

## Solid-Solid Transitions in Titanium and Zirconium at High Pressures\*

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The body-centered cubic to hexagonal close-packed transformations in titanium and zirconium have been studied by means of differential thermal analysis at pressures in the range 0–65 kbar and at cooling and heating rates of 3–5°C/sec. The transitions occurred at different temperatures upon heating and upon cooling and these hysteresis intervals did not appear to vary much with increasing pressure and/or contamination. Alloying with the tantalum containers and consequent lowering of the transition temperatures was unavoidable in most of the experiments. The Ti transition decreases only slightly in temperature with increasing pressure; a zero pressure volume change of less than 0.3% is suggested. The Zr transition exhibits a slope of about  $-2.4^{\circ}\text{C}/\text{kbar}$  until a new transition is encountered near 58 kbar; the transition from body-centered cubic to the new Zr polymorph is without much hysteresis, and the phase boundary exhibits a slope of about  $0.6^{\circ}\text{C}/\text{kbar}$ . Discontinuities of about 17% in resistance at room temperature are detected near 51–59 kbar for Zr and 80–90 kbar for Ti, there being a decrease for Zr and an increase for the resistance of Ti.

### I. INTRODUCTION

**T**ITANIUM, zirconium, and hafnium crystallize in the hexagonal close-packed (hcp) structure at low temperatures and transform to the body-centered cubic (bcc) structure before melting. The bcc-hcp transformations apparently are diffusionless and relatively insensitive<sup>1,2</sup> to the rate of heating or cooling; the equilibrium transition temperatures are near  $882^{\circ}\text{C}$ ,<sup>3</sup>  $870^{\circ}\text{C}$ ,<sup>4</sup> and  $1750 \pm 20^{\circ}\text{C}$ <sup>5</sup> for Ti, Zr, and Hf, respectively. Many features of the bcc-hcp transitions remain poorly understood because of the ease of contamination at these high temperatures.

No previous investigations of the bcc-hcp transitions in Ti, Zr, and Hf at high pressures have been reported. Bridgman has measured the resistance<sup>6</sup> of Ti, Zr and Hf to about 75 kbar (revised pressure scale) and the volume<sup>7</sup> of Ti and Zr to about 100 kbar at room temperature. The only discontinuity detected was for the resistance of Zr—a decrease near 59 kbar; however, Bridgman did not find any change in volume at this pressure. Very recent high-pressure x-ray diffraction experiments by Jamieson<sup>8</sup> indicate that both Ti and Zr transform from hcp to a hexagonal (3 atoms/unit cell) structure, hereafter referred to as  $\omega$ . The transition pressures are not known from Jamieson's work; the volume differences relative to hcp seem to be  $\sim 1.5\%$  for Ti and  $\sim 3\%$  for Zr, as inferred from the x-ray

densities<sup>8</sup> obtained for the  $\omega$  phases retained at zero pressure.

In the present investigation, the bcc-hcp transitions in Ti and Zr at high pressure were followed by differential thermal analysis. An effort was also made to verify the resistance discontinuity reported<sup>6</sup> near 59 kbar for Zr. One of us (A.J.) carried out room-temperature resistance measurements to much higher pressures in the laboratory of Professor H. G. Drickamer. Although most of the present experiments were completed prior to Jamieson's work, some additional experiments were undertaken in order to verify these results insofar as is possible with the present apparatus.

### II. EXPERIMENTAL PROCEDURES

For pressures up to 45 kbar a single stage piston cylinder apparatus and above this a double staged apparatus were used.<sup>9,10</sup> In the former, the pressure is generated by a  $\frac{1}{2}$ -in.-diam, 2-in.-long carboloy piston moving inside a supported carboloy chamber of similar dimensions. In this the pressures attainable are limited by the crushing strength of the carboloy piston, but this can be extended by giving piston support, through the double stage scheme. This is done by immersing the high-pressure piston ( $\frac{1}{2}$  in. diam, 2 in. long) in a compressed column of bismuth, contained in a supported steel core 1 in. in diameter and 2 in. long, forming the lower stage. A 1-in.-diam carboloy piston pushes the high-pressure piston into the high-pressure stage ( $\frac{1}{2}$  in. in diameter by 2 in. long) and compresses at the same time the bismuth column which gives support to the high pressure piston. The pressure in the upper stage can be accurately computed when the supporting bismuth is in transition, because the load on the bismuth can then be calculated from the known transition pressure and the area of the column and then subtracted from the

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<sup>1</sup> L. P. Srivastava and J. G. Parr, *Trans. AIME* **224**, 1295 (1962).

<sup>2</sup> P. Duwez, *J. Metals* **3**, 765 (1951).

<sup>3</sup> A. D. McQuillan, *J. Inst. Metals* **18**, 249 (1950).

<sup>4</sup> G. B. Skinner and H. L. Johnston, *J. Chem. Phys.* **21**, 1383 (1953).

<sup>5</sup> D. K. Deardorff and H. Kato, *Trans. AIME* **215**, 876 (1959).

<sup>6</sup> P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **81**, 165 (1952).

<sup>7</sup> P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **76**, 55 (1948).

<sup>8</sup> J. C. Jamieson, *Science* **140**, 72 (1963).

<sup>9</sup> G. C. Kennedy and R. C. Newton, *Solids under Pressure* (McGraw-Hill Book Company, Inc., New York, 1963).

<sup>10</sup> A. Jayaraman, W. Klement, R. C. Newton, and G. C. Kennedy, *J. Phys. Chem. Solids* **34**, 7 (1963).

total ram pressure to yield the pressure on the sample. The pressure for the Bi I-II transition varies with temperature from 25.4 kbar at 25°C to about 17 kbar at 190°C. In experiments involving extended high-temperature runs, such as the study of hcp-bcc transformations in Ti and Zr, the bismuth column becomes heated, resulting in the onset of the transition at pressures lower than for a room temperature run. The problem is then one of accurately estimating transition pressure—for even a small change in this pressure greatly influences the load absorbed by the bismuth column and, consequently, the accuracy with which the pressure on the sample is known. The temperature of the column could not be directly measured with the present setup and, hence, an indirect method was used to estimate the transition pressure. In this, experiments with the same amount of bismuth and with identical sample assemblies were run with and without heating. Any difference in the ram pressures at the onset of the bismuth transition was attributed to the heating of the column. In several runs, the bismuth transition occurred at 500 bars oil pressure on the main ram, with heating, and at 530 bars without heating. The transition pressure for the heated bismuth was calculated to be 2.5 kbar less than the room temperature value of 25.4 kbar, indicating a temperature of nearly 75°C at the bismuth column. Accordingly, in extended runs at 700–800°C, the bismuth transition pressure was scaled down by 2.5 kbar and the pressure on the sample chamber computed on this basis. The heating of the column would be different for different temperature ranges and the experiment outlined has to be carried out for every such range.

Friction corrections were estimated as before<sup>11</sup> and pressures are believed accurate to  $\pm 1.0$  kbar for the single-stage and  $\pm 2$  kbar for the double-stage apparatus.

Differential thermal analysis (DTA)<sup>9,12</sup> was employed to detect the heats of transition upon both heating and cooling at rates of 3–5°C/sec. Temperatures were measured with chromel-alumel thermocouples, using values from the standard tables in the absence of reliable pressure corrections. These temperatures could be, at best, estimated to within  $\pm 3^\circ\text{C}$ .

Samples were machined into cylinders 0.150 in. diam by 0.2 in. long and were encapsulated in tantalum or molybdenum containers. Both titanium and zirconium were high purity, iodide grade.

For resistance measurements on Ti, the high pressure electrical resistance cell described by Balchan and Drickamer<sup>13</sup> was used; this device uses pyrophyllite for piston support and is capable of generating several hundred kbar. A Bridgman-type anvil device with a  $\frac{3}{8}$  in. diam flat was used for the Zr and Hf experiments;

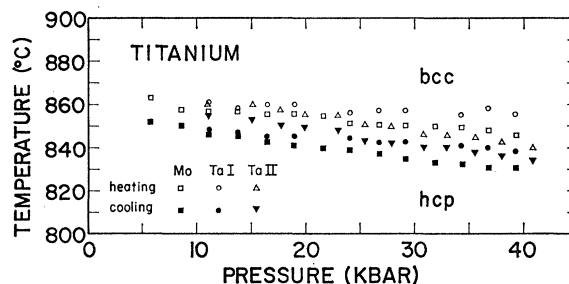


FIG. 1. Transition temperatures for titanium encapsulated in tantalum and molybdenum, as obtained on both heating and cooling. Pressures have been corrected for friction.

this device has an upper limit of 100 kbar before the carbonyl badly deforms. Silver chloride was employed as the pressure medium in all of the experiments and resistances were measured by observing changes in potential across the sample, for a small constant direct current. Generally, pressures in the lower ranges are somewhat less reliable with the high-pressure resistance cell and it is believed that they are accurate to within 15% in the range, 50–100 kbar. In the Bridgman-type apparatus, the pressures are probably accurate to  $\pm 4$  kbar.

### III. EXPERIMENTAL RESULTS

#### Titanium

The transformation temperatures for titanium, encapsulated in molybdenum and tantalum, are displayed in Fig. 1. These data are from the first compression runs only; those at the higher pressures undoubtedly reflect the effects of increasing contamination. Corrections for friction have, therefore, been made on the basis of previous experience<sup>11</sup> with the present geometry, since progressive contamination results in a lowering of the transition temperatures to an extent which cannot be readily estimated. The temperatures on the second compression runs, as compared to the first cycles, were at least 4, 6, and 10°C lower for Ti in the Mo, Ta I, and Ta II containers, respectively. A "smearing-out" of the DTA signals on heating (for the Ta I sample especially) was further evidence of alloying; all DTA signals on cooling were, however, abrupt and distinct.

A few runs were also made with a chromel-alumel thermocouple directly in contact with a titanium sample in a BN sleeve. In these experiments, the transition temperatures, on heating, progressively decreased from an initial value of 855°C to about 830°C upon repeated thermal cycling at about 10 kbar. Increasing the pressure to 40 kbar resulted in only a slight further decrease in the transition temperature.

#### Zirconium

Results for several runs of zirconium encapsulated in tantalum are shown in Fig. 2. These data are from the first compression runs only; on the second compression

<sup>11</sup> W. Klement, A. Jayaraman, and G. C. Kennedy, *Phys. Rev.* **129**, 1971 (1963).

<sup>12</sup> W. Klement, A. Jayaraman, and G. C. Kennedy, *Phys. Rev.* **131**, 1 (1963).

<sup>13</sup> A. S. Balchan and H. G. Drickamer, *Rev. Sci. Instr.* **32**, 308 (1961).

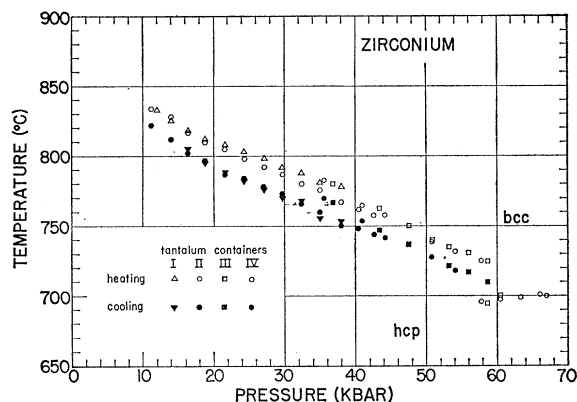


FIG. 2. Transition temperatures for zirconium, as obtained on both heating and cooling. Pressures have been corrected for friction.

for Zr in Ta I and Ta II, transition temperatures fell 3–4°C lower, indicating contamination, but to a lesser degree than for Ti. In one run where the sample was surrounded by a BN sleeve with a platinum sheet to avoid contact with the thermocouple, transition temperatures were 15–20°C lower than when encapsulated in tantalum.

Data from the four runs, representing transition temperatures obtained on heating as well as on cooling, are plotted in Fig. 2. The results from the two single-stage runs (Ta I and II) are in good agreement at the lowest pressures but diverge somewhat at the higher pressures, due presumably to differing amounts of contamination. The results from the two double-stage runs (Ta III and IV) are in good agreement at all pressures; these temperatures are slightly higher at the lowest pressure (~35 kbar) compared with the single-stage results with the more contaminated specimens. The hysteresis interval associated with the bcc-hcp transition is about 15–20°C and does not appear to vary with pressure or increasing contamination. The transition temperatures also appeared to be independent of the rate of heating or cooling, at rates from 3–5°C/sec and even up to 20°C/sec. DTA signals on cooling were always quite distinct, while those obtained on heating were fairly clear.

Near 58 kbar and 695°C, another strong thermal arrest was detected, in which the signals were very clear and pronounced and had very little hysteresis. The heat associated with this new transition may be ~3–4 times greater than that of the bcc-hcp transition, as estimated from the thermal arrests. The boundary between bcc and the new phase does *not* intersect the bcc-hcp phase boundary, if the latter is taken to lie somewhere in the hysteresis interval according to the usual conventions. Two more runs were made with the Zr again encapsulated in tantalum, in order to determine whether the abnormal position of this new transition was the result of some effect due to contamination. In these runs, the sample was compressed at room temperature to  $\geq 60$

kbar and then heated through the transformation; the data thus obtained coincide exactly with those from the Ta III and IV runs, thereby showing that the transition temperatures are not altered by the result of contamination but are a real characteristic of the transformation. After these thermal arrests were recorded, the sample was cooled to room temperature at a pressure  $\geq 60$  kbar and then unloaded. Examinations of the sample in an x-ray diffractometer indicated that the  $\omega$  phase predominated with some of the strong, low-angle hcp peaks also detectable. Similar examinations of samples cooled in the stability field of the hcp phase did not indicate any  $\omega$  phase. Almost complete conversion to  $\omega$  phase was obtained for a sample compressed to about 66 kbar at room temperature.

### Hafnium

The bcc-hcp transformation is reported<sup>5</sup> to occur normally at  $1750 \pm 20^\circ\text{C}$  for hafnium. One DTA run was made with Hf (1.8 at.%Zr as primary impurity) encapsulated in tantalum, using a Pt-Pt10Rh thermocouple. No definite thermal arrests could be detected up to 1500°C, where the run had to be given up because of the high temperature problems.

### Resistance Measurements

The results of the resistance measurements for Ti, Zr, and Hf are presented in Fig. 3.

The resistance of Ti decreases with pressure up to 80–90 kbar, at which point there is a sharp rise of about 17% followed by a somewhat rapid decrease up to 200 kbar. At higher pressures, the decrease is very gradual. The curve marked Ti<sub>1</sub> was obtained with a set of pistons which had incipient cracks and, hence, the transition pressure cannot be considered as very reliable for the reason that the calibration could have changed somewhat. However, the curve is reproduced to show the resistance behavior of Ti beyond 200 kbar. The curve marked Ti<sub>2</sub> was obtained with freshly calibrated set of pistons, but the run was terminated soon after the transition for fear of cracking the pistons. The resistance discontinuity is most likely to be closer to the transition pressure in this run than in the previous one. The sharp discontinuous rise is believed to be associated with a first-order phase transition.

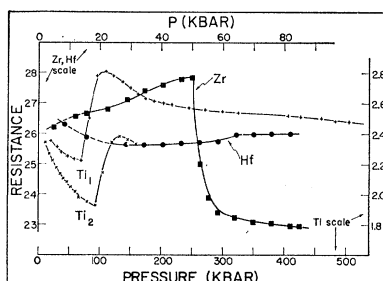


FIG. 3. Resistance measurements for Ti, Zr, and Hf as a function of pressure. Note the different scales for Ti and for Zr and Hf. Resistances are plotted in arbitrary units.

For Zr, the resistance increases with pressure up to about 51 kbar, where it begins to decrease sharply up to about 60 kbar, gradually decreasing at higher pressures. The present resistance curve differs from that<sup>6</sup> of Bridgman in two respects. First, there is a positive slope instead of a small decrease before the precipitous drop and, second, the discontinuity is near 50 kbar rather than 60 kbar. Bridgman<sup>6</sup> experienced difficulty in inducing this transition and, in some experiments, failed to obtain any evidence at all for it. The transition could not be produced by the present investigators in several resistivity runs to about 60 kbar, carried out under nearly hydrostatic conditions in a piston-cylinder apparatus.<sup>10</sup> It might be that a certain amount of shear is necessary to effect the transformation.

The resistance change with pressure for Hf is rather small and there appears to be a broad, shallow minimum around 35 kbar, with a break at about 62 kbar, beyond which the resistance varies only slightly with pressure. These features were observed in both of the runs that were made. It is doubtful whether the break in resistance for Hf is indicative of a first-order phase transformation. Bridgman's data for Hf show a somewhat larger drop up to about 40 kg/cm<sup>2</sup> and thereafter the decrease is small and the curve is rapidly flattening near 100 kg/cm<sup>2</sup>. The resistance changes involved are quite small.

#### IV. DISCUSSION

##### Titanium

It is well known<sup>14,15</sup> that both Ta and Mo lower the  $M_s$  in Ti, while the presence of solutes such as oxygen and nitrogen raise the transformation temperatures. The bcc-hcp transition temperatures, on both heating and cooling, were progressively lowered during the present experiments, indicating interdiffusion of a few at.% Ta or Mo from the container into the titanium sample, similar to the mechanism previously proposed in the uranium study.<sup>11</sup> The present results (Fig. 1) do not seem to indicate any systematic variation in the hysteresis interval with increasing contamination or with increasing pressure. Indeed, the data are scattered and cannot be considered as highly reproducible.

It may be concluded, however, that pressure does decrease the bcc-hcp transition temperature to a small extent. Smoothed boundaries for the transformation upon heating and cooling are shown in Fig. 4. These boundaries are compensated for the increased contamination at the higher pressures (i.e., near the end of the run) from the transformation temperatures obtained in a second compression cycle (see Sec. III, Titanium) but otherwise are fairly close to the actual data, as presented in Fig. 1. The connection with the presently accepted zero-pressure values is not too good. It may be

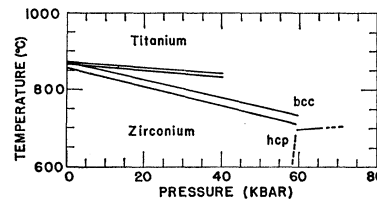


FIG. 4. Transition temperatures for titanium and zirconium, as obtained on both heating and cooling. The temperatures for the bcc-hcp transitions have been corrected for contamination effects. The dashed line for Zr indicates the hcp-Zr III boundary and is a linear interpolation between the room temperature resistance discontinuity and the region of the "triple point."

that this is a drop due to an initial rapid contamination of the sample, but it is also possible that the published zero-pressure data of 882°C is higher due to oxygen contamination of the sample which is very difficult to avoid. It is believed that the resistance discontinuity noted at ~80 kbar indicates a first-order transition.

The slope of the bcc-hcp phase boundary at zero pressure may be estimated as about  $-0.8^{\circ}\text{C}/\text{kbar}$ . For  $\Delta S$  (transition) = 0.88 entropy units (eu)<sup>16</sup> and a molar volume at the transition of  $\sim 10.9$  cm<sup>3</sup>/mole,<sup>17</sup> the change in volume is estimated as about 0.03 cm<sup>3</sup>/mole.

##### Zirconium

The effects of pressure on the bcc-hcp transformation in Zr are more pronounced than for Ti. As for Ti, Ta is known<sup>14</sup> to lower the  $M_s$  in Zr while oxygen and nitrogen raise<sup>14</sup> the bcc-hcp transformation temperatures. The progressive lowering of the Zr transition temperatures, as clearly indicated in the present experiments, is almost certainly due to alloying with the tantalum containers. The effects of this alloying are not understood quantitatively but appear to be less than for titanium and lowering of the transformation temperatures due to pressure is much more than that due to contamination.

Smoothed boundaries for the transformation upon heating and cooling are shown in Fig. 4. These boundaries are compensated for the effects of contamination, insofar as possible, but are generally close to the actual data (Fig. 2). The connection with the presently accepted zero-pressure values is fair. The distinct negative slope of the phase boundary is qualitatively in agreement with the trajectory expected from zero-pressure data. From the present experiments, the slope of the transition may be estimated as  $-2.4^{\circ}\text{C}/\text{kbar}$ ; the value of  $-5^{\circ}\text{C}/\text{kbar}$  calculated from  $\Delta S \approx 0.9$  e.u.<sup>18</sup> and  $\Delta V \approx 0.19$  cm<sup>3</sup>/mole,<sup>17</sup> is, however, in poor agreement.

The discontinuity in the resistance of Zr found at

<sup>14</sup> M. Hansen and K. Anderko, *Constitution of Binary Alloys*, (McGraw-Hill Book Company, Inc., New York, 1958).

<sup>15</sup> P. Duwez, *Trans. Am. Soc. Metals* **45**, 934 (1953).

<sup>16</sup> R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values for the Thermodynamic Properties of Metals and Alloys* (John Wiley & Sons, Inc., New York, 1963).

<sup>17</sup> W. B. Pearson, in *Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958).

<sup>18</sup> L. Kaufman, *Acta Met.* **7**, 575 (1959).

pressures in the neighborhood of 50–59 kbar at room temperature is almost certainly indicative of a first-order transformation. Although room for doubt may have existed previously since Bridgman<sup>7</sup> did not detect any volume discontinuity corresponding to the resistance discontinuity, the discovery of the thermal arrest at higher temperatures, corresponding to a new phase boundary, is strong evidence for a first-order transition. Since no other thermal arrests were detected, it is reasonable to assume that the high pressure polymorph found at room temperature is the same as that which transforms to bcc above about 60 kbar and 695°C; the dotted line near the “triple point” in Fig. 4 indicates the possible phase boundary between hcp and the new polymorph.

The problem of the “triple point” is particularly perplexing. Careful experiments rule out the possibility of strong curvature of the hcp-bcc boundary near the triple point. The effects of contamination on the bcc-hcp, hcp-bcc and bcc-Zr III transitions have been fairly well accounted for (Fig. 4) and yet the thermodynamically impossible situation arises wherein the phase boundaries do not intersect in a triple point when the bcc-hcp equilibrium boundary is taken to lie somewhere in the hysteresis interval

One possibility is the existence of another phase boundary above 700°C, which intersects the bcc-hcp equilibrium boundary. If the heat of this transition is very small, it might have escaped detection with the present technique.

Another possibility is that the presently determined bcc-Zr III boundary is not an equilibrium boundary and that, at lower rates of cooling and heating, the equilibrium boundary would be found at higher temperatures and with a proper thermodynamic intersection at a triple point. The equilibrium, low-temperature phase would not then necessarily have the  $\omega$  structure, which would have to be regarded as metastable.

An understanding of the kinetics must be based on a knowledge of the crystal structures at high pressure and temperature. The weight of the evidence<sup>8</sup> at present is that Zr III occurs in the  $\omega$  structure, although decisive evidence can be produced only for the element equilibrated within the stability region of the high pressure polymorph and investigated there. Most of the  $\omega$  phases, previously known in Ti- and Zr-base alloys, are apparently metastable transition phases obtained on cooling from the high-temperature bcc stability fields. The crystallographic similarities between the  $\omega$  and bcc structures are well recognized and it is generally considered that bcc to  $\omega$  proceeds without diffusion. It is not clear whether  $\omega$  can be produced through a diffusionless transition from hcp or face-centered cubic (fcc). Some of the present hesitation in accepting  $\omega$  as the high-pressure polymorph of Zr and Ti stems from these considerations as well as the extensive stability field of Ti III indicated by resistance measurements.

### Structural Analogies Among Ti, Zr, Hf, and Tl

It has been recognized for some time that there is a good deal of similarity between thallium and the isomorphous, fourth-column transition elements, titanium, zirconium and hafnium. For instance, the similarity in the diffusionless, bcc-hcp transformations<sup>2</sup> has been established. At room temperature and zero pressure, it is generally agreed<sup>17</sup> that the axial ratio for these four hcp structures is less than ideal, i.e.,  $c/a < \sqrt{8/3}$ , although there is some disagreement upon the precise values. As pointed out recently,<sup>12</sup> the effect of hydrostatic pressure is almost always to increase the coordination within an anisotropic structure and, for an hcp structure, this means that the axial ratio is altered toward  $c/a = 1.6330 \dots$ . Elastic moduli data have recently become available for Ti,<sup>19</sup> Zr,<sup>19</sup> Hf,<sup>19</sup> and Tl.<sup>20</sup> The quantity<sup>12</sup>

$$\xi \equiv \left( \frac{c}{a} \right) \left( \frac{C_{33} - C_{13}}{C_{11} + C_{12} - 2C_{13}} \right)$$

is greater than unity for an increase in  $c/a$ , less than unity for a decrease;  $\xi = 1.5$ , 1.8, 1.7, and 2.0, for Ti, Zr, Hf, and Tl, respectively, indicating increasing axial ratios under hydrostatic pressure. The axial ratios also increase with temperature for Ti,<sup>17</sup> Zr,<sup>17</sup> and probably Hf and Tl.<sup>21</sup>

The phase diagram for thallium up to 50 kbar is now well established due to the work of Jayaraman *et al.*<sup>10</sup>; Piermarini and Weir<sup>22</sup> have verified that the structure of the high-pressure polymorph is fcc. Although there is considerable hysteresis in the bcc-hcp transition for thallium, the bcc-fcc transformation<sup>10</sup> occurs at nearly the same temperature on heating and cooling, for a given pressure. The transformation between bcc Zr and the high-pressure polymorph reported in this paper exhibits negligible hysteresis. The volume change for the hcp-fcc transition in Tl is about<sup>10</sup> 0.6% and the difference in Helmholtz free energy between the two polymorphs is, therefore, small. Furthermore, it is expected<sup>23</sup> that the stacking fault energy is also relatively small since there is some proportionality between stacking fault energy and bulk free energy, although the precise relations are not yet clear.<sup>24,25</sup> The stacking fault energy of Ti has been estimated<sup>25</sup> as  $\sim 10$  ergs/cm<sup>2</sup>, indicating only a small difference in free energy between hcp and fcc polymorphs. Although no direct evidence exists at present for pressure-induced fcc in Ti and Zr, the

<sup>19</sup> E. S. Fisher and C. J. Renken, *Bull. Am. Phys. Soc.* **8**, 65 (1963); E. S. Fisher (private communication).

<sup>20</sup> R. W. Ferris, M. L. Shepard, and J. F. Smith, *J. Appl. Phys.* **34**, 768 (1963).

<sup>21</sup> R. W. Meyerhoff and J. F. Smith, *J. Appl. Phys.* **33**, 219 (1962).

<sup>22</sup> G. J. Piermarini and C. E. Weir, *J. Res. Nat. Bur. Std.* **66A**, 325 (1962).

<sup>23</sup> L. Kaufman, *Acta Met.* **9**, 896 (1961).

<sup>24</sup> W. Klement, *J. Chem. Phys.* **38**, 298 (1963).

<sup>25</sup> J. Spreadborough, *Phil. Mag.* **3**, 1167 (1958).

occurrence of such close-packed structures in alloys at high pressure must be considered as a possibility.

There are further similarities among Ti, Zr, and Tl in that the bcc-hcp transition temperatures decrease with pressure, giving rise to the situation where transitions to a structure of lower coordination (bcc) from a nearly close-packed structure (hcp) may be obtained by isothermal compression. Whether these transformations involve a discontinuous change in the "atomic size" and are to be considered as "electronic" transitions remains to be seen. The bcc-hcp transition<sup>26</sup> in beryllium, which normally occurs at  $1254 \pm 5^\circ\text{C}$ , also may be expected to decrease in temperature with increasing pressure and yet it is extremely unlikely that any localization of an electron could take place. It would seem more useful to attempt to take into account the covalent contributions

to the bonding in these elements. With the presence of appreciable covalent contributions, any approximations for the atoms as rigid spheres become of dubious validity.

#### ACKNOWLEDGMENTS

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<sup>26</sup> V. M. Amonenko, V. Ye. Ivanov, G. F. Tikhinskii, V. A. Finkels, and I. I. Chaporava, *Phys. Metals Metallog.* **12**, 77 (1961).

## Fundamental Optical Absorption, Electrical Conductivity, and Thermoelectric Power of Calcium Oxide\*

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The opacities of thin backed films of CaO were measured at room temperature over the energy range 5.5 to 11.3 eV. At energies below 6 eV the opacity was low. A sharp peak, attributed to the formation of excitons, was observed at about 7.0 eV. A second strong peak was observed at 8.3 eV. This peak appears to have a doublet splitting of about 0.2 eV and probably should also be ascribed to excitons. Other peaks were observed at higher energies but were less reproducible. The width of the forbidden band was estimated to be near 7.7 eV. The electrical conductivity and thermoelectric power of sprayed aggregates of CaO were measured, as a function of temperature, for several states of activation and were found to exhibit the characteristics of a pore conductor. Using these data and the theory for pore conduction, the electron affinity for CaO was estimated to be 0.7 eV.

### I. INTRODUCTION

THE work on calcium oxide to be reported here is part of a larger program whose purpose is the investigation of the electronic structure of the alkaline earth chalcogenides.<sup>1-3</sup> Interest in this family of compounds stems not only from the practical applications of the heavier oxides in oxide coated cathodes, but also because this family represents a divalent counterpart to the alkali halide family. Fundamental optical

absorption studies have previously been reported for fourteen of the sixteen members of this family and, with the work being presented here, only magnesium sulfide remains unstudied.<sup>2,3</sup> The thermoelectric properties of calcium oxide being reported here represents an extension of similar work carried out on the heavier oxides which was primarily concerned with the pore conduction properties of porous aggregates of these materials.<sup>4-6</sup>

Although much of the early work on oxide-coated cathodes involved the use of calcium oxide, not until very recently has anything relating to the electronic structure of this material appeared in the modern

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<sup>2</sup> G. H. Reiling and E. B. Hensley, *Phys. Rev.* **112**, 1106 (1958).

<sup>3</sup> G. A. Saum and E. B. Hensley, *Phys. Rev.* **113**, 1019 (1959).

<sup>4</sup> J. R. Young, *J. Appl. Phys.* **23**, 1129 (1952).

<sup>5</sup> E. B. Hensley, *J. Appl. Phys.* **23**, 1122 (1952).

<sup>6</sup> E. B. Hensley, *J. Appl. Phys.* **27**, 286 (1956).