

X-RAY DIFFRACTION EVIDENCE FOR A CRITICAL END POINT FOR CERIUM I AND CERIUM II*

BRIANT L. DAVIS† and LEASON H. ADAMS

Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California

(Received 12 August 1963)

Abstract—A beryllium pressure vessel has been used to investigate the two face-centered phases of cerium at various temperatures and pressures along the phase boundary. X-ray diffraction records of the strong 111 peak of both phases show that the two peaks coalesce with increasing temperature and pressure along the boundary. The P - t region for the critical end point of the boundary is obtained by extrapolation of the change in d -spacing with distance along the boundary, and is found to be 350–400°C and 20–22 kb.

The X-ray data also show that the compressibility and thermal expansion of the high-pressure (II) phase are greater than those of the low-pressure (I) phase.

Rate studies indicate that under pressure phase I persists into the phase II stability field with lowering temperature. Considerable overstepping of pressure into this field is also possible before complete transformation of I-II will take place.

1. INTRODUCTION

THE RARE earth element cerium (first of the lanthanum series) has been studied in great detail in the last 30 years with respect to atomic structure, magnetic susceptibility, alloy properties, and phase stability including polymorphism. HULL⁽¹⁾ and KLEMM and BOMMER,⁽²⁾ recognized two polymorphs of cerium having identical densities, a close-packed hexagonal (h.c.p.) structure, and a face-centered (f.c.c.) cubic structure.

BRIDGMAN⁽³⁾ at first found the compressibility of cerium to decrease in a normal way with pressure and found no transitions up to 12 kg/cm². In a second series of experiments BRIDGMAN⁽⁴⁾ located a transition in cerium at 7600 kg/cm² and 30°C, and also noted that the compressibility of the low-pressure-phase increased with increasing pressure, and decreased with increasing temperature. BRIDGMAN⁽⁵⁾ again studied cerium of presumably high purity, this time finding no transition until he reached 12,430 kg/cm², with the compression data,

however, in agreement with the results of 1927. In these and subsequent papers (BRIDGMAN⁽⁶⁻⁹⁾) these inconsistencies were explained to be the result of impurity differences, with the pure samples requiring higher pressures for transformation.

An anomalous behavior in thermal expansion was observed for the low-pressure phases of cerium by BARNSON, LEGVOLD and SPEDDING.⁽¹⁰⁾ The expansion coefficient, α , decreased with increasing temperature to a minimum at 200°C (where $\alpha = 6 \times 10^{-3}/^\circ\text{C}$) and then increased regularly to 700°C. The minimum was suggested to be the result of formation of mixtures of both h.c.p. and f.c.c. phases.

The stability regions of the low- and high-pressure phases (hereafter called phases I and II, respectively) were determined using volume methods by LIKHTER, RYABININ and VERESCHAGIN.⁽¹¹⁾ Their results give a linear phase boundary with slope 23.8° C/kb and a transition pressure at 30°C of 8.7 kb.

From magnetic susceptibility measurements, TROMBE⁽¹²⁾ and TROMBE and FOEX⁽¹³⁾ noted a transformation with hysteresis and large volume change at low temperatures (100–200°K). More recent work with magnetic susceptibilities of

* Publication No. 305, Institute of Geophysics and Planetary Physics, University of California, Los Angeles 24, California.

† Now at Department of Geology and Geological Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakota.

ON

erg cm⁻²)

$\lambda\sigma$	σ
065	19.701
050	19.039
143	43.168
119	41.731
175	52.793
219	53.411
206	62.116
216	62.057
181	20.339
146	19.801
397	44.568
348	43.301
486	54.504
625	54.871
572	64.130
624	64.048
145	21.339
114	20.816
318	46.759
273	45.515
388	57.186
497	57.628
457	67.284
493	67.294

REFERENCES

- R., *Proc. phys. Soc. Lond.* A62, 182 (1959).
- SAISNYS J. R. and JURA G., *J. Phys.* 11, 182 (1959).
- BALK P. and WHITE P., *J. chem. Phys.* 29, 302 (1959).
- DEMPSEY E. and BALK P., *J. chem. Phys.* 33, 26 (1961).
- FREEMAN P. I. and DEMPSEY E., *J. chem. Phys.* 33, 26 (1961).
- FREEMAN P. I. and DEMPSEY E., *J. chem. Phys.* 39, 302 (1963).
- B. M. E. and BENSON G. C., *Canad. J. Phys.* 31, 1087 (1953).
- F. and BENSON G. C., *J. chem. Phys.* 27, 1087 (1957).
- and INGHAM A. E., *Proc. Roy. Soc. Lond.* A252, 925 (1959).
- and RICE W. E., *J. chem. Phys.* 22, 843 (1954).

cerium by LOCKE⁽¹⁴⁾ and BATES and NEWMANN⁽¹⁵⁾ show further anomalies. Bates and Newmann also show that although the atomic radii of Ce and Th are 1.82 Å and 1.80 Å, respectively, there is a decrease in cell parameter (below 1.80 Å) when a small amount of Ce is present in Th; this slight decrease terminates and the cell parameter remains constant to about 35 per cent Ce in Th, after which the cell parameter increases with added Ce to the value for the pure metal.

To explain the above effect and also the temperature dependence of magnetic susceptibility of alloys in the Ce-Th system, Bates and Newmann suggest that the Ce ions resonate between the Ce³⁺ and Ce⁴⁺ state, thereby effectively producing a proportion of smaller ions with no 4f electrons. This concept is in keeping with the findings of WERNICK and GELLER⁽¹⁶⁾ who found that of all of the cobalt rare earth and nickel rare earth compounds having the Cu₅Ca structure only the cerium compounds depart from the plot of atomic volume vs. atomic number. The atomic volumes of Co₅Ce and Ni₅Ce are much too small for structures in which cerium is in the trivalent state. The promotion of the 4f electron into the 5d state, with corresponding contraction in ion size, is the explanation suggested by Wernick and Geller.

Evidence for a transition in cerium being due to electronic collapse has been found from neutron diffraction studies at low temperatures by WILKINSON, *et al.*,⁽¹⁷⁾ and from X-ray diffraction studies at low temperatures by SCHUCH and STURDIVANT⁽¹⁸⁾ and from high-pressure X-ray diffraction studies by LAWSON and TANG⁽¹⁹⁾ and ADAMS and DAVIS.⁽²⁰⁾ In all cases the high-pressure or low-temperature pattern conformed to a f.c.c. structure. Lawson and Tang obtained a cell constant of $a_0 = 4.84 \pm 0.03$ Å at room temperature and 15,000 atm. for the high-pressure phase ($a_0 = 5.14$ Å for the low-pressure phase at room temperature). The over-all volume change given by them is 16.5 per cent. Adams and Davis give $a_0 = 4.82_4$ at room temperature and transition pressure of 7 kb, with a volume change of 14 per cent at the transition and 18 per cent over-all.

PONIATOVSKII⁽²¹⁾ observed during a thermographic analysis of the two phases across the boundary that the heat of transition diminished to the point where it could not be separated from experimental error. This point was roughly 280°C

and 18.9 kb, thus indicating a critical end point for the phase boundary, although Pontiatovskii stated that the observed point where the heat of transition could not be detected was not necessarily the correct position for the end point.

Further volume work by HERMANN and SWENSON⁽²²⁾ and BEECROFT and SWENSON⁽²³⁾ confirms this result. The transition volumes decrease with increasing temperature and pressure along the boundary; Beecroft and Swenson extrapolate their data to 357°C and 20,000 atm as the point at which there is no volume change. Of importance in a later discussion will be the fact that Beecroft and Swenson observed a spreading out of the transition pressure at higher temperatures and a considerable increase in thermal expansion of cerium (presumably phase II) at 20,000 atm, over that of cerium at room pressure. The earlier work of HERMANN and SWENSON⁽²²⁾ revealed considerable hysteresis to the transition at room temperature, whereas the later work, using the cerium from the same source, revealed little or no hysteresis at room pressure.

2. EXPERIMENTAL METHOD

The apparatus is similar to that previously described by DAVIS and ADAMS.⁽²⁴⁾ A sketch of the supported beryllium pressure vessel is given in Fig. 1. The complete vessel with cap stands less than 6 cm high and is seated on a ram mounted at the base of a small press. The press, with attached spindle is inserted into the X-ray goniometer of a Norelco diffractometer as seen in the general experimental arrangement, Fig. 2.

The beryllium cylinder is encased in a steel jacket (C, Fig. 1) that is screwed into the hardened steel outer casing. In the present arrangement there is a selection of several bore sizes of Plug C and corresponding piston sizes (A and D) to allow for different sample sizes and pressure ranges for the pump system now in use. The sample and piston diameter used throughout the study was 4.6 mm. The sample pellet is separated from the piston face by a 4.6 mm × 1.25 mm. beryllium pellet to act as the window for the X-rays. The X-ray beam passes through slots in the outer casing (Fig. 1, inset), through the beryllium cylinder and pellet, and onto the sample. The "reflection" path is similar. The dial gauge arm operates a height indicator, the main function of which is to warn of excessive sample extrusion or deformation of the internal parts of the vessel.

Not shown in Fig. 1 is the heating jacket made from No. 24 (Brown and Sharpe) Nichrome V wire wound into a length of coil and fashioned into a zig-zag belt. The belt was insulated by an inner and outer layer of alundum cement baked at 500°C, or by layers of Transite and pure (99.9%) SiO₂ cloth held together by an

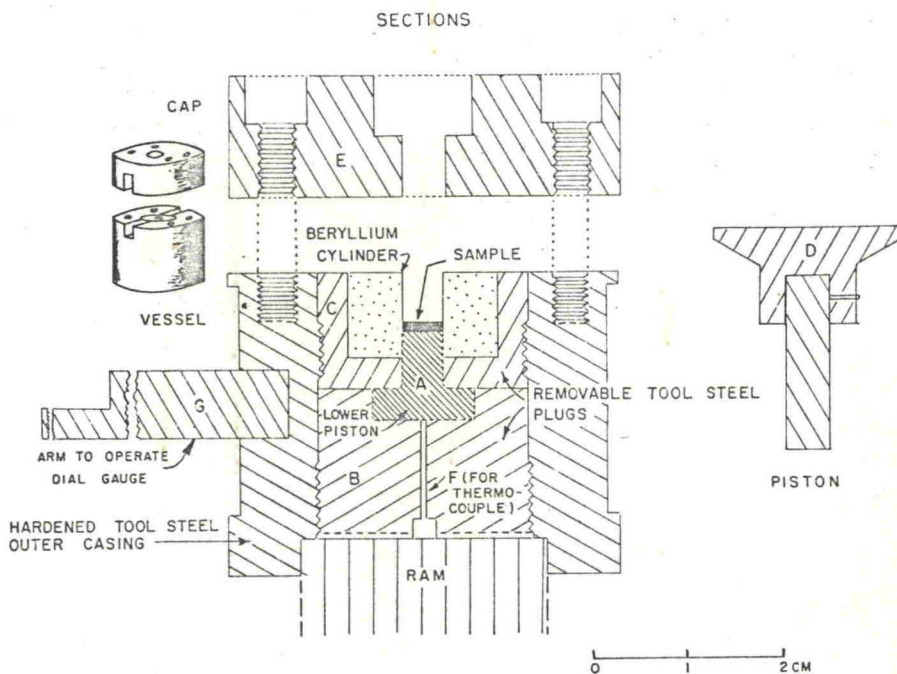


Fig. 1. Beryllium pressure vessel, sectional view, including cap and piston. Beryllium cylinder is stippled. Inset shows view of vessel and cap, and relations between casing slots and beryllium cylinder.

exterior band of copper or brass sheeting (see Fig. 2). A special cooling jacket was constructed to fit around the ram and goniometer spindle.

The temperature was measured by means of a Chromel-alumel thermocouple insulated and inserted into hole F of plug B, Fig. 1. The temperature was read from a Leeds-Northrup potentiometer (with a "reference junction" to approximate the cold-junction correction). Insertion of a mercury thermometer into the bomb window at 175°C gave results within two degrees of that read from the potentiometer. Work with the transition point of $\text{KNO}_3\text{-II-KNO}_3\text{-I}$ (128.3°C) showed that thermocouple readings were correct to within ± 2 deg. A similar uncertainty can be assigned to the results of this investigation. Excessive heat flow out through the vessel was eliminated by placing a 4-mm disk of Transite between the piston base and plug base (B, Fig. 1).

Preliminary experiments were carried out to determine the difference between nominal and internal pressures. This was done by making a standard run using a highly compressible material, such as KI or RbI, as a sample. Previously determined equations giving $\Delta v/v_0$ as a function of pressure allow calculation of internal pressures from peak shift on the diffraction chart. To correct for the peak shift due to change in sample height (mainly due to compression of Transite pad and beryllium pellet above the sample) a thin layer of diamond powder was placed on top of the sample pellet. Effective reflecting

depths of diamond powder and sample material would be almost identical after a slight amount of pressure was applied to imbed the diamond into the sample.

The calibration runs carried out specifically for this study agreed closely with results obtained previously with the same vessels. Using a piston that fits easily into the cylinder, there is very little frictional loss of pressure on going up in pressure. After perhaps 20 kb had been attained the return run indicated considerable lag of the internal pressure above nominal pressure. At $P = 0$ (nominal) on the return run, the internal pressure may be as much as 4 kb. One up-pressure run at 150°C indicated that there is less frictional resistance than at room temperature, after taking into account the change in compressibility of sample with temperature. There is still some pressure uncertainty stemming from the deformation of the beryllium pellet and vessel walls, especially at higher temperatures. This deformation is most likely responsible for the pressure lag on the return leg of the runs as well as increased frictional resistance when repeating a run with the same sample and beryllium pellet used previously. A pressure uncertainty of ± 1 kb is appended to all pressure values, and at temperatures below 100°C this figure is considered to be quite conservative.

Radiation used was $\text{MoK}\alpha$, with applied power of 40 kV and 20 mA. A scintillation counter combined with pulse-height analyser comprised the detection,

licating a critical end point for although Pontiatovskii stated point where the heat of transition was not necessarily the end point.

work by HERMANN and SWENSON and SWENSON⁽²³⁾ confirms transition volumes decrease with pressure and pressure along the line and Swenson extrapolate to 20,000 atm as the point of volume change. Of importance will be the fact that Beecroft observed a spreading out of the transition at higher temperatures and a change in thermal expansion of phase II) at 20,000 atm, over pressure. The earlier work of SWENSON⁽²²⁾ revealed the transition at room temperature work, using the cerium revealed little or no hys-

EXPERIMENTAL METHOD

to that previously described. A sketch of the supported vessel is given in Fig. 1. The vessel is less than 6 cm high and is mounted at the base of a small press. The spindle is inserted into the vessel as seen in the arrangement, Fig. 2.

The vessel is encased in a steel jacket into the hardened steel outer casing there is a selection of different sample sizes and corresponding piston system now in use. The sample used throughout the study is separated from the vessel by a 25 mm. beryllium pellet to X-rays. The X-ray beam is directed through the outer casing (Fig. 1, inset), around the piston and pellet, and onto the sample. The dial gauge is used to measure the main function of the vessel, the main function of the vessel, the main function of the vessel.

The heating jacket made from Nichrome V wire wound around the vessel is fashioned into a zig-zag belt. The inner and outer layer of the jacket is held together by an

discrimination, and amplification circuit; records were taken on a Brown strip-chart recorder.

The sample (A.D. MacKay, Inc., 99.9 per cent pure) consisted of a thin disk punched from rolled sheet and sanded to remove oxide. The pellet thickness was usually between 0.5 mm and 0.8 mm and always 4.6 mm in diameter. Two major experimental difficulties were encountered at high pressures and temperatures. First, cerium oxidizes quite rapidly at room temperature, and when exposed to air at 150°C the peaks of the cerium are nearly gone in 5 min. To avoid such oxidation, a few hundred bars pressure was applied to the sample when raising the temperature 200–300° for a pressure run at constant temperature. Secondly, cerium flows very rapidly at 200°C and 15 kb, so much so that movement up alongside the beryllium pellet cut off the X-ray beam to the extent that several runs had to be abandoned. Furthermore, the cerium flows around the lower piston so that the lower plug and upper plug (B and C, Fig. 1) could only with difficulty be removed upon cooling. Much better results were obtained by making the pellet 3.2 mm in diameter so that it was entirely surrounded by and constrained by the 4.6 mm beryllium pellet.

3. RESULTS

Figure 3 is the phase diagram of cerium-I and cerium-II as established from the X-ray data of several runs. Runs were made at both constant pressure and constant temperature. To establish which phase was growing, the integrated intensities of the strong 111 peaks of both phases were compared. The slope of the phase boundary was found to be 25.5 deg/kb and the room temperature (300°K) transition pressure, 7.6 kb. Comparison with results of other workers are made in Table 1, from which it can be seen that there is considerable variation in the transition pressure given for room temperature. The heat of transition ΔH , is not given for Bridgman's data because the only value for the volume change given corresponded to the 8 per cent he found at 12,430

kg/cm².⁽⁵⁾ The value for ΔH given by Likhter, *et al.*, was given in the original paper as 0.023 eV, which is equivalent to 530 cal/g atom.

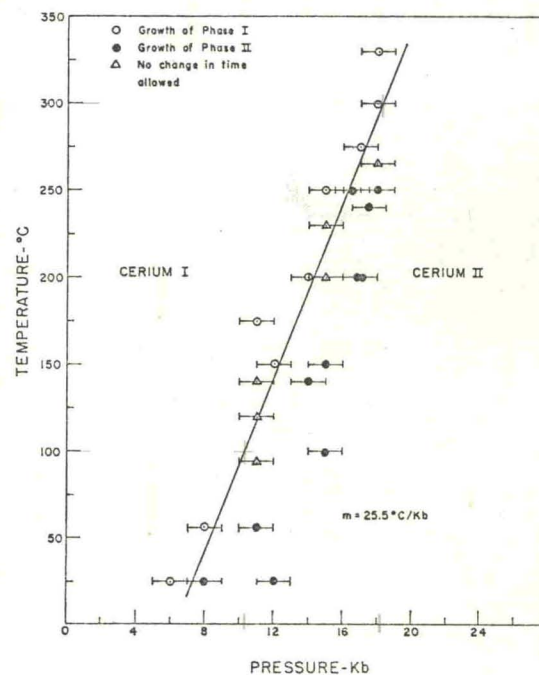


FIG. 3. Partial phase diagram of cerium showing stability regions of phases I and II as determined by X-ray data. Horizontal bar at each point indicates pressure uncertainty.

The cerium I–cerium II transformation is sluggish enough to allow X-ray examination of both phases in a region of pressure and temperature considerably removed from the phase boundary. As a result of several runs at constant pressure and

Table 1

	Transition pressure* (kb)	dT/dP (°C/kb)	ΔH^* (cal/g. atom)
Bridgman ⁽⁴⁾	8.0	29.7	-----
Hermann and Swenson ⁽²²⁾	7.4	20.8	1150 ± 100
Likhter, <i>et al.</i> ⁽¹¹⁾	8.5	23.8	530
Poniatovskii ⁽²¹⁾	8.0	22.0	-----
Beecroft and Swenson ⁽²³⁾	6.5	23.6	800 ± 50
Davis and Adams ⁽²⁹⁾ and this paper	7.6	25.5	798

* All at room temperature.

DAMS

value for ΔH given by Likhter, the original paper as 0.023 eV, to 530 cal/g atom.

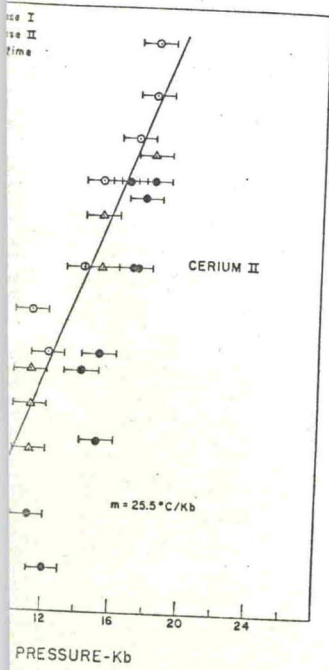


Diagram of cerium showing stability of Cerium II as determined by X-ray data. Each point indicates pressure and temperature with a certain uncertainty.

The Cerium II transformation is sluggish. X-ray examination of both phases as a function of pressure and temperature from the phase boundary. Measurements were made at constant pressure and constant temperature.

ΔH^* (cal/g. atom)
± 100
± 50

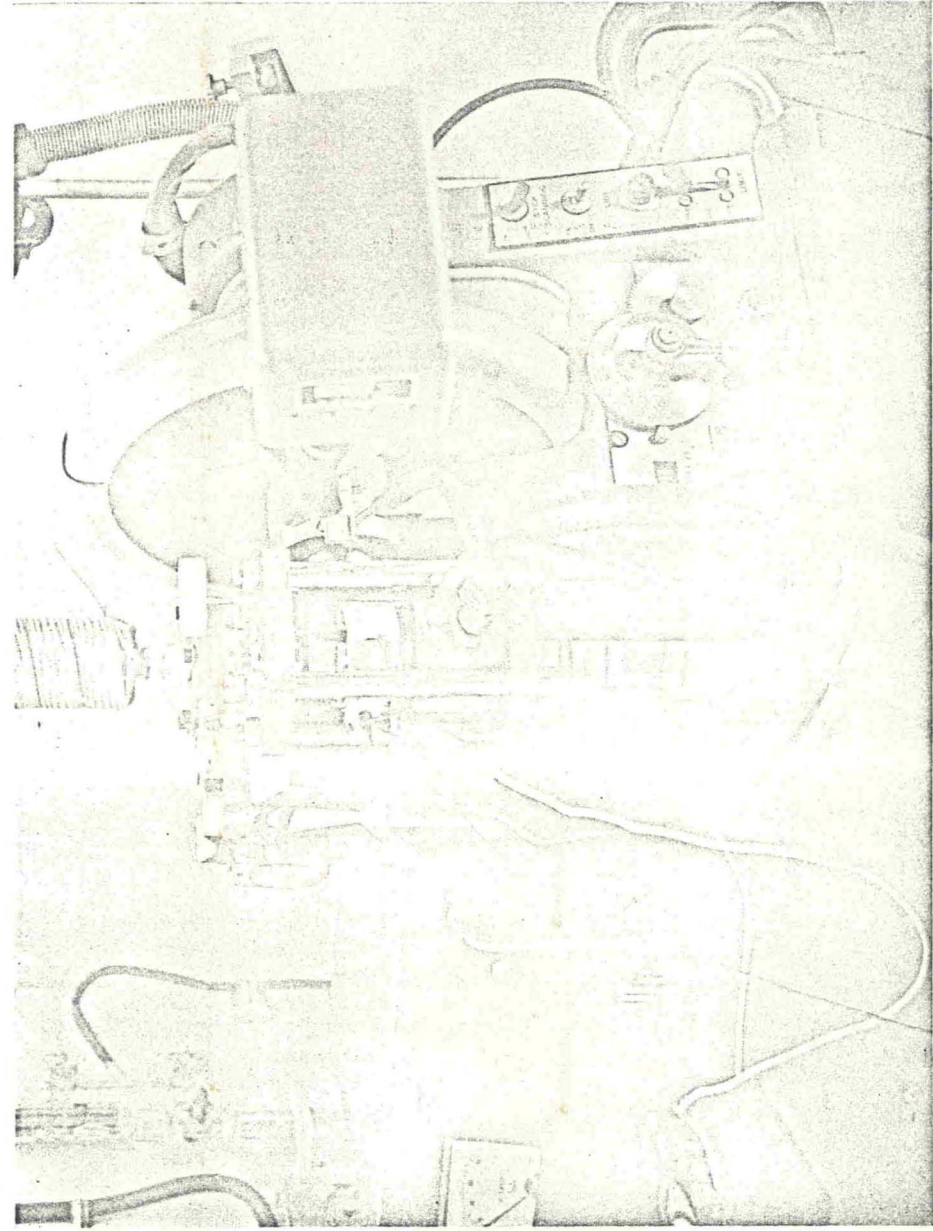


FIG. 2. Close-up view of vessel mounted in press inserted into the goniometer of the diffraction unit. The large hose is the pressure line and the small hoses are water lines leading to the cooling jackets on the ram and spindle. Wires are power leads and thermocouple. X-ray shields have been removed.

constant temperature it can be concluded that, in the P - t region studied (see Fig. 3), the high-pressure phase, cerium II, has both a higher compressibility and higher thermal expansion than the low-pressure phase.

For example, at 200°C as the pressure is increased from 14 to 17 kb, the reduction in d -spacing for the high-pressure phase is twice that for the low pressure phase. Even more surprising is the fact that in two independent runs (using diamond internal

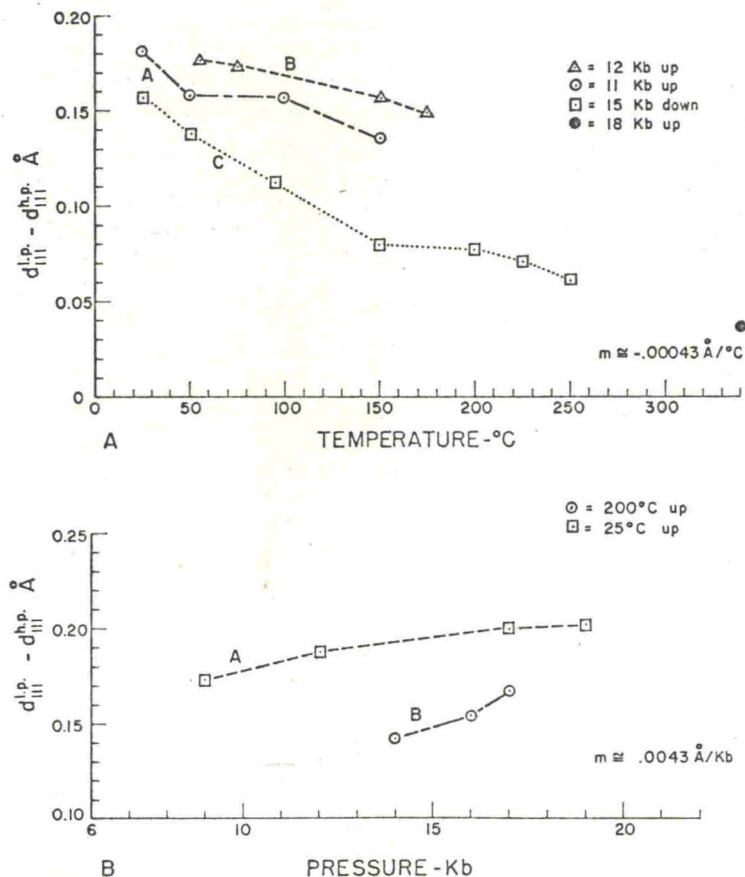


FIG. 4. Spacing differences of the 111 peak of phase I and II of cerium as a function of (a) temperature and (b) pressure. The value for the slope given is the best fit for all the data present.

This phenomenon was observed by noting the relative positions (centers of gravity) of the 111 diffraction peak of each phase. On all runs at constant temperature the two peaks diverged in Bragg angle with increasing pressure, whereas at constant pressure the two peaks converged with increasing temperature. The results are expressed as a variation in Δd_{111} with pressure and temperature in Fig. 4, a and b. It is also apparent that the change in Δd_{111} is almost entirely due to a change in the spacing of the high-pressure phase.

standard) the results indicated a contraction by a very small amount (approximately 0.2 per cent) of the low-pressure phase compared to an expansion of about 1 per cent of the high-pressure phase for an increase of about 125°C at 11 kb. In another run, with an increase of 60° at 14 kb, the change was approximately +0.6 per cent for the high-pressure phase and again -0.2 per cent for the low-pressure phase. Even if one regards the measurement of the small changes for the low-pressure phase to be in error, one cannot escape

the conclusion that the thermal expansion of cerium II is many times that of cerium I. This phenomenon has been reported by BEECROFT and SWENSON⁽²³⁾ who found that at 20,000 atm the thermal expansion of the phase present (presumably cerium II) is a factor of 10 greater than at zero pressure, certainly an anomalous behavior in comparison with most other metals.

The primary purpose for this investigation was to try to obtain sufficiently definitive diffraction records to see if the strong 111 peaks of both high- and low-pressure phases would coalesce as the

In order to show more clearly the convergence of the two 111 peaks, all of the data collected by this method have been schematically reproduced in Fig. 6. The separation of the triangles equidistant from the $P-t$ point are accurately drawn to represent the peak separation at that point. Note that there is not a gradual decrease in Δd_{111} along the boundary but a more or less sudden decrease at or above 200°C. This is qualitatively in agreement with the findings of BEECROFT and SWENSON who noted an approximately constant value for ΔH (and therefore for Δv) up to 500°K (227°C).

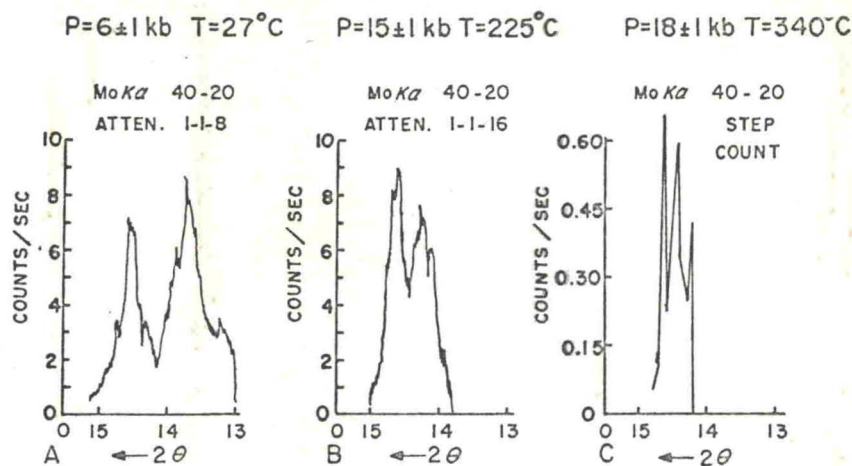


FIG. 5. Records of peak separation for the 111 spacing of phases I and II of cerium for various pressures and temperatures close to the phase boundary. The power values for the X-ray tube given are in kV and mA. The attenuation given is in the order; scale factor, multiplier, and time constant. For diagram C the step counting interval was 132 sec/step.

reported critical end point along the phase boundary was approached. The diffraction charts taken at the higher temperatures and pressures of the boundary indeed show this coalescence; portions of three actual records are reproduced here in Fig. 5, and were taken at roughly equidistant intervals along the phase boundary. The peaks of Fig. 5(C) were obtained from step counting at intervals of 0.05 deg (2θ) with a counting time of 132 sec/step. These peaks might actually be one, although their positions and resolution were reproduced twice. The peak separation is much too great to be a $K\alpha_1-K\alpha_2$ separation. Because of the weak diffraction count superimposed on high background scatter, the records obtained by scanning did not give consistent results.

Extrapolation of Δd_{111} along the boundary could be accomplished by using only those points lying close to the boundary. However, in order to help eliminate the effects of experimental error and inconsistencies in results due to sample history, the following procedure was undertaken. The approximate slopes $\Delta d/^\circ\text{C}$ and $\Delta d/\text{kb}$ were established from the data of Fig. 4, a and b. These slopes show that for every kilobar increase in pressure there must be a decrease of 10° in order to maintain constancy of volume. With the assumption that this relationship does not change significantly with temperature and pressure, the data points of Fig. 6 were extrapolated into the phase boundary. This allows a plot of Δd_{111} as a function of distance along the phase boundary; the results are thus given in

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° in 2θ . 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.

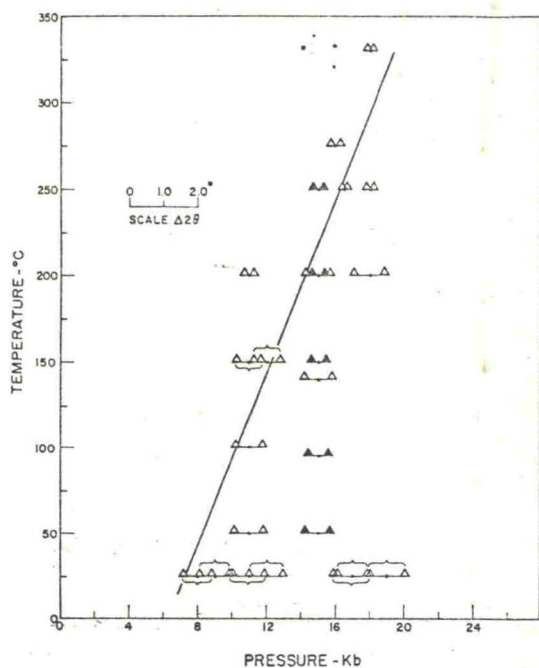


FIG. 6. Plot of $\Delta 2\theta$ (θ = Bragg angle), for the 111 peaks of cerium phases I and II, at various points in the vicinity of the phase boundary. See text for explanation of symbols.

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^(5, 7) SCHUCH and STURDIVANT,⁽¹⁸⁾ HERMAN and SWENSON,⁽²²⁾ BEECROFT and SWENSON,⁽²³⁾ WILKINSON, *et al.*⁽¹⁷⁾ and LAWSON and TANG⁽¹⁹⁾ 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°C and 20 - 22 kb. This is in fair agreement with the value of 357°C and $20,000$ atm given by BEECROFT and SWENSON.⁽²³⁾

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 Δd_{111} along the
or less sudden decrease at or
s qualitatively in agreement
Beecroft and Swenson who
ely constant value for ΔH
up to 500°K (227°C).

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

40 - 20
STEP
COUNT

14 13
20

and II of cerium
ary. The power
n given is in the
e 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° 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

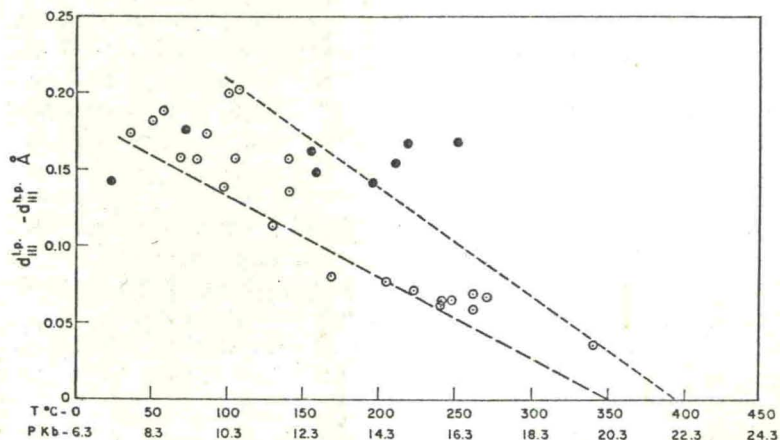


FIG. 7. Plot of differences in spacing of the 111 plane of phases I and II of cerium vs. distance along the phase boundary from 0°C. See text for explanation of symbols.

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 ± 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 ± 1 kb; after 12 min there was still 50 per cent of phase II present. The pressure was dropped further to about 4 ± 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⁽¹⁵⁾ and WERNICK and GELLER⁽¹⁶⁾ already mentioned above.

Similar phenomena need explanation here. First, there is the fact that the change in Δd_{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⁽⁹⁾ showed a change in $\Delta v/v_0$ for phase I in the interval 5000–10,000 kg/cm² of 0.0315, and for phase II in the interval 15,000–20,000 kg/cm² 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

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 $350-400^\circ\text{C}$ 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).



ases I and II of
C. See text for

b; after 12 min there was still
e II present. The pressure was
about 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,
reduction in volume from
the result of promotion of the
state, is presently well ac-
planation is insufficient, how-
omalies involving cerium is
work of BATES and NEW-
CK and GELLER⁽¹⁶⁾ already

need explanation here. First,
the change in Δd_{111} during
nsion results almost entirely
acing of the high-pressure
icates 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-
explained if the compress-
ured included part of the

9. BRIDGMAN P. W., *Proc. Amer. Acad. Arts Sci.* **83**, 1 (1954).
10. BARNSON F., LEGVOLD S. and SPEDDING F. H., *Phys. Rev.* **105**, 418 (1957).
11. LIKHTER A. I., RYABININ YU N. and VERESCHAGIN L. F., *Sov. Phys. J. exp. theor. Phys.* **6**, 469 (1958).
12. TROMBE F., *C.R. Acad. Sci., Paris* **198**, 1591 (1934).
13. TROMBE F. and FOEX M., *Ann. Chem.* **19**, 417 (1944).
14. LOCKE J. M., *Proc. phys. Soc. Lond.* **B70**, 566 (1957).
15. BATES L. F. and NEWMANN M. M., *Proc. Phys. Soc. Lond.* **72**, 345 (1958).
16. WERNICK J. H. and GELLER S., *Acta Cryst.* **12**, 662 (1959).
17. WILKINSON M. K., CHILD H. R., MCHARGUE C. J., KOELLER W. C. and WOLLAN E. D., *Phys. Rev.* **122**, 1409 (1961).
18. SCHUCH A. E. and STURDIVANT J. H., *J. chem. Phys.* **18**, 145 (1950).
19. LAWSON A. W. and TANG TING-YUAN, 2nd Annual Report to ONR on High Pressure Research, 1948-49, pp. 88-91, Univ. of Chicago Press.
20. ADAMS L. H. and DAVIS B. L., *Proc. Nat. Acad. Sci.* **48**, 982 (1962).
21. PONIATOVSKII E., *Sov. Phys. Dokl.* **3**, 498 (1958).
22. HERMANN R. and SWENSON C. A., *J. chem. Phys.* **29**, 398 (1958).
23. BEECROFT R. I. and SWENSON S. A., *J. Phys. Chem. Solids* **15**, 234 (1960).
24. DAVIS B. L. and ADAMS L. H., *Z. Krist.* **117**, 399 (1962).
25. MCHARGUE C. J. and YAKEL H. L., Jr., *Acta Met.* **8**, 637 (1960).
26. BRIDGMAN P. W., *Proc. Amer. Acad. Arts Sci.* **52**, 57 (1915).