The Pressures of Some Solid-Solid Transitions[1]

Cs, Bi, Tl, Te, Ba

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Abstract. A free piston gage capable of measuring pressures to 60 kb has been constructed. The basic element of the gage is a supported carbide vessel entered by a rotating piston. With this apparatus the pressures of various transitions have been determined with fair precision. We find the following pressures: Teflon, 5.43 kb; $AgNO_3$ I–$AgNO_3$ II, 9.78 kb; KI I–KI II, 17.48 kb; KBr I–KBr II, 17.88 kb; KCl I–KCl II, 19.28 kb; KCN I–KCN II, 19.72 kb; Ice VI–Ice VII, 21.42 kb; $AgNO_3$ II–$AgNO_3$ III, 21.2 kb; Cs I–Cs II, 22.6 kb; Bi I–Bi II, 25.38 kb; Bi II–Bi III, 26.92 kb; Tl II–Tl III, 36.69 kb; Te I–Te II, 40.12 kb; Cs II–Cs III, 41.7 kb; Ba II–Ba III, 59.6 kb. These results are in close agreement with earlier measurements of discontinuities in volume made by Bridgman.

INTRODUCTION

A number of new high-pressure devices and systems have been described within the last few years. Among these are the tetrahedral anvil device of *Hall* [1958], the piston-cylinder device described by *Boyd and England* [1960], and the belt apparatus described by *Hall* [1960]. Certain fixed pressure points are needed for the evaluation of friction in these and related types of apparatus. Without a number of fixed pressure points, it is exceedingly difficult to correlate force on a ram with pressure inside a pressure vessel.

Most recent pressure calibrations have been based on the discontinuities in electrical resistivity at polymorphic fixed points in various metals, as determined by *Bridgman* [1952]. Unfortunately Bridgman's 1952 data on discontinuities in electrical resistivity, with the exception of the Bi I–Bi II transition, do not agree with his own previously determined data for volume discontinuities. Most of Bridgman's electrical measurements of polymorphic discontinuities were obtained in a piston-anvil device, whereas his measurements of volume discontinuities were obtained in a piston-cylinder device. *Boyd and England* [1960] redetermined the Tl II–Tl III transition pressure by electrical measurements. Their value of 37 kb is somewhat lower than the value reported by *Bridgman* [1952, 1935] by both electrical and volume discontinuity measurements. Our new determination of the transition pressure of thallium, by volume measurement, closely agrees with that of Boyd and England.

volume measurements

Our own experimental apparatus and techniques as well as some preliminary results have been previously described [*Kennedy and La Mori,* 1961] and will not be repeated here.

EXPERIMENTAL RESULTS

Results of our new experiments are shown in Tables 1 and 2. Insofar as the temperature coefficient of the transition was known, all runs were corrected to 25°C.

Corrections of our rough values were made for the weight of the main ram. No corrections were made, however, for the dilation of the ram cylinder or of the high-pressure piston. These corrections have been evaluated and lie well within the uncertainty of the method. Corrections applicable to a free piston gage are discussed at length by *Johnson and Newhall* [1953].

Table 1 shows a mean value and a best value for the pressure for each transition studied. Our mean value is the average of the means for the various experiments. These means for the various experiments were determined by averaging the up-stroke transition pressure and the down-stroke transition pressure. Our best value was selected in a different fashion. It was assumed

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TABLE 1. Experimental Data for Each Transition

TABLE 1. Continued

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Up Corrected Pressure, bars	Down Corrected Pressure, bars	Mean Pressure, bars (at 25°C)	Uncertainty, bars
Bismuth I–Bismuth II			
25,480	25,370	25,425	±55
25,375	25,285	25,330	±45
25,535	25,380	25,460	±80
25,615	25,245	25,430	±185
25,520	25,300	25,410	±110
25,480	25,300	25,390	±90
25,422	25,350	25,385	±35
	Mean	25,405 ± 80	
	Best value	25,380 ± 20	
Bismuth II–Bismuth III			
27,157	26,784	26,972	±185
27,144	26,770	26,957	±185
27,171	26,756	26,964	±205
27,171	26,743	26,956	±210
	Mean	26,962 ± 195	
	Best value	26,965 ± 180	
Thallium II–Thallium III			
36,835	36,535	36,685	±150
36,805	36,585	36,695	±110
	Mean	36,690 ± 100 bars	
Cesium I–Cesium II			
23,250	21,950	22,600	±600
Cesium II–Cesium III			
42,700	40,750	41,700	±1000
43,350	40,450	41,900	±1400
	Mean	41,800 ± 1000 bars	
	Best value	41,725 ± 1000 bars	
KCl I–KCl II			
19,488	18,896	19,192	±295
19,551	19,062	19,307	±245
19,504	18,951	19,227	±280
	Mean	19,240 ± 270	
	Best value	19,275 ± 210	
KBr I–KBr II			
17,997	17,392	17,694	±300
17,939	17,566	17,752	±190
17,987	17,820	17,900	±80
	Mean	17,782 ± 190	
	Best value	17,880 ± 60	

TABLE 1. Continued

Up Corrected Pressure, bars	Down Corrected Pressure, bars	Mean Pressure, bars (at 25°C)	Uncertainty, bars
KI I–KI II			
17,729	17,151	17,440	±290
17,772	17,241	17,505	±265
	Mean	17,470 ± 280	
	Best value	17,485 ± 240	
$AgNO_3$ I–$AgNO_3$ II			
10,807	8,269	9,538	±1300
10,246			
10,813	9,307	10,060	±750
	Mean	9,800 ± 1000	
	Best value	9,775 ± 470	
$AgNO_3$ II–$AgNO_3$ III			
23,075	20,810	21,943	±1130
21,598	20,105	20,854	±750
	Mean	21,400 ± 940	
	Best value	21,200 ± 400	
Teflon II–Teflon III			
5,642	5,338	5,490	±150
	5,280		
5,529	5,286	5,407	±120
	Mean	5,450 ± 135	
	Best value	5,430 ± 95	
Ice VI–Ice VII			
21,462	21,310	21,386	±75
21,533	21,370	21,452	±80
	Mean	21,420 ± 75	
	Best value	21,416 ± 45	
KCN II–KCN IV			
20,154	19,282	19,718	±435
20,167	19,172	19,670	±500
	Mean	19,695 ± 465	
	Best value	19,720 ± 430	
Tellurium I–Tellurium II			
43,538	36,693	40,125	±3500
44,030	36,361	40,195	±3800
	Mean	40,160 ± 3600	
	Best value	40,120 ± 3500	

that the true transition pressure must lie somewhere below the lowest transition pressure obtained on the up-stroke and somewhere above the highest transition pressure obtained on the down-stroke. We have taken the average of these two values to obtain our best value. The difference between up-stroke and down-stroke transition pressures depends very much on the material involved. Certain substances with extremely sluggish transitions, such as tellurium, showed very large hysteresis loops even after extended piston rotation over a long time interval. The uncertainty we cite for each value indicates the breadth of the hysteresis loop. However, with the assumptions that residual friction is reasonably symmetrical and that the hysteresis loop is reasonably symmetrical around the true value of the transition pressure, our best value is probably much closer to the true transition pressure than is indicated by the plus or minus uncertainty. In almost all cases our best value and the mean value of the various determinations are fairly close to each other.

Bismuth. The bismuth used in the experiments was supplied by the American Smelting and Refining Company and had a purity of 99.999%. Stated impurities, as determined by standard spectrographic methods, are Mg < 0.0001%, Pb < 0.0001%, Fe < 0.0001%, Cu < 0.0001%, and Ag < 0.0004%.

The Bi I–Bi II transition was readily determined. This transition occurs exceedingly rapidly. Only a few minutes are required until equilibrium is reached. It contrasts sharply with the Bi II–Bi III transition, which appears to be very sluggish and is thus much more difficult to determine. The mean transition pressure of Bi I–Bi II is 25,405 ± 80 bars. All seven determinations of the pressure lie well within the uncertainty.

Bismuth was the only material studied in which the hysteresis loop of the transition pressure was effectively zero. In fact, in one measurement of the up-stroke transition pressure, we obtained a value slightly lower than the highest value obtained on one of the down-stroke measurements. Thus our best value of 25,380 bars for the Bi I–Bi II transition pressure was about 25 bars below the mean value obtained. Our uncertainty in determining the transition pressure for the Bi I–Bi II transition is approximately the uncertainty in reading our Heise-Bourdon tube gage which monitored the oil pressure in the main ram. Our determination is in excellent agreement with *Bridgman's* [1940*a*] best volume-measurement value of 25,150 bars corrected to 25°C. The friction on Bridgman's runs ranged from 4 to 9 per cent, however. The close agreement between the two results is due to the fact that the friction is 'symmetrical'; i.e., up-stroke and down-stroke friction are the same, and thus Bridgman's midpoint with large friction is very close to our free-piston value for which friction is almost entirely relieved.

The Bi II–Bi III transition occurs at 26,975 ± 190 bars. The mean of four determinations of this pressure is the same. This value is also in close agreement with *Bridgman's* [1940] value of 26,540 bars. *Bridgman* [1952] reported similar values for the Bi II–Bi III transition determined by electrical resistivity measurements.

Thallium. A supply of thallium was obtained from the American Smelting and Refining Company. It has a stated purity of 99.95+%. The impurities detectable by standard spectrographic methods are Pb < 0.009%, Cu < 0.0004%, Fe < 0.0001%, and Bi < 0.0001%. The thallium metal was jacketed in a thin-walled steel tube because of the very deleterious effects of thallium on the carbide high-pressure container. Our value for the Tl II–Tl III transition pressure is 36,690 ± 100 bars. This determination is in good agreement with *Boyd and England's* [1960] electrical measurement of 37.1 kb. It is somewhat lower than *Bridgman's* [1935, 1952] volume measurement of 41 kb and his electrical measurement of 44 kb.

Cesium. Our supply of cesium was obtained from the American Potash and Chemical Company. It had a stated purity of 99.0 per cent with determined impurities Rb = 0.5%, K = 0.04%, Na = 0.02%, and Li = 0.005%. The cesium was golden in color, suggesting the presence of some dissolved cesium oxides. The mean value for two determinations of the Cs II–Cs III transition pressure is 41,800 ± 1000 bars. The large uncertainty is believed to be due to the fact that the cesium was encapsulated in aluminum, and the aluminum was in contact with the piston. Our cesium was certainly impure, and this value is presented as a tentative

TABLE 2. Comparison of Present Results with Those of Bridgman

Transition	Kennedy and La Mori, kb	Bridgman (Volume), kb	Bridgman (Electrical), kb
Teflon	5.43 ± 0.09		
$AgNO_3$ I–II	9.78 ± 0.47	9.56	
		9.35	
KI I–II	17.48 ± 0.24	17.85	
KBr I–II	17.88 ± 0.06	18.05	
KCl I –II	19.28 ± 0.21	19.65	
KCN II–IV	19.72 ± 0.43	19.85	
Ice VI–VII	21.42 ± 0.04	21.82	
$AgNO_3$ II–III	21.2 ± 0.4		
Cs I–II	22.6 ± 0.6	22.5	22.5
Bi I–II	25.38 ± 0.02	25.15	24.5
Bi II–III	26.96 ± 0.18	26.54	
Tl II–III	36.69 ± 0.10	41.0	44.0
Te I–II	40.1 ± 3.5	39.3	44–58
Cs II–III	41.7 ± 1.0	44.1	53.9
Ba II–III	59.6 ± 1	59–64	60–80

one. Further efforts with better encapsulating material and purer cesium are required. Our disagreement with Bridgman's value is not to be taken seriously. Bridgman has reported two values for the cesium transition pressure, a 1948 volume discontinuity measurement of 44 kb and a 1952 electrical discontinuity measurement of 54 kb. However, the mean pressure value of his compression and decompression experiments on the electrical conductivity discontinuity was approximately 43 kb.

We have determined the Cs I–Cs II transition pressure to be approximately 22,600 ± 600 bars. This is in close agreement with *Bridgman's* [1938] value of 22.5 kb.

Potassium halides—KCl, KBr, KI. Baker and Adamson reagent-grade chemicals were used in the determination of transition pressures in the potassium-halides, KCl, KBr, and KI. The various salts were dried for several hours at 110°C before use. Each salt was precompressed at 5 kb in a mold slightly smaller in diameter than the pressure vessel. This solid salt slug was then wrapped with a .002-inch sheet of lead foil and inserted in the pressure vessel.

Each of the three salts showed transitions with very large volume changes. However, the salts also had high internal friction, and the transitions do not occur with anything like the desired sharpness. Each point required 4 to 5 hours of slow piston rotation before a good value could be obtained. Our best value for the KCl I–KCl II transition pressure is 19,275 bars. The KBr I–KBr II transition occurs at 17,880 bars, and the KI I–KI II transition occurs at 17,485 bars. As can be seen in Table 2 these values are very close to those obtained by *Bridgman* [1940*b*]. Our new values average approximately 1 per cent lower than the corresponding Bridgman value.

Silver nitrate. The silver nitrate used in our experiments was Baker and Adamson reagent grade. It was precompressed and dried in the way described for the potassium halides. Two somewhat sluggish transitions were found. $AgNO_3$ I–$AgNO_3$ II at room temperature occurs at approximately 9775 ± 470 bars. Our value for the pressure for this transition agrees closely with the 9.5 kb found by *Bridgman* [1937*a*]. A second transition in $AgNO_3$ was found with a best pressure value of 21,200 ± 400 bars; this transition was readily observed in twelve successive experiments. Pressure excursions up to 50 kb did not show any further transitions in $AgNO_3$. These results contrasted markedly with the phase diagram of $AgNO_3$ presented by *Bridgman* [1937*a*], who reported a $AgNO_3$ II–$AgNO_3$ III transition at approximately 32 kb and a $AgNO_3$ III–$AgNO_3$ IV transition at approximately 41 kb, both at room temperature. Bridgman did not report the transition in $AgNO_3$ which we found at 21 kb, and we failed to confirm his two higher-pressure transitions. *Bridgman* [1937*a*] notes a peculiar behavior of $AgNO_3$ and he states: 'On one occasion the modification II was held at room temperature at approximately 20,000 kg/cm² for forty-two hours; it had then apparently lost the capacity to change to either of the high-pressure modifications, two excursions to the maximum pressure at 60°C did not give any transition at all.' This represents a most unusual behavior, and we find it most difficult to believe that a high-pressure transition can be depressed by holding a material for a long time at a lower pressure.

Teflon. A cylinder of Teflon, ½ inch in diameter and 1¾ inches long, was machined from our laboratory stock. A sharp transition was encountered at 5430 ± 95 bars. This compares with

a value of approximately 5460 bars for the Teflon II–Teflon III transition reported by *Weir* [1953].

Water. The phase diagram for water published by Bridgman in 1937 suggests that the Ice VI–Ice VII transition should provide an excellent fixed point in the high-pressure scale. This transition has a large volume change and a very low temperature coefficient in the vicinity of room temperature.

Distilled water was placed in a cup of Wood's metal. A cap of Wood's metal was sealed on the cup with a soldering iron. Wood's metal has very low strength and serves as an excellent pressure-transmitting medium. Two determinations of the Ice VI–Ice VII transition pressure were made and are reported in Table 1. Our best value is 24,416 ± 45 bars. This is a very sharp transition and the uncertainty could probably be reduced by further effort. Our value for the transition pressure is in fair agreement with *Bridgman's* [1937*b*] value of 22,275 bars at 25°C. Because of the sharpness of this transition, the ready availability of material of very high purity, and the lack of temperature sensitivity of the transition, further effort should be made on the Ice VI–Ice VII transition. This could well be established as a fixed point with very high precision for calibration of high-pressure apparatus.

Potassium cyanide. Baker and Adamson reagent-grade KCN was dehydrated, precompressed, and sheathed as described for the potassium halides. Two determinations were made of the KCN II–KCN IV transition pressure. These are reported in Table 1. Our best value is 19,720 ± 430 bars.

Bridgman [1937*a*] reported the phase diagram for KCN. The diagram is somewhat complicated; at least four phases are present at various pressures and temperatures. Bridgman reported the KCN II–KCN IV transition to occur at approximately 19.8 kb at room temperature. A further transition, KCN I–KCN II, presumably occurs at about 5 kb but is so sluggish that it cannot be observed at room temperature. Our agreement with Bridgman's value is excellent, but we find the KCN II–KCN IV transition to be rather sluggish, and the transition pressure could not be accurately measured.

Tellurium. A supply of tellurium was obtained from the American Smelting and Refining Company. The material was of semiconductor grade, of stated purity 99.999 per cent. It was kept sealed in an argon-filled container until ready for use. Stated impurities are Mg < .0001%, Si < .0001%, Se < .001%, and Cu < .0001%.

Two determinations were made of the Te I–Te II transition pressure. Our best value is 40,120 ± 3500 bars. Unfortunately, tellurium has a very high shear strength, and it is extremely difficult to detect the onset of this transition. The hysteresis in the transition is large. Tellurium does not make a satisfactory calibration material.

Bridgman [1940*b*] reported that the Te I–Te II transition occurs at approximately 39.4 kb. This contrasts somewhat with his earlier studies [*Bridgman,* 1935], in which he reported two transitions at room temperature, one occurring at approximately 35 kb and a second at approximately 43 kb. Our determinations of volume versus pressure give no indication of a double transition of this sort, and Bridgman apparently did not encounter the double transition in his later work in 1940. *Bridgman* [1952] examined the electrical resistance of tellurium in his piston-anvil device. He found a large drop of resistance 'at a pressure never lower than 45,000 kg/cm² and never higher than 59,000 kg/cm².' He attributed the higher values to superpressing and accepted the lower value as general confirmation of the pressures achieved in his piston-anvil device.

Barium. A transition at high pressures is known in barium and has been widely used as a calibration point. *Bridgman* [1942] reported on volumetric measurements of barium at high pressures. In the table of results accompanying his paper, he listed the transition pressure as 60,000 kg/cm². *Bridgman* [1952] reported that the transition in barium, as determined by electrical resistivity measurements, occurs at approximately 80,000 kg/cm² on the increasing pressure stroke and at approximately 60,000 kg/cm² with decreasing pressure. Unfortunately, the barium transition lies at just the upper limit of pressures obtainable in our apparatus. We have a preliminary value of 59.6 kb from a single run during which a piston broke just as the transition was entered. Further work will be done on this transition.

Discussion

The results of our volume measurements on the pressures at which certain transitions take place are in very close agreement with similar measurements by Bridgman. Our determinations of pressures of transitions for most of the substances we have studied average approximately 1 per cent below those cited by Bridgman. However, in the specific case of bismuth which we have studied most extensively, we find our transition pressure slightly above that cited by Bridgman. Our results and his are summarized in Table 2. The uncertainty we cite represents one-half the double value of friction and hysteresis in our apparatus for each transition. Only if all friction and hysteresis were one-sided would the uncertainty be as great as is indicated. Because sluggishness, hysteresis, and friction are more or less the same on both up and down strokes, the mean value we cite for a transition is probably much better than is indicated by the plus or minus uncertainty. The problem of systematic error or systematic bias in our experiments toward higher or lower value is a much more difficult matter. We can, however, see no inherent reason for a systematic bias toward high or low results in the method of our measurement.

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