



FIG. 7. Plot of differences in spacing of the 111 plane of phases I and II of cerium vs. distance along the phase boundary from 0°C. See text for explanation of symbols.

phase I has been converted to phase II. At room temperature and 5 kb above the phase boundary, about 50 per cent conversion to phase II will take place in 1 hr. At this temperature and about 18 kb nearly all of phase I is almost immediately converted to phase II. Temperature increase accelerates the transformation and at  $11 \pm 1$  kb and 200°C cerium that is 1/3 phase I will completely transform to this phase in about 20 min.

One experiment merits special mention here. The data for curve C, Fig. 4(a), and the filled peak symbols of Fig. 6 were taken at  $P = 15 \pm 1$  kb and with decreasing temperature from 250 to 27°C. The purpose of the experiment was to observe the divergence of the 111 peaks of phases I and II and to compare the results with up temperature runs. As can be seen in Figs 4 and 6 the divergence at low temperatures is not as great as for up-temperature runs, although the slope  $\Delta d/^\circ\text{C}$  is the same. Moreover, the proportion of phases did not change significantly until 150°C, and then at 95°C nearly complete conversion took place. The temperature for this run was lowered very slowly (at 2–5°C intervals) and allowed to come to equilibrium over a period of 10–15 min before a record was taken. Thus it appears that persistence of phase I into the phase II region of stability is easily accomplished by quenching, at least under conditions of moderate pressure.

In this same run, after the temperature had dropped to room value, the pressure was lowered

suddenly to  $6 \pm 1$  kb; after 12 min there was still 50 per cent of phase II present. The pressure was dropped further to about  $4 \pm 1$  kb; 15 hr later there was still about 20 per cent of phase II present.

#### 4. DISCUSSION

The explanation given in previous papers for the identical structures of the two cerium phases, namely that the large reduction in volume from phase I to phase II is the result of promotion of the 4f electron to the 5d state, is presently well accepted. That this explanation is insufficient, however, to explain all anomalies involving cerium is made evident by the work of BATES and NEWMANN<sup>(15)</sup> and WERNICK and GELLER<sup>(16)</sup> already mentioned above.

Similar phenomena need explanation here. First, there is the fact that the change in  $\Delta d_{111}$  during compression and expansion results almost entirely from a change in spacing of the high-pressure (II) phase. This indicates an anomalously high compressibility and thermal expansion for phase II compared to phase I. BRIDGMAN<sup>(9)</sup> showed a change in  $\Delta v/v_0$  for phase I in the interval 5000–10,000 kg/cm<sup>2</sup> of 0.0315, and for phase II in the interval 15,000–20,000 kg/cm<sup>2</sup> of only 0.0209. This decrease in compressibility of the high-pressure phase is opposite that observed by us. The contradiction might be explained if the compressibility Bridgman measured included part of the