ases I and II of
C. See text for

b; after 12 min there was still
II present. The pressure was
bout 4 ± 1 kb; 15 hr later there
er cent of phase II present.

DISCUSSION

given in previous papers for
res of the two cerium phases,
e reduction in volume from
the result of promotion of the
l state, is presently well ac-
lanation is insufficient, how-
nomalies involving cerium is
work of BATES and NEW-
ICK and GELLER[16] already

need explanation here. First,
the change in Δd_{111} during
nsion results almost entirely
acing of the high-pressure
cates an anomalously high
ermal expansion for phase II
RIDGMAN[9] showed a change
n the interval 5000–10,000
for phase II in the interval
of only 0·0209. This de-
lity of the high-pressure
observed by us. The con-
xplained if the compres-
ured included part of the

volume change of transition. The technique employed by Bridgman requires that transformation be complete in order to measure the correct compressibility of phase II; likewise, the correct compressibility of phase I can be measured only if undisturbed by the volume change of an oncoming transition. As opposed to this, the present technique will permit measurement of compressibility of mixtures of the two phases without such error because it is determined from a shift of peaks of each phase.

Secondly, it has been observed that at higher temperatures and pressures along the phase boundary, the phase II peak would shift (phase I peaks remaining constant in position) until it emerged with the peak of phase I of same hkl index, as transformation of phase II to phase I progressed. Occasionally the two separate peaks would merge into one broad, flat-topped hump. This indicates diffraction coming from spacings intermediate between the theoretical spacings that would exist at the phase boundary in that $P–t$ vicinity. A possible explanation for the hump would be the distortion of the structures (presumably both phases) resulting from the volume increase of the II–I transformation, and reduction of grain size during the transformation.

It also should be mentioned that the increase in transformation rate for I–II with increased pressure-overstepping of the phase boundary at constant temperature could be due in part to deformation of the sample. McHARGUE and YAKEL[25] have shown that transformation of phase I to phase II at low temperatures is accelerated by working of the metal surface with a vibrating tool. Although no complete rate curve has been recorded in this study it is very likely that as strains in the bulk sample are removed by growth of strain-free grains of the new phase, the rate of transformation will decrease.

The lag in transformation of I–II with lowering temperature at 15 ± 1 kb (see p. 386) also needs explanation. In this instance there is a decrease in volume. As the temperature was lowered deep into the stability region of phase II the sudden completion of the transformation merely demonstrated the long accepted fact that considerable overstepping of $P–t$ conditions beyond the phase boundary is often necessary to accomplish a solid-state transformation (e.g., see BRIDGMAN).[26]

The actual process may involve both nucleation and growth, and the rates of these processes increase as the difference in free energy between the stable (II in this case) and metastable phases increases.

5. CONCLUSIONS

Direct X-ray examination under pressure of metallic cerium has shown that the dimensions of both face-centered cubic cells become identical at high temperatures and pressures along the cerium I–cerium II phase boundary. The data used for the extrapolation of Δd_{111} to zero along this boundary show marked scatter, some of which is suggested to be the result of previous sample history. The extrapolation data give an end point region of 350–400°C and 20–22 kb.

The transformation rate of cerium I $\rightleftharpoons$ cerium II is a function of the proximity to the phase boundary, as well as temperature, and it is possible to quench phase I so that it persists into the phase II stability region.

It appears that both the compressibility and thermal expansion of the high-pressure (II) phase are greater than those of the low-pressure (I) phase.

The peculiar coalescence of the 111 peaks with time as phase II transforms to phase I at high temperature is best explained as a distortion of the structures of both phases as well as a breakdown in grain size as the transformation proceeds.

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3