

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.

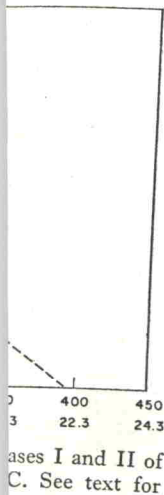
It appears that both the compressibility and thermal expansion of the high-pressure (II) phase are greater than those of the low-pressure (I) phase.

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.

Acknowledgements—The writers wish to thank Dr. A. JAYARAMAN, Dr. GEORGE KENNEDY, and Dr. W. KLEMENT for helpful suggestions during this study. Financial assistance from the National Science Foundation is also gratefully acknowledged.

REFERENCES

- HULL A. W., *Phys. Rev.* **18**, 88 (1921).
- KLEMM W. and BOMMER H., *Z. anorg. Chem.* Bd. **321**, S. 138-171.
- BRIDGMAN P. W., *Proc. Amer. Acad. Arts Sci.* **58**, 166 (1923).
- BRIDGMAN P. W., *Proc. Amer. Acad. Arts Sci.* **62**, 207 (1927).
- BRIDGMAN P. W., *Proc. Amer. Acad. Arts Sci.* **76**, 55 (1948).
- BRIDGMAN P. W., *Proc. Amer. Acad. Arts Sci.* **76**, 71 (1948).
- BRIDGMAN P. W., *Proc. Amer. Acad. Arts Sci.* **79**, 125 (1951).
- BRIDGMAN P. W., *Proc. Amer. Acad. Arts Sci.* **81**, 165 (1952).



Phases I and II of C. See text for

b; after 12 min there was still phase II present. The pressure was about 4 ± 1 kb; 15 hr later there was 10 per cent of phase II present.

DISCUSSION

As given in previous papers for cerium, the reduction in volume from phase I to phase II is the result of promotion of the cerium to the high-pressure state, is presently well accounted for. The explanation is insufficient, however, for the anomalies involving cerium. The work of BATES and NEWKOME⁽¹⁵⁾ and GELLER⁽¹⁶⁾ already

needs explanation here. First, the change in Δd_{111} during the transformation results almost entirely from the compression of the high-pressure phase. This indicates an anomalously high thermal expansion for phase II. BRIDGMAN⁽⁹⁾ showed a change in Δd_{111} in the interval 5000 - $10,000$ psi for phase II in the interval of only 0.0209 . This deviation from the high-pressure behavior is not observed by us. The compression is explained if the compressed part of the