The powder was then loaded under argon in a glove box, with P_2O_5 present, to ~5-mm lengths in 1.59 mm OD platinum tubes of 0.13 mm wall thickness, which were then crimped before being brought into air for the sealing in an oxyacetylene flame. Typically, the capsule held ~7 mg of $CaCO_3$. Two runs were made. In the first run, the measuring thermocouple of 0.13 mm diam chromel and alumel wires was lashed against the sample capsule with 0.13 mm diam chromel wire. In order to ensure good thermal contact, the sample capsule for the second run was compressed under argon to ~0.5 kbar at room temperature, and 0.32 mm diam platinum wire was used to lash the thermocouple, made of 0.25 mm diam chromel and alumel wire, to the capsule. The reference junction was within less than 2 mm of the measuring junction. The arrangement of sample capsule, thermocouples, and the hydrostatic pressure apparatus using argon have been described elsewhere.

In the DTA runs, temperature was mostly varied at ~0.5°C/sec and the maximum temperature difference between measuring and reference thermocouples was usually less than 2°C (especially in the second run). Sensitivities in recording temperature and differential temperature were 0.2 mV/cm and as much as 4 μV /cm, respectively, on the two-pen recorder. The temperatures corresponding to the peak or the abrupt change in direction of motion of the differential signal were observed on heating and cooling and these always agreed to within 1°C, usually to within 0.5°C. Two or more cycles were usually made at each pressure and data were obtained on both increasing and decreasing pressure. Pressures were read to ±5 bar on a Heise bourdon pressure gauge.

Near 0.69 kbar, the discernability of the signals was examined at different heating and cooling rates. The signals could be identified unambiguously at ~0.3°C/ sec, but at ~0.1°C/sec were more or less lost in the background. No variation in transition temperature with rate could be observed.

An in situ calibration of the thermocouple used in the second run was made using the melting point of silver as a standard. Silver 99.99+% pure from American Smelting and Refining Company was sealed in a pyrex capillary of 1.63 mm diam and 0.2 mm wall thickness which was then lashed to the measuring thermocouple as before. With heating rates of 0.1–0.3°C/sec and temperature differences between measuring and reference thermocouples of less than 1°C, the signal for the onset of melting was less distinct than that which indicated the end of the melting. The latter corresponded to 959.5° ± 0.25°C, which was compared with the accepted value (Rossini 1970) of 961.9° ± 0.2°C. Hence, all temperatures presented here have been corrected upward by this amount, which is approximately corroborated by the manufacturer's calibration corrections for the reels of thermocouple wire used here.

The data from the two runs, plotted in figure 1, appear to be consistent among themselves, and with a linear fit, to within 2°C. The extrapolated transition temperature at 1 bar is near 985°C. The data may be fitted by straight lines of slopes 3.0 ± 0.3°C/kbar and no curvature seems to be indicated, within the experimental precision.
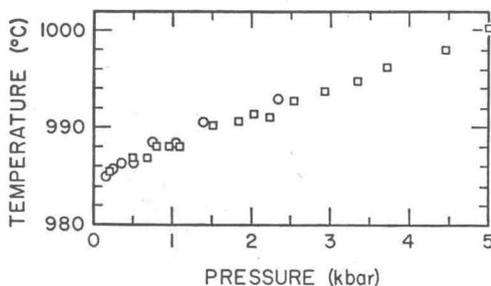

Fig. 1.—Temperatures for the transition in calcite at various pressures: *circles* denote data from the first run, *squares* those from the second run.

DISCUSSION

It is exceedingly probable that the transition investigated here is identical to the one discovered by Boeke (1912) and confirmed by Eitel (1922); no significance is attached to the slight difference in reported transition temperatures at the lower pressures.

It seems possible that Smyth and Adams (1923) did not observe the transition because their heating and cooling rates of $\sim 0.1°C/sec$ (as read from their fig. 4) were too slow and hence the signals for this subtle transition were smeared out and lost in the background. In discovering the transition, Boeke (1912) used heating and cooling rates of $\sim 1°C/sec$ (as read from his fig. 7). Because of the difficulty in using piston-cylinder apparatus below a few kilobars, Goldsmith and Newton (1969) probably spent most of their fruitless search near the kink in the calcite-argonite boundary, where no confirmation of a transition in calcite has yet been made.

It is not clear if the calcite transition is first-order, and it seems likely that any possible volume discontinuity be quite small since single crystals can be cycled through the transition and recovered intact (e.g., Smyth and Adams 1923). The strongest evidence for the structure of the high-temperature polymorph probably comes from the high-temperature X-ray diffraction work of Chang (1965) on $CaCO_3$-$SrCO_3$ and $CaCO_3$-$BaCO_3$ alloys. Chang (1965) extrapolated his alloy data to pure

$CaCO_3$, inferring a transition temperature of $\sim 955°C$, but the extrapolations may readily be made so as to be consistent with the present value of $985°C$. The X-ray data for the alloys (Chang 1965) are consistent with a model of disordered anions for the high-temperature polymorph. If all the entropy of disordering the anions were to appear discontinuously at the transition temperature, the associated volume change would be $(dT/dp) \cdot R\ln2 \sim 0.17$ cm^3/mole, which would be $\sim 0.5\%$ if the molar volume near the transition temperature is estimated by extrapolation of the data of Rosenholtz and Smith (1949).

That the high-temperature transition temperature might increase with pressure was apparently first "tentatively indicated" by Rapoport (1966) in his discussion of the many, confusing high-pressure results for $CaCO_3$. The present determination of the trajectory of the high-temperature transition in calcite does not suggest any ready resolution of the morass of conflicting data at higher pressures (e.g., Rapoport 1966), except to eliminate the speculation that the high-temperature transition is related to the break in the calcite-aragonite boundary near $480°C$ and 9.4 kbar (Boettcher and Wyllie 1967) or $500°C$ and 10 kbar (Goldsmith and Newton 1969).

REFERENCES CITED

BOEKE, H. E., 1912, Die Schmelzerscheinungen und die umkehrbare Umwandlung des Calciumcarbonats: Neues Jahrb. Mineralogie Abh., v. 1, p. 91–121.

BOETTCHER, A. L., and WYLLIE, P. J., 1967, Revision of the calcite-aragonite transition, with the location of a triple point between calcite I, calcite II and aragonite: Nature, v. 213, p. 792–793.

CHANG, L. L. Y., 1965, Subsolidus phase relations in the systems BaCO$_3$-SrCO$_3$, SrCO$_3$-CaCO$_3$, and BaCO$_3$-CaCO$_3$: Jour. Geology, v. 73, p. 346–368.

EITEL, W., 1923, Über das binäre System CaCO$_3$-

Ca$_2$SiO$_4$ und den Spurrit: Neues Jahrb. Mineralogie Beil. Band, v. 48, p. 63–74.

GOLDSMITH, J. R., and NEWTON, R. C., 1969, P-T-X relations in the system CaCO$_3$-MgCO$_3$ at high temperatures and pressures: Am. Jour. Sci., v. 267A, p. 160–190.

JAMIESON, J. C., 1957, Introductory studies of high-pressure polymorphism to 24,000 bars by X-ray diffraction with some comments on calcite II: Jour. Geology, v. 65, p. 334–343.

JOHANNES, W., and PUHAN, D., 1971, The calcite-aragonite transition, reinvestigated: Contr. Mineralogy and Petrology, v. 31, p. 28–38.