole of the  $\alpha$  and  $\beta$  phases,  $v_0$  is the volume per mole in some convenient reference state (say in the  $\alpha$  phase),  $\epsilon_{ij}{}^{\alpha}$  is the strain in going from the reference state to the phase boundary, and  $\epsilon_{ij}{}^{\beta}$ is greater than  $\epsilon_{ij}{}^{\alpha}$  by the strain  $\Delta \epsilon_{ij}$  associated with the transition. Holding all components of the stress constant except  $\sigma_{k1}$  and eliminating the common term  $v_0 d\langle P \rangle$  from both sides of (C5), we obtain the slope of the phase boundary in the  $\sigma_{k1} - T$  plane

$$M_{kl} \equiv -(\partial T_{\alpha-\beta}/\partial \sigma_{kl})_{\sigma\neq\sigma_{kl}}$$

$$= v_0 \Delta \epsilon_{kl} / \Delta s$$
 (C6)

Thus, the increase of transition temperature with stress varies for the different components of stress proportionally to the corresponding component of the transformation strain.

Note that (C6) reduces to the standard Clapeyron equation 10 in the case of hydrostatic pressure (set k = l and sum, with  $d\sigma_{11} = d\sigma_{22} = d\sigma_{33} = -dP$ ). It is also closely analogous to the asymptotic relations derived for  $\lambda$  transitions. If the changes  $\Delta s$  and  $\Delta \epsilon_{kl}$ are assumed to occur continuously in a very small interval of temperature or stress around the transition boundary, we see that an expression like (7) or (8) can be obtained by dividing both numerator and denominator of (C6) by either  $\Delta T$  or  $\Delta \sigma_{ij}$ , respectively.

Since deriving equation C6 we have found it stated without proof and applied to the transi-

tion in the indium-thallium alloy system by Burkart and Read [1953], as well as a onedimensional form of it used by Flory [1956] to deal with a reversible transition in protein fibers. A brief derivation is given by Forsbergh [1956, p. 357] with reference to the dependence of the Curie point on stress in ferroelectrics, which is valid, even though his statement that the generalization of the Gibbs free energy that he uses reduces to the standard one for hydrostatic pressure is incorrect (p. 346).

This treatment of coherent first-order transitions can be compared with other theories of nonhydrostatically stressed solids that have some features in common. Verhoogen [1951] presented a theory in which the chemical potential (G per mole) is uniform within a homogeneously stressed solid and the orientation of the phase boundary plays no role in thermodynamic equilibrium. These are two of the distinguishing characteristics of the above development, but his conclusion that it is sufficient to a first approximation to replace P in the hydrostatic equations by  $\langle P \rangle \equiv (-\sigma_{11} - \sigma_{22})$  $-\sigma_{33}$  /3 in order to deal with a general stress is in agreement with our equations C5 and C6 only in the special case in which the transformation strain is isotropic (no shape change:  $\Delta \epsilon_{kl} = \Delta v/3v_0$  for  $k = l, \Delta \epsilon_{lk} = 0$  for  $k \neq l$ .

*McLellan* [1968] distinguished coherent and incoherent interfaces in his general treatment of phase equilibriums, but he also appears to have limited his consideration to isotropic transformation strains. Thus our expression for equilibrium between coherent  $\alpha$  and  $\beta$  single component phases related by an infinitesimal transformation strain  $\Delta \epsilon_{kl}$ ,  $g^a = g^{\beta}$  can be rewritten

$$u^{\alpha} - Ts^{\alpha} + \langle P \rangle v_{0}^{\alpha}$$

$$= u^{\beta} - Ts^{\beta} + \langle P \rangle v_{0}^{\alpha} - v_{0}^{\alpha} \sigma_{ij} \Delta \epsilon_{ij}$$

$$= u^{\beta} - T_{s}^{\beta} + \langle P \rangle v_{0}^{\beta} - v_{0}^{\alpha} \sigma_{ij}$$

$$\cdot [\Delta \epsilon_{ij} - \delta_{ij} (\Delta \epsilon_{11} + \Delta \epsilon_{22} + \Delta \epsilon_{33})/3]$$
(C7)

where the reference state of stress and strain is taken to be in the  $\alpha$  phase right at the transition and  $\delta_{ij}$  is 1 for i = j and 0 for  $i \neq j$ , whereas *McLellan* [1968, his equation 40b] requires

$$u^{\alpha} - T_s^{\alpha} + \langle P \rangle v^{\alpha}$$

$$= u^{\beta} - Ts^{\beta} + \langle P \rangle v^{\beta} \qquad (C8)$$

In general, these two formulations of equilibrium are contradictory, but (C7) becomes identical to (C8) when  $\Delta \epsilon_{ij}$  is isotropic.

Kumazawa [1963] recognized the importance of shape as a thermodynamic parameter, and his discussion of the effect of stress on twinning in calcite (p. 185) is similar to our procedure. However, he does not consider coherent polymorphic transitions in which a discontinuity in entropy occurs (latent heat) and thus does not derive nor use the nonhydrostatic analogy of the Clapeyron relation (C6).

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#### 4948

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