overshoots seem to depend upon the particular geometry used. Gibson (1928, Fig. 3) and also Bates and Phelps (1927–28) report signals of the same sort. The present geometries are not equivalent to the geometries used by Gibson and by Bates and Phelps, and no trends are clear with respect to the details of the signals for the varying geometries. Such signals were not reported for the high pressure studies of the inversion in powdered material by Yoder (1950) or KvGtH (1973) nor in the detailed 1 bar work of Keith and Tuttle (1952). DTA signals in all the geometries used here showed abrupt departures from baseline on heating through the inversion but less abrupt departures on cooling. All data reported here, however, are from thermal analysis and not DTA, since the thermal analysis signal was clear and abrupt (Fig. 1); when analyzed, DTA data agreed closely with thermal analysis data.

In runs 2 and 3, heating and cooling signals were examined at different rates of temperature change. For run 2 at 1 bar, the temperature variation with rate was $\lesssim 0.1_5°$ for rates from ~2-1/2 to 15 deg min^{-1}. For run 3 near 0.23 kbar, variation was $<0.1°$ for rates from ~0.2 to 6 deg min^{-1}. In this run, an attempt was made to obtain semiquantitative data for the effect of rate on magnitude of the anomalies in the temperature *vs* time signals. Straight lines were drawn tangent to the thermal analysis curves from below the inversion to above, and the areas isolated between each curve and the corresponding straight line were estimated by counting squares. No systematic variations could be established over the range of heating/cooling rates used. Hystereses, as defined as the difference between the initiation of the inversion on heating and the initiation of the inversion on cooling, were different (values are given below) for the different runs, but effects of different geometries cannot be isolated. From run 3, the variation in hysteresis with pressure appeared to be $\lesssim 0.1$ deg kbar^{-1}. Likewise the variation of hysteresis with heating/cooling rate at given pressures appeared negligible, within the present precision, and no change was apparent in the nature of the thermal analysis signal at different pressures.

The peculiar thermal analysis signal was well documented in the early work by Bates and Phelps (1927–28) who, in 1 bar work with thin plates, noted a drop of ~0.5° after initiation of the inversion on heating and a rise of ~0.1–0.2° on cooling; Gibson (1928) graphically shows a drop of ~1/2° on heating (at an unspecified pressure) with cylin-

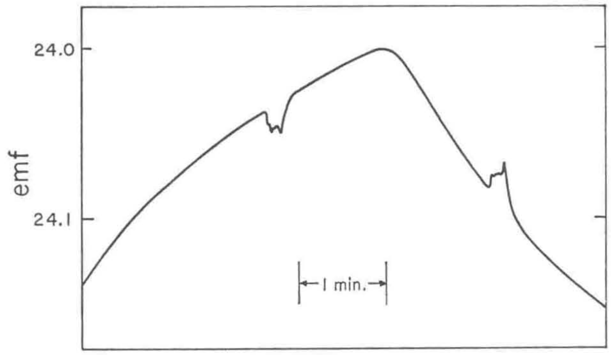

FIG. 1. Recorder trace of typical heating and cooling cycle for high-low quartz inversion, near 0.23 kbar. Ordinate is chromel-alumel thermocouple millivoltage, as referenced to 0°C, and abscissa is time, increasing from left to right. The peculiar nature of the signal for the inversion in the single crystal, on both heating and cooling, is evident. Data from run #3.

drical geometry. The present observations agree with these magnitudes for the effects. Shape of the signal is almost certainly influenced by geometrical factors, anisotropic thermal diffusivities of the two phases, the efficiency of heat transfer between sample and thermocouple, *etc,* with each factor being unknown. Sosman (1965, p. 88 *et seq.*) reviews thermal and other physical property measurements relevant to this phenomenon and also discusses suggested mechanisms, none of which seem to have been convincingly demonstrated.

Hystereses corresponding to the different runs were ~0.7° (run 1), ~0.5° (2), ~1.4 ± 0.2° (3) and (4), with only negligible variation with rate or with pressure being observed here. Larger hystereses have been reported in single-crystal (Bates and Phelps, 1927–28) and powdered crystal (Keith and Tuttle, 1952) experiments, with much slower rates of temperature change (and different geometries). Trends for the variation of hystereses among these reports are not obvious and there is also the problem as to whether the hystereses inferred from thermal analyses are verified by other techniques. Höchli (1970) found evidence from ultrasonic work which suggests coexistence of high and low quartz over ≈1° and hysteresis vanishing for rates of temperature change of less than ≈1 deg hr^{-1}.

Critical Review of Previous Data for the Trajectory of the Inversion

Since high pressure results so far indicate the trajectories of the inversion on heating and on cooling to be nearly parallel in *p-T* space, it would seem that the equilibrium phase boundary lies somewhere within the hysteretic interval and probably parallel to the trajectories obtained for the inversion on heating and on cooling. Correlation of thermodynamic data obtained at 1 bar yields virtually no useful constraint on the slope (dT/dp) or the curvature (d^2T/dp^2) for the first-order components of the transition, which require discontinuous changes in volume and entropy; however, correlation of the rapidly varying thermal expansions, specific heat, and elastic compliances yields not unconvincing bounds on the slope, as compared with the experimental work at high pressures (Cohen and Klement, 1967; Klement and Cohen, 1968).

It is well-established (*e.g.*, Keith and Tuttle, 1952) that the inversion temperatures at 1 bar vary with the samples; therefore, disagreements among 1 bar data, obtained either directly or by extrapolation, are here considered only minor. It is not yet known if the trajectory of the transition is significantly sample-dependent. Indeed it would be gratifying if the slope could be bounded and if the sign of the curvature could be established, but detailed analysis of results must necessarily involve detailed examination of experimental techniques.

Gibson's (1928) pioneering work—using single crystals and chromel-alumel thermocouples (no correction attempted for effect of pressure) in a carbon dioxide apparatus wherein pressures were obtained from a bourdon tube gauge calibrated against dead weights (Smyth and Adams, 1923)—yielded 12 data, at 1 bar, 0.13 kbar, and then up to 2.64 kbar, which were fitted by a least square quadratic with initial slope ≈ 21 deg kbar^{-1} and $d^2T/dp^2 > 0$. Precision in pressure seemed to be $\approx \pm 5$ bars and $\approx \pm 0.1°$ in temperature although deviations from the fitted curve were often nearly 1°.

Yoder's (1950) work with powdered samples and iron-constantan thermocouples was carried out in an argon apparatus, wherein pressures were deduced from the resistance of a manganin wire coil calibrated at the pressures of the CCl_4 transition at 20°C and the freezing point of mercury at 0°C. The latter value is now suggested as 7.5692 $\pm$ 0.0015 kbar (*e.g.*, Dadson and Grieg, 1965) as compared with the value of 7.492 kbar used by Yoder (1950). From 60 data, at 1 bar, ≈ 0.524 kbar and then up to 10 kbar, a quadratic was fitted with initial slope ≈ 28.7 deg kbar^{-1} and $d^2T/dp^2 < 0$. Revision of the pressure calibration may lower the estimated initial slope by perhaps 1–2 percent, but the greatest uncertainty probably remains in the still unknown effect of pressure on emf of the iron-constantan thermocouples. Data of Freud and LaMori (1971), if extrapolated, suggest a considerable effect of pressure on constantan but data for iron are lacking.

Cohen and Klement (1967) investigated the inversion over the range 6–35 kbar in quasi-hydrostatic apparatus, using several types of thermocouples and without any attempt to correct for the effect of pressure on thermocouple emf. They suggested an initial slope of ≈ 26 deg kbar^{-1} and $d^2T/dp^2 < 0$.

Coe and Paterson (1969) carried out experiments above 1 kbar with single crystals using a chromel-alumel thermocouple at 1 bar; data from nonhydrostatic experiments, from which results for hydrostatic conditions were calculated over the range 1–6 kbar, yielded a slope of 25.8 $\pm$ 0.3 deg kbar^{-1} and negligible curvature. Overall accuracy in temperature was estimated as $\pm 2°$ and the pressure (estimated from change in resistance of manganin coil) was considered accurate to ± 1 percent.

KvGtH (1973) used powdered samples with Pt–Pt + 10% Rh thermocouples (uncorrected for pressure effect) in an argon apparatus wherein pressures were measured with a 5 kbar bourdon gauge to 3 kbar and by extrapolation via a manganin coil to 10 kbar, the accuracy being considered to be 1 percent. Precision in temperature was considered to be within $\pm 1°$. Results from the heating and cooling cycles were tabulated separately, but the problem of hysteresis was not discussed. For 24 data on each cycle, at 1 bar, 34-1/2 bars and thence to $\sim$10.1 kbar, their quadratic regression of all the data yielded an initial slope of 25.1 deg kbar^{-1} and $d^2T/dp^2 > 0$ with a standard error of 1.34°. However, KvGtH (1973) chose to fit their data by two quadratics: from 0.001 to 1.065 kbar, the initial slope is 15.5 deg kbar^{-1}, $d^2T/dp^2 > 0$, and standard error 0.11°; from 0.88 to 10.2 kbar, the initial slope is 26.5 deg kbar^{-1}, $d^2T/dp^2 < 0$, and standard error 0.7°. Thus a "hitch", with lack of continuity in slope and curvature, is claimed for the trajectory $\lesssim$1 kbar.

Present Data for the Inversion Trajectory; Discussion and Conclusions

In the present experiments, at least two heating and cooling cycles were made in the vicinity of a given pressure so that the actual data points are clustered within the given pressure ranges. Data were subjected to regression analysis to obtain initial slopes (coefficient of p term) and initial curvatures