

The α - β Inversion in Quartz: A Coherent Phase Transition under Nonhydrostatic Stress

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FEB 11 1970

Experiments on oriented cores from a single crystal of quartz show that the temperature of the α - β transition is raised $10.6 \pm 0.4^\circ\text{C/kb}$ and $5.0 \pm 0.4^\circ\text{C/kb}$ 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 σ between 0 and 10 kb: $|(d^2T_{\alpha-\beta}/d\sigma^2)| < 0.05^\circ\text{C/kb}^2$. The increase of transition temperature with hydrostatic pressure of $25.8 \pm 0.3^\circ\text{C/kb}$ 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 α - β inversion is either a λ 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 self-diffusion 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. *MacDonald* [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 first-order transitions. He pointed out, however, that, when ΔS and ΔV of a first-order transition are very small, the terms involving elastic anisotropy become significant, and he therefore predicted that the α - β 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 self-diffusion 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], *MacDonald* [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 α - β 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 α - β 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 α - β 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 λ 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 T and 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 λ 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 α to the β 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 λ transition is that the strain ϵ_{ki} is assumed to undergo a first-order change, i.e., there is a nonzero $\Delta\epsilon_{ki}$ at the transition.

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