

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 λ transitions. Thus, the fact that our experimental results fit the first-order formula as well as the λ -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 mech-

anism 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 α - β transition, then describe the experimental procedure, present the data, and discuss the results with 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 α - β QUARTZ TRANSITION

When low or α quartz (trigonal class 32) is heated at atmospheric pressure, it transforms to high or β 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 α 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 V and entropy S . Because the expansion is isotropic in the plane perpendicular to the C axis (from symmetry [*Nye*, 1957, p. 23]), the change of V with temperature T can be inferred from the relative changes in length par-

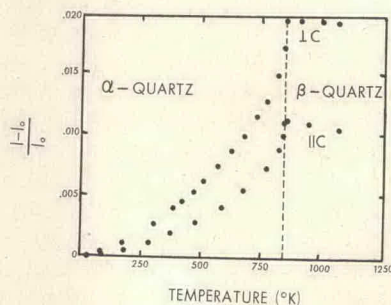


Fig. 1. Relative elongations of quartz parallel ($\parallel C$) and perpendicular ($\perp C$) to the C axis as a function of absolute temperature [after *Mayer*, 1960].

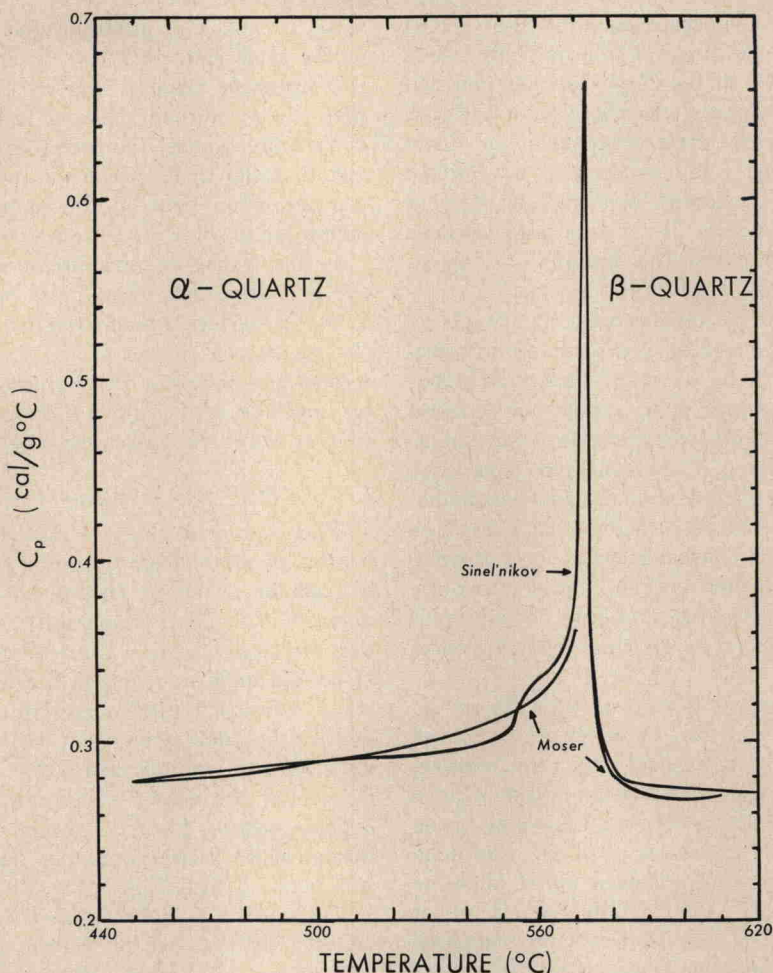


Fig. 2. Specific heat of quartz according to Moser [1936] and Sinelnikov [1953].

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 measure-