

“ordered” and “partly ordered” samples. Peacor’s X-ray diffraction data<sup>10</sup> on single-crystal cristobalite, indicating a volume discontinuity of  $\approx 1.3 \text{ cm}^3 \text{ mol}^{-1}$  at  $220^\circ\text{C}$ , also do not agree well with the other data.<sup>1,8,9</sup> The sources of these discrepancies are not known but presumably can be attributed to differences among samples.

At a given pressure, the volume increase for the low $\rightarrow$ high transition is numerically less than the volume decrease for the high $\rightarrow$ low transition. This result is derived from combining the data<sup>8,9</sup> showing greater thermal expansion for low cristobalite than for high cristobalite with the experimental observation that the low $\rightarrow$ high transition occurred at higher temperature than the high $\rightarrow$ low.

Krisement *et al.*<sup>11</sup> obtained, by microcalorimetry, the most extensive data for heats of transition. For samples exhibiting transition temperatures of  $244^\circ$  to  $270^\circ\text{C}$  (low $\rightarrow$ high) and  $215^\circ$  to  $235^\circ\text{C}$  (high $\rightarrow$ low), Krisement *et al.*<sup>11</sup> found the heats of transition greater for the high $\rightarrow$ low transition than for the low $\rightarrow$ high. There appears to be no systematic variation of heat of transition with transition temperature but the heat (high $\rightarrow$ low)  $\leq 0.30 \text{ kcal mol}^{-1}$  and the heat (low $\rightarrow$ high)  $\geq 0.25 \text{ kcal mol}^{-1}$ . Krisement *et al.*<sup>11</sup> suggest that the specific heat of high cristobalite is greater than that of low cristobalite over the temperature range of transformation.

The Clausius-Clapeyron equation,

$$dT/dp = \Delta V/\Delta S \quad (1)$$

correlates the several independently determined quantities. For the low $\rightarrow$ high transition,  $dT/dp$  (Fig. 1)  $\approx 51.1 \text{ deg kbar}^{-1}$ , with an extrapolated 1-bar intercept of  $\approx 232^\circ\text{C}$ ; for the 1-bar volume decrease at that temperature, Ref. 8 data yield  $\Delta V \approx 0.95 \text{ cm}^3 \text{ mol}^{-1}$  and Ref. 9  $\approx 1.09 \text{ cm}^3 \text{ mol}^{-1}$  (with uncertainties  $\approx \pm 0.03 \text{ cm}^3 \text{ mol}^{-1}$ ). Peacor’s data<sup>10</sup> indicate a volume discontinuity of  $\approx 1.3 \text{ cm}^3 \text{ mol}^{-1}$  at  $220^\circ\text{C}$ . From Eq. (1),  $\Delta S \approx 0.44 \text{ cal deg}^{-1} \text{ mol}^{-1}$  (from Ref. 8 data) or  $0.51$  (from Ref. 9 data). Data from Ref. 11 suggest  $\Delta S \leq 0.55$  to  $0.58 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . For the high $\rightarrow$ low transition,  $dT/dp$  (Fig. 1)  $\approx 53.6 \text{ deg kbar}^{-1}$ , with an extrapolated 1-bar intercept of  $\approx 209^\circ\text{C}$ ; for the 1-bar volume increase at that temperature, Ref. 8 data suggest  $\approx 0.99 \text{ cm}^3 \text{ mol}^{-1}$  and Ref. 9,  $\approx 1.13$  (both  $\approx \pm 0.03 \text{ cm}^3 \text{ mol}^{-1}$ ). From Eq. (1),  $\Delta S \approx 0.44 \text{ cal deg}^{-1} \text{ mol}^{-1}$  (Ref. 8) or  $0.50$  (from Ref. 9). Ref. 11 data suggest  $\Delta S \geq 0.49$  to  $0.51 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . The consistency of these data is fairly good, with those of Ref. 11 and Ref. 9 resulting in the greatest consonancy. The conclusion most clearly demonstrated here is that the somewhat steeper initial slope of the high $\rightarrow$ low transition (as compared to the low $\rightarrow$ high) can be quantitatively correlated with the greatly different thermal expansion coefficients of low and high cristobalite and the appreciable hysteresis in the transition.

It is expected that, at pressures higher than obtained here, the trajectories of the low $\rightarrow$ high and high $\rightarrow$ low transitions will be essentially parallel, i.e. with constant hysteresis. Within the precision of the present data (Fig. 1), no curvature is apparent in either phase boundary beyond the low-pressure region, and there is no prediction as to where the trajectories become essentially parallel. Linear extrapolations of the present data suggest an intersection at  $\approx 9 \text{ kbar}$ , which is impossible but perhaps indicative of the rapidity with which the trajectories are converging with increasing pressure. It is clearly seen (Fig. 1) that the hysteresis in the inversion, whatever its origin, varies with pressure and cannot be considered as constant.

Ignoring the small differences in various quantities for the inversion on heating and on cooling, the equation

$$\frac{d^2T}{dp^2} = \frac{1}{\Delta S} \left[ \left( \frac{\partial \Delta V}{\partial p} \right)_T + 2 \left( \frac{dT}{dp} \right) \left( \frac{\partial \Delta V}{\partial T} \right)_p - \left( \frac{dT}{dp} \right)^2 \left( \frac{\partial \Delta S}{\partial T} \right)_p \right] \quad (2)$$

may be examined under two assumptions for  $d^2T/dp^2$ . For  $(\partial \Delta V/\partial T)_p \approx -1.6 \times 10^{-3} \text{ cm}^3 \text{ deg}^{-1} \text{ mol}^{-1}$ <sup>8,9</sup> and  $(\partial \Delta S/\partial T)_p \approx (50 \text{ cal mol}^{-1}) (30 \text{ deg})^{-1} (500 \text{ deg})^{-1}$  (from Ref. 11 results) and  $d^2T/dp^2 \approx 0$ ,  $(\partial \Delta V/\partial p)_T \approx 0.55 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$ . If  $|d^2T/dp^2| \leq 0.1 \text{ deg kbar}^{-2}$  (as a possible upper limit obtained from the

present experiments), the above value for  $(\partial \Delta V/\partial p)_T$  is scarcely altered. Therefore, it is concluded that  $(\partial \Delta V/\partial p)_T > 0$ , and this is not usual since, for most transitions, the high-temperature phase is more compressible than the low-temperature phase.

The initial fractional rate of change of transition entropy with pressure may be calculated since

$$\frac{d\Delta S}{dp} = \left( \frac{\partial \Delta S}{\partial p} \right)_T + \frac{dT}{dp} \left( \frac{\partial \Delta S}{\partial T} \right)_p \quad (3)$$

and  $(\partial \Delta S/\partial p)_T = -(\partial \Delta V/\partial T)_p$ . Rearrangement of Eq. (3) and use of values given above suggest that  $(1/\Delta S)(d\Delta S/dp) \approx +0.08 \text{ kbar}^{-1}$ . For the slope to remain nearly constant, as observed, the volume change for the transition must increase accordingly and the greater compressibility of low cristobalite, compared to high cristobalite, contributes to this effect.

The anomalous curvature found at the lowest pressures (Fig. 1) is not understood but is possibly related to the polycrystallinity. Bogardus and Roy<sup>12</sup> reported that grinding increases the high-low inversion temperatures somewhat in both cristobalite and quartz, both showing increases in transition temperature with hydrostatic pressure; on the other hand, they<sup>12</sup> also showed that grinding lowers the transition temperature in  $\text{BaTiO}_3$ , for which  $dT/dp$  is also positive. The role of residual stresses, probably of importance in these refractory materials, is yet to be clarified for these transitions.

From the decrease in transition temperature in cristobalite and quartz under neutron bombardment, Roy and Buhsmer<sup>13</sup> suggested the effect of the neutrons was akin to that of negative hydrostatic pressure. The more extensive investigation by Schenk<sup>14</sup> on the effects of neutron irradiation on the high-low cristobalite inversion does not corroborate the Roy and Buhsmer data,<sup>13</sup> which nevertheless may be looked at anew. Plotting high-low quartz inversion temperatures vs high-low cristobalite inversion temperatures for the same neutron dose gives an approximately straight line; thus these data<sup>13</sup> suggest that a given dose of neutrons lowers the cristobalite inversion temperature  $\approx 9 \pm 2$  times as much as the quartz inversion temperature. By comparison, application of hydrostatic pressure raises the cristobalite inversion temperature nearly twice as much as the quartz inversion temperature.<sup>4</sup> Thus the correlation between hydrostatic pressures and neutron bombardment, if any, is difficult to quantify. The absence of any compressibility data for cristobalite continues to hamper such theory.

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