

Fig. 7. The most apparent feature of the plot is the large scatter. Consideration of sources for the scatter first led to the belief that it was mainly due to uncertainties in pressure. That this cannot be a major factor, however, is indicated by previous vessel calibration as well as by the fact that in order to bring the points of greatest deviation into line with the others the pressure would have to be reduced or increased into the region of phase growth that would be opposite that observed at nearby points and by other workers. Errors in chart reading could not account for such scatter, inasmuch as this would mean a reading error of  $0.3^\circ$  in  $2\theta$ . Nor could reasonable error in the  $\Delta d/^\circ\text{C}$  and  $\Delta d/\text{kb}$  observed above alone account for the deviation. If so, it would not only require a very different magnitude for the  $\Delta d/^\circ\text{C}$  but also a difference in sign.

Although combinations of error from several of the above factors could account for part of the scatter, it is very likely that a change in physical behavior due to previous history is important also.

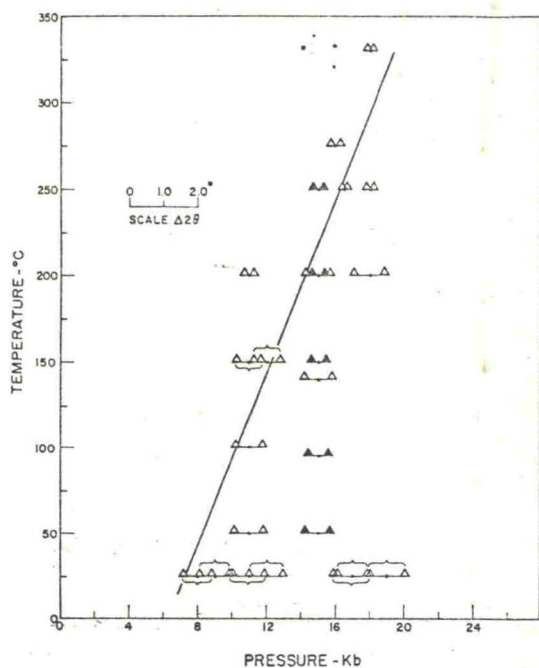


FIG. 6. Plot of  $\Delta 2\theta$  ( $\theta$  = Bragg angle), for the 111 peaks of cerium phases I and II, at various points in the vicinity of the phase boundary. See text for explanation of symbols.

For example, the run giving the greatest scatter of Fig. 7 (solid circles) differed from the others in that the pressure was increased at constant temperature until the phase boundary was crossed, diffraction patterns being taken at desired points; the temperature would then be increased at constant pressure until the boundary was crossed again, this time back into the region of stability of phase I. The temperature was then kept constant while the pressure was again increased until crossing of the boundary was again indicated by growth of phase II. In this manner a zig-zag course was followed along the phase boundary. It can be seen in a striking way by the solid circles of Fig. 7, that the data gathered in this way agree in no way with the data of other runs, even though the stability relations indicated by these same data fall in line with those of the other runs.

In fact, the irregular but definite trend of the data of Fig. 7 is gratifying to see when regarding the inconsistencies of data on the cerium transition as reported in the literature. BRIDGMAN<sup>(5, 7)</sup> SCHUCH and STURDIVANT,<sup>(18)</sup> HERMAN and SWENSON,<sup>(22)</sup> BEECROFT and SWENSON,<sup>(23)</sup> WILKINSON, *et al.*<sup>(17)</sup> and LAWSON and TANG<sup>(19)</sup> all report inconsistencies, most of which are ascribed to previous sample treatment. That the transition can even be effected, the value for the transition pressure at a certain temperature, the number and proportion of phases present (including the h.c.p. phase), and the presence or absence of hysteresis phenomena, all appear to depend upon such factors as thermal cycling, mechanical deformation, quickness of cooling, and impurity content.

The best indication of the position of the critical point can be gained by ignoring the anomalous data (solid circles) of Fig. 7, and extrapolating the slightly convergent band of data down to  $\Delta d_{111} = 0$ . When this is done, as indicated by the dashed lines of Fig. 7, the  $P$ - $t$  field roughly defining the critical end point is  $350$ - $400^\circ\text{C}$  and  $20$ - $22$  kb. This is in fair agreement with the value of  $357^\circ\text{C}$  and  $20,000$  atm given by BEECROFT and SWENSON.<sup>(23)</sup>

#### Rate of transformation

Several of the runs allowed a semi-quantitative estimate of transformation rate to be made. The rate at low temperatures is so small that considerable overstepping is possible before most of

AMS

more clearly the convergence of  
of the data collected by this  
schematically reproduced in  
of the triangles equidistant  
are accurately drawn to repre-  
tion at that point. Note that  
l decrease in  $\Delta d_{111}$  along the  
or less sudden decrease at or  
s qualitatively in agreement  
Beecroft and Swenson who  
ely constant value for  $\Delta H$   
up to  $500^\circ\text{K}$  ( $227^\circ\text{C}$ ).

1 kb  $T=340^\circ\text{C}$

40 - 20  
STEP  
COUNT

14 13  
20

and II of cerium  
ary. The power  
given is in the  
step counting

along the boundary could  
ng only those points lying  
However, in order to help  
experimental error and in-  
due to sample history, the  
undertaken. The approxi-  
 $\Delta d/\text{kb}$  were established  
and b. These slopes show  
ncrease in pressure there  
 $10^\circ$  in order to maintain  
with the assumption that  
change significantly with  
the data points of Fig. 6  
the phase boundary. This  
function of distance along  
results are thus given in