PHYSICAL PROPERTIES OF QUARTZ AT AND NEAR THE TRANSITION*

by

R. A. YOUNG

Georgia Institute of Technology, Atlanta, Georgia

EXTENDED ABSTRACT

THE α–β transition at 573°C has been shown to be first order by a detailed single crystal X-ray study of atomic positions and thermal vibrations throughout the temperature range 450°C—650°C. As the transition temperature is reached, the thermal vibrations of the oxygen atom carry it physically past a point of unstable equilibrium and the α–β transition results.

In this X-ray study the coordinate parameters and thermal ellipsoids were determined as a function of temperature by least squares refinements at eight temperatures from 450°C to 650°C. R-factors are generally less than 4 per cent. Specially collected data allowed a particularly good determination of the 600°C β-structure to be made ($x = 0.4137 \pm 0.0015$). The choice of a single over a double minimum model for the configurational potential energy in the β-phase was based on continuous intensity versus temperature data for selected reflections; an unambiguous choice was possible on the basis of qualitative aspects, alone, of certain reflections.

The transition proper is generally preceded by a special type of secondary transition consisting of the development of extensive small-scale Dauphiné twinning. This twinning, and the strain associated with it, are probably responsible for the fuzzing of optical signals and occasional literature suggestions of an intermediate phase. Both extent and temperature range of the micro-twinned condition vary among specimens over wide ranges including zero, but are reproducible in any one specimen.

In the neighborhood of the transition, many physical properties and their temperature dependences are mechanistically understandable at an atomic level through correlation with the present results. For example, the small size of the latent heat, ~ 0.08 kcal/mol, is a consequence of the fact that the principal atomic-scale change at the transition is an approximately 50 per cent increase of the thermal vibrational amplitude of the oxygen atom in one direction only. Previous uncertainties about the existence of a latent heat in good calorimetric experiments are probably due to the combination of the small size and the fact that, because of real differences among specimens, varying amounts of Dauphiné twin-associated strain energy were available to reduce the required external heat input at the transition proper.

Increasingly marked temperature dependence of various physical properties (e.g. specific heat, thermal expansion, elastic constants, infrared spectral details, etc.) as the transition is approached from below, can be at least qualitatively accounted for on the basis of increased anharmonicity in the atomic thermal vibrations and changes of atomic equilibrium positions. The accounting is potentially quantitative in all cases. For example, the piezo-electric constant for shear is quantitatively shown to depend linearly on the displacement of the atoms from their ultimate higher symmetry position in the β-phase.

* Supported in part by the Air Force Office of Scientific Research.