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# Yet More Observations on the High-Low Quartz Inversion: Thermal Analysis Studies to 7 kbar with Single Crystals

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**Abstract**

The peculiar nature of the thermal analysis signal for the high-low inversion in quartz single crystals is verified. For each sample, no change in the nature of the signal or the temperature difference between heating and cooling signals is observed either by varying pressure (up to 7 kbar) or by changing heating/cooling rate. The initial slope, $dT/dp$, of the trajectory of the inversion is verified to be at least 26 deg kbar$^{-1}$; within the pressure range to 7 kbar, decisive evidence that the curvature, $d^2T/dp^2$, is nonzero is lacking. Precision and accuracy of measurement in these and similar data make detailed comparisons of results difficult.

## Introduction

As the high-low quartz inversion is studied in greater detail, more complexities are encountered. This note reports precise studies on the inversion at high pressures using single crystals and thus is to be compared especially with the very recent work of Koster van Groos and ter Heege (1973) ("KvGtH") to 10 kbar with powdered samples. In the precise work being done with this inversion, the problems of uniformity among samples, thermocouple calibrations at ambient and elevated pressures, *etc,* are conspicuous, and it seems impossible to make detailed comparisons among the different sets of data.

## Experiments

The internally-heated argon gas apparatus described by Goldsmith and Heard (1961) was used with minimal modifications. Pressures were read from 1, 3, or 7 kbar Heise bourdon tube gauges; after these experiments were completed, the 1 and 3 kbar gauges were calibrated to 1 bar within the 2.7 kbar limit of a deadweight tester. Temperatures in the gas apparatus were varied manually, using a ten-turn potentiometer to control a silicon-controlled rectifier. Instead of the thermocouple arrangement shown in Figure 1 of Goldsmith and Heard (1961), three thermocouple leads were introduced through a closure piston which was made from a tungsten carbide cylinder having a 3.2 mm diam. axial hole. A steel end-plug, slightly smaller than the diameter of the carbide piston, was soft-soldered or epoxied to the high pressure end of the piston. The steel plug contained an alumel and two chromel leads which were made to hold gas pressure in the manner of the original design. Steel 0–80 screws in the tapered plugs clamped the respective thermocouple wires to the leads.

Experimental samples were cylinders of clear, single-crystal Brazilian quartz cored parallel to the *c* axis. A slot approximately 0.2 mm wide was cut with a wire saw parallel to the axis of each cylinder and approximately to a depth of the radius; location of the slot was difficult to control and was not always

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on a radius. Sample temperature was measured with a butt-welded 0.127 mm diam. chromel-alumel thermocouple placed in the slot; the junction was located approximately mid-way from the ends of the sample. The cylinder used in run 1 was 2.4 mm diam. and 2.5 mm long; that in run 2 was 1.7 mm diam. and 1.7 mm long; the sample used in runs 3 and 4 was 1.2 mm diam. and 1.2 mm long, with a mass of ~3 mg. The reference junction, a butt-welded 0.32 mm diam. thermocouple, was located within a piece of 4-bore mullite thermocouple tubing of 1.6 mm o.d. and 0.39 mm bore. Mullite thus became the DTA reference material. The measuring junction was pulled tightly against the quartz, and its leads run into the other holes of the mullite tubing. In runs 3 and 4, silver conductive paint was applied to the measuring junction to assure good thermal contact between quartz and thermocouple. The reference junction and quartz cylinder were placed side-by-side and then the cylinder was wired to the mullite tube containing the reference junction. Reference and measuring junctions were therefore less than 2 mm apart. So as to minimize temperature fluctuations caused by convection in the horizontal furnace, the sample assembly was inserted into a 22 mm long, 5 mm i.d. gold tube which, in turn, was surrounded by a stainless steel tube closed at one end and push-fitted at the other. Isothermality was demonstrated by the DTA baseline varying less than $\pm 1/2°$ over the temperature range and also by all the quartz samples remaining intact during the runs; no cracking, often reported for samples in thermal gradients while passing through the inversion, was noted.

Emfs corresponding to temperature were recorded on a 25 cm wide two-pen strip chart recorder at 5 mV full scale for the first two runs, and 1 mV full scale for the second two runs. Emfs corresponding to differential temperature were recorded on full scales corresponding to as little as 0.1 mV. Heath/Schlumberger voltage reference sources provided calibrated voltage suppression for the temperature measuring circuit, and also compensated lead wires and an ice bath reference junction were used throughout. Thermocouple emfs were often read to ~0.001 mV. In order to avoid roundoff and interpolation errors arising from the use of standard thermocouple tables, which are tabulated at 0.10 mV intervals, a set of chromel-alumel thermocouple tables was computer-generated using the interpolation scheme and key values suggested by ASTM (1963). A similar routine was used to convert millivoltage directly to temperature. No attempt was made to correct for the effect of pressure on thermocouple emf because the data of Getting and Kennedy (1970) suggest that any correction within the present range would be less than 1°; this relatively small effect was an important consideration in the choice of chromel-alumel thermocouples here.

Heating and cooling rates were usually in the range of ~4 to 15 deg $min^{-1}$ although some data were taken at other rates. In the heating/cooling cycles through the inversion, the maximum temperatures attained were 10° or less above the inversion temperature.

In run 1, data[2] were taken over the intervals, ~205 → 6955 bars and 6955 → 210 bars. In run 2, data were taken over the successive intervals, 1 → 6235 → 1 bars. A 7 kbar pressure gauge was used for both these runs. In run 3 (using a 3 kbar pressure gauge), data were taken over the successive intervals, 84 → 2711, 229 → 854 and near 2100 bars. In run 4 (using both 1 and 3 kbar gauges simultaneously), data were taken over the range 19-1/2 → 997 and near 508 and then 1 bar. When pressure was decreased rapidly, at least 15 min. were allowed for the Bourdon tubes in the pressure gauges to equilibrate to room temperature. This wait appears to be necessary for precise work, since upon decreasing pressure to ambient pressure, it had been noted that the pressure gauges initially read below zero, presumably because of adiabatic cooling.

In run 2, the 1 bar data after the first pressure cycle were $\lesssim 0.2°$ lower than the initial values. In run 3, the data in the second pressure cycle were $\lesssim 0.1°$ lower below 0.85 kbar and also near 2.1 kbar, where comparison with the data from the first cycle could be made. In run 3, the thermocouple drift was $<0.1°$ near 0.5 kbar. Extensive experiments (Potts and McElroy, 1961; McElroy, 1958) on the drift with time of chromel-alumel thermocouples at 1 bar have shown the behavior to be complex and plausibly of the same order as encountered here.

## Nature and Variations of the Thermal Analysis Signals

A typical temperature *vs* time signal is shown in Figure 1. The details of the signal beyond the initial

[2] To obtain a complete table of runs (37 pages), order NAPS Document 02418 from ASIS, c/o Microfiche Publications, Division of Microfiche Systems Corporation, 305 East 46th Street, New York, N. Y. 10017. Please remit in advance $1.50 for microfiche or $5.00 for photocopies. Please check the most recent issue of this journal for the current address and prices.

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.

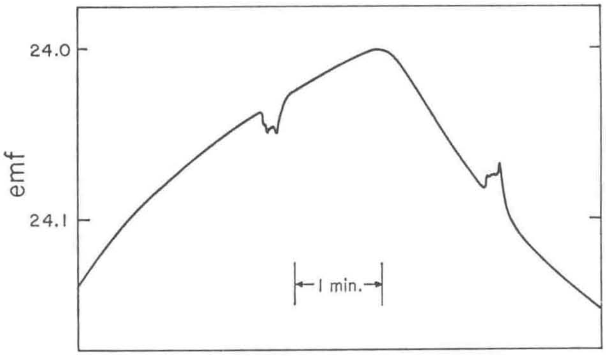


FIG. 1. Recorder trace of typical heating and cooling cycle for high-low quartz inversion, near 0.23 kbar. Ordinate is chromel-alumel thermocouple millivoltage, as referenced to 0°C, and abscissa is time, increasing from left to right. The peculiar nature of the signal for the inversion in the single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

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 cylindrical 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 ($\mathrm{d}T/\mathrm{d}p$) or the curvature ($\mathrm{d}^2T/\mathrm{d}p^2$) 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 $\approx$21 deg kbar$^{-1}$ and $\mathrm{d}^2T/\mathrm{d}p^2 > 0$. Precision in pressure seemed to be $\approx\pm5$ bars and $\approx\pm0.1°$ 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, $\approx$0.524 kbar and then up to 10 kbar, a quadratic was fitted with initial slope $\approx$28.7 deg kbar$^{-1}$ and $\mathrm{d}^2T/\mathrm{d}p^2 < 0$. 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 $\approx$26 deg kbar$^{-1}$ and $\mathrm{d}^2T/\mathrm{d}p^2 < 0$.

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 $\pm2°$ and the pressure (estimated from change in resistance of manganin coil) was considered accurate to $\pm1$ 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 $\pm1°$. 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 $\mathrm{d}^2T/\mathrm{d}p^2 > 0$ 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$^{-1}$, $\mathrm{d}^2T/\mathrm{d}p^2 > 0$, and standard error 0.11°; from 0.88 to 10.2 kbar, the initial slope is 26.5 deg kbar$^{-1}$, $\mathrm{d}^2T/\mathrm{d}p^2 < 0$, 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 (coefficient of $p^2$ term); polynomials of order >2 yielded only negligible improvement in the curve fitting and are thus not necessary. Only when data from run 3 (below) were separated into adjacent ranges and curves fitted to each range were polynomials of order >2 occasionally found to be significant.

Run 1 was primarily exploratory; from 30-some data on heating and cooling cycles respectively, the initial slope was $\sim 26._2$ deg kbar$^{-1}$, with a standard error of $\sim 0.5°$ and the initial curvature was essentially zero ($<0.1$ deg kbar$^{-2}$). Run 2 was meant primarily to investigate the effect of considerably smaller sample size on the peculiar thermal analysis signal and also to collect more closely spaced data; from 60-some data on heating and cooling cycles respectively, the initial slope was $\sim 26._8$ deg kbar$^{-1}$, with a standard error of $\sim 0.5°$ and initial curvature $(d^2T/dp^2) \sim -0.2$ deg kbar$^{-2}$. For run 3, thermal contact between thermocouple and sample was enhanced by use of the silver conductive paint. Yet more data, more closely spaced, were obtained, particularly at the lower pressures. From 70-some data on heating and cooling cycles respectively, the initial slope was $\sim 26._0$ deg kbar$^{-1}$, with a standard error $\sim 0.12°$ and negligible curvature. Systematic deviations from this fit were noted below $\sim 0.3$ kbar, and regression analyses showed that somewhat better fits could be obtained if the data below 0.8, 0.6, or 0.4 kbar were fitted by one curve and those above by another. The curves for the higher pressure data essentially coincided with the curve obtained for all the data, whereas the curves for the lower pressure data suggested higher initial slopes and greater curvatures ($d^2T/dp^2 < 0$). Run 3 can also be considered as a search for the existence of a "hitch" in the inversion such as KvGtH (1973) interpreted from their data. It is not clear whether fitting curves to piecewise sections of data, or even to overlapping sections, is a method for discovering "hitches."

Because data at the lower pressures are perforce more important for comparison with the various thermodynamic data at 1 bar, run 4 was intended to improve the statistical reliability of the results at the lower pressures and to try to pin down existence and characteristics of a "hitch," if any, in the trajectory of the inversion below 1 kbar. The initial slope thus obtained from 50-some data on heating and cooling respectively were $28._6$ deg kbar$^{-1}$ with a standard error of 0.08°, and the curvature $(d^2T/dp^2) \sim -4$ deg kbar$^{-2}$.

Thus the results from run 4, the most intensive investigation thus far of the range below 1 kbar, suggest greater initial slope and curvature than indicated hitherto by the data at higher pressures. It is hoped that the very recent recalibration of the 1 and 3 kbar pressure gauges is sufficient precaution to insure confidence in the pressures given here. Thermocouple calibrations are, of course, another problem. It is believed that the calibrations most relevant to the present experiments should be made *in situ; in situ* calibrations at 1 bar have been made with the Curie point of iron (Cohen and Klement, 1973) and with the solid-liquid transition of lead (Cohen and Klement, 1974) but do not seem to be accurate enough for the present experiments. Nothing in the present experiments suggests drastic variations for the chromel-alumel thermocouples, beyond the instabilities already recognized (Potts and McElroy, 1961) for these materials. Although the effect of pressure on emf of chromel-alumel thermocouples is considered to be considerably smaller than for Pt–Pt + 10% Rh thermocouples over the present *p-T* range (Getting and Kennedy, 1970), it is worthwhile to examine what seems to be the variation within the range of the present experiments. According to Getting and Kennedy (1970), the maximum correction voltage may be of the order of 20 $\mu$V (observed temperatures $\sim 1/2°$ higher than actual), increasing from zero at 1 bar and then decreasing to zero again and changing arithmetical sign at higher pressures; more details for the variation are not known (see also Freud and LaMori, 1971). Unfortunately, a correction of $\sim 1/2°$ at, say, 0.5 kbar yields an apparent initial slope $\sim 1$ deg kbar$^{-1}$ higher than actual, which is the suggested sign of direction of the variation of the present data at the lowest pressures as compared to the data for all pressures.

If one applies approximate corrections (Getting and Kennedy, 1970) for the effects of pressure on the emf of Pt–Pt + 10% Rh thermocouples to the KvGtH (1973) data, it becomes moot as to whether there is nonzero curvature; likewise the slope above 1 kbar becomes $\gtrsim 26$ deg kbar$^{-1}$. Whether there is actually a hitch in the trajectory of the transition for their samples depends upon the requisite knowledge of pressure and of temperature and the manner in which the data are reduced and interpreted. The KvGtH (1973) report of an initial slope as low as $\sim 15$ deg kbar$^{-1}$ is not corroborated in the present work, or elsewhere.

Until more convincing experiments can be carried out, it is suggested that (1) there is no evidence yet for the initial slope of the high-low quartz inversion being sample-dependent; (2) the initial slope is $\gtrsim 26$ deg kbar$^{-1}$, with $\sim 28$ deg kbar$^{-1}$ being a suggested upper limit; (3) considering uncertainties in the pressure effects on thermocouples, there is no evidence yet that the curvature is nonzero within the 7 kbar range of the present experiments.

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