DECEMBER 1, 1935 PHYSICAL REVIEW VOLUME 48

Polymorphism, Principally of the Elements, up to 50,000 kg/cm^2

P. W. BRIDGMAN, *Research Laboratory of Physics, Harvard University*

(Received September 26, 1935)

A new technique is described by which pressures of 50,000 kg/cm^2 and more may be applied to solids, and the parameters of any transitions measured. A systematic examination has been made for polymorphism of many of the elements in the new pressure range. New modifications are found for Bi, Hg, Tl, Te, Ga, and I_2, and the transition parameters measured. A beginning has been made of a systematic study of polymorphism of compounds, and results obtained for KCl, KBr, and KI, which assume at about 20,000 kg/cm^2 presumably the CsCl type of structure.

THE NEW TECHNIQUE

HITHERTO nearly all my high pressure measurements have been restricted to a range of about 20,000 kg/cm^2, and by far the larger part have reached only 12,000. The limit has been set by the bursting strength of the cylinders. By subjecting the cylinders to an initial stretching considerably beyond the elastic limit it is possible to put them into such a state of internal stress that the best grades of steel will withstand pressures of the order of 40,000 kg/cm^2, but the benefit of any such treatment rapidly tapers off with time, so that 20,000 is as high as I have found it profitable to go, and even then rupture is frequent. The practical limit of the pistons with which pressure is produced is considerably higher, around 40,000 kg/cm^2.

It is evident, and in fact a number of persons have independently made the suggestion to me, that it would be ideally possible to reach any pressure whatever by making a nest of pressure apparatuses, one within the other, each inner apparatus being exposed to a uniform hydrostatic pressure all overexerted by the next outer apparatus. The extreme mechanical difficulty of carrying out this idea, even in an apparatus of only two stages, has hitherto deterred me from any such attempt at extending the pressure range. It is quite conceivable, however, that it would be possible to accomplish the desired end by subjecting the internal apparatus to a less complete support than would be afforded by a hydrostatic pressure all over its external surface. Such, has in fact, proved to be easy, and in the following results are given for a large number of routine experiments made with such an apparatus up to 50,000 kg/cm^2.

The cylindrical vessel exposed to internal hydrostatic pressure may be supported with sufficient effectiveness by applying an external pressure to the curved surface only of the cylinder. A very simple calculation by elasticity theory shows the effectiveness of such support. Consider, for example, two cylinders both initially of the same internal diameter, one with infinitely thick walls, and the other with an external diameter four times the internal diameter. To the first cylinder is applied a certain pressure, and to the second cylinder the same pressure and at the same time an external pressure equal to one-half the internal pressure. Calculation by the conventional formulas, as for example in Love's *Elasticity*, shows that the radial stretch at the inner surface of the second cylinder is only 0.28 as great as that of the first. A factor so advantageous as this cannot be gained by cold working. If the ratio of external to internal pressure could be automatically maintained in some way as the internal pressure increases, the second cylinder could obviously be carried to a much higher pressure without rupture than could the first cylinder with its infinitely thick walls.

A simple scheme by which the external pressure may be automatically maintained at a predetermined fraction of the internal pressure is illustrated in Fig. 1. The external walls of the cylinder are given a conical shape like a stopper, and this steel "stopper" is pushed into an external sleeve by the same force with which the piston is driven into the cylinder, compressing the material within it. The friction on the walls of the cone is of course a complicating factor that must be allowed for empirically, but by using carefully polished surfaces, and a graphite and vaseline lubricant the purpose is accomplished with about the proportions shown, and

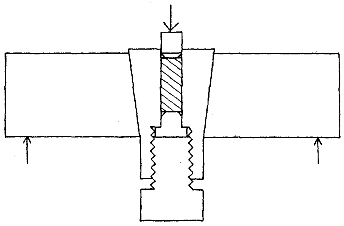

FIG. 1.

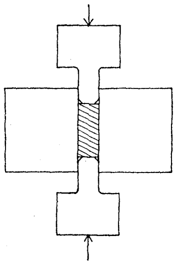

FIG. 2.

FIG. 1. Illustrates the new arrangement by which an external pressure is automatically applied to keep pace with the internal pressure. The diagram is approximately to scale; the diameter of the "stopper" at the upper end is 2.5 cm.

FIG. 2. The double ended cylinder and pistons by which the transitions of bismuth were measured.

the stopper comes back out of the sleeve without sticking on release of pressure.

As already stated, with this arrangement many routine measurements have been made to 50,000 kg/cm^2. The weak part of the apparatus is now the piston, 50,000 being beyond the reach of any steel that I have been able to find. Fortunately carboloy, the recently developed cemented carbide of tungsten and cobalt, turns out to have a much higher compressive strength than the hardest steel, and 50,000 kg/cm^2 or even considerably more may be easily reached with it; I am exceedingly indebted to Dr. Zay Jeffries of the Carboloy Company of America, through whose kind offices I was presented with sufficient carboloy in the form of rods about 6 mm in diameter to make 100 pistons 6 mm long. It is usually possible to use a single piston for half a dozen excursions to 50,000 kg/cm^2 before it breaks.

Full details of the apparatus are deferred to another paper, only a few of the more important points will be mentioned here. The simple apparatus sketched in Fig. 1 is evidently capable of yielding quantitative information about polymorphic transitions by merely determining the position of the piston as a function of pressure, which is exactly the method used in my former work at lower pressures. It is probable that the apparatus can also yield information about compressibility, although this second use has not been seriously attempted yet. There will obviously be complications because of hysteresis and friction, which, however, I believe can be overcome. In any event, the accuracy cannot be as high as in my previous work, in which pressure is truly hydrostatic and is transmitted by a true liquid. But such experiments are no longer possible at ordinary temperatures at pressures as high as this, for nearly everything freezes to the solid. The substance which would longest resist freezing is doubtless helium; Simon's[1] extrapolation indicates that even it will freeze at room temperature at a pressure in the neighborhood of 100,000 kg/cm^2, a pressure which I have actually reached under special conditions on one occasion. It has been a suprise, however, to find that the apparatus is capable of accuracy not much lower than that of the former apparatus, as has been established on several occasions when measurements of the same transition have been made with the two types of apparatus. In any event, the field is sufficiently new, and the results to be expected of sufficient interest to justify the use of methods not of the highest accuracy.

One reason that the pressure fails to be truly hydrostatic arises from the friction exerted on the walls by the material undergoing compression as it moves down into smaller volume. If the ratio of length to diameter is high, enormously high friction may be developed in this way, so that the pressure at the lower end may be only a small fraction of the pressure immediately under the piston. In this apparatus the dimensions were such, however, 6 mm diameter and length of the order of 9 mm, that the friction could not be an important fraction of the mean hydrostatic pressure. The friction is less when soft materials are used, because of their low plastic limit, and it is this kind of material that has been used in most of these investigations. Harder materials can be experimented with by embedding them in a sheath of some softer material, such as lead or even copper. Such a sheath becomes a positive necessity for many materials, particularly above 100°. In my early work I had found that mercury amalgamates and breaks the cylinder at a few thousand kilograms pressure. Action quite similar to this takes place with many of the low melting metals at these new higher pressures. Sodium, for example,

---

[1] F. Simon, M. Ruhemann and W. A. M. Edwards, Zeits. f. physik. Chemie **B6**, 62 (1929).

cannot be used directly in contact with steel at any temperature, but alloys with it and ruptures it. Tin, bismuth and others act similarly. Also such substances as sulfur attack chemically the steel, which must be protected from direct contact.

In addition to the friction of the material under compression, there is also considerable friction at the closure under the piston, which is an arrangement utilizing a conical ring as shown. The effect of both sorts of friction was eliminated from the transition pressure by taking mean values obtained with increasing and decreasing pressure. One serious result of the very considerable friction, however, was loss of sensitivity; a number of substances were found to have probable transitions by a shearing method, described in a previous paper, but showed nothing large enough to be measurable by this direct volumetric method.

Temperature control was effected through a temperature bath, which consisted of a pan soldered to the conical supporting sleeve. Solid carbon dioxide temperatures were easily reached in this way, and by means of an electric heater in oil, temperatures up to the softening point of the steel were reached. 200°C was about the limit for measurements to 50,000; at higher temperatures the cylinder softens perceptibly, as does also the carboloy piston, which seems to be notably stronger at the lower temperatures.

The detailed results now follow. First are given those elements for which it has been possible to carry through a full determination of all the thermodynamic parameters, namely, transition pressures and accompanying change of volume as a function of temperature. Next those elements are enumerated for which negative results were found, with a list repeated for the sake of completeness from a previous paper of those elements which the shearing method has shown to be probably polymorphic. Finally are given the transition parameters for the potassium halides, with a mention of other exploratory work for a few simple compounds.

DETAILED RESULTS FOR THE ELEMENTS

Bismuth

This metal was found to be polymorphic at high pressures over a year ago, and part of the results have been already summarized in print.[2] The first work with bismuth was done with a different type of apparatus from that described above, not capable of nearly such high pressures, but of sufficient usefulness to justify a brief description. In general idea it is not dissimilar from a method used by Tammann.[3] The method is sufficiently well indicated in Fig. 2. The bismuth is contained in a short cylinder, and compressed from both ends by two pistons pushed together by a hydraulic press. By the use of two pistons friction is very materially reduced, and the sharpness of the readings increased. Mechanical stability is increased by the large ends shown on the pistons. The cylinder is made of "Solar" steel; this is a water hardening silicon-manganese steel of very materially higher tensile characteristics than the chrome-vanadium steel used hitherto in my work. In fact, it was the availability of this new grade of steel that gave the impetus to all this attempt to reach higher pressures. The solar steel cylinder of Fig. 2 was treated by an initial stretching exactly as my former cylinders. Temperature was varied by means of a heating coil wound over the outside of the cylinder. With this arrangement measurements could be made up to 30,000 kg/cm^2 or perhaps more.

With this first apparatus two new high pressure forms of bismuth were discovered, and measurements were made on the transition lines I–II and II–III between 79° and 182°C. At 197° the pressure of the melting of I was located, 15,700 kg/cm^2, increasing pressure from the domain of the solid to that of the liquid. The pressure found in this way agreed well with the pressure extrapolated from former measurements up to 12,000. The melting pressure had not been held for longer than two minutes, however, when the cylinder broke, amalgamated by the liquid bismuth; the amalgamation was very obvious in the fracture.

With the "stopper" apparatus an exploration was made for other modifications at still higher pressures. The I–II and II–III transitions were first located at 134° and the change of volume determined. At somewhat less than 30,000 at

---

[2] P. W. Bridgman, Phys. Rev. **47**, 427 (1935).

[3] G. Tammann, Zeits. f. anorg. u. allgem. Chemie **199**, 209 (1931).

this temperature the cylinder broke, amalgamated by the solid bismuth. The changes of volume and also the transition pressure so found agreed well enough with the values obtained with the first apparatus. A new cylinder was now used and the bismuth enclosed in a copper sheath. This was successfully carried to 50,000 at 20°. At the upper end of the pressure range there was considerable plastic yield of the cylinder, so that a small transition might have escaped notice. On release of pressure, a very small discontinuity in the volume of not more than 5 percent of the volume change of the other transitions was found near 40,000. No special significance was attached to this at the time. But on making shearing measurements with the apparatus described in the previous paper, there appeared unmistakable evidence that this discontinuity must have been really a transition. The experiment was then repeated with two different set-ups of the "stopper" apparatus at $-79°$ and 0°C. On each occasion the break was found with decreasing pressure and there seems no doubt of the reality of the transition. The "region of indifference" of this transition unfortunately appears to be rather wide, the transition occurring with increasing pressure so near to 50,000 that it is obscured by volume creep in the cylinder. It was therefore not possible to determine the average of the transition pressure with increasing and decreasing pressure, so that the true transition pressure is restricted to a much broader region of uncertainty than is usually possible. The width of the band of indifference did not seem to be importantly less at 20° than at $-79°$, and for this reason the attempt was not made to get more accurate values by increasing the temperature, a procedure which would ordinarily be effective, but here would have been of doubtful value because of the rapid increase of plastic creep with higher temperatures. The volume change was so small that it could be determined with only small accuracy; the actual value found at $-79°$ was a little more than one-half that at 20°.

At solid CO_2 temperature the two transition points I–II and II–III are so close together that it was not possible to separate them. The total change of volume, I–III, found at this point was 0.0073, which agreed exactly with the sum of the values for I–II and II–III extrapolated from readings at higher temperatures. In view of the breaking of the cylinder when melting of I took place, no attempt was made to obtain points on the melting curves of II or III. The parameters at the triple points given in Table I were obtained by calculation. The parameters for the melting of II and III are very rough, since they involve extrapolations and the difference of nearly equal quantities. The parameters of the transition III–IV given in the table are also very rough.

The transition parameters are collected in Table I, and the phase diagram is shown in Fig. 3 and the changes of volume in Fig. 4. It will be seen that there is a rough analogy between the phase diagram of bismuth and that of water, which possibly may be of significance.

Mercury

The transition was first found at CO_2 temperature at about 14,000 kg/cm². The mercury

TABLE I. *Transition parameters of bismuth.*

PRESSURE (kg/cm²)	TEMPERATURE (°C)		$\frac{d\tau}{dp}$	Δv (cm³/g)	LATENT HEAT (kg cm/g)	LATENT HEAT (g cal./g)
			LIQUID–I			
1	271.0		−0.00342	0.00345	−549	−12.87
5,000	251.9		418	386	485	11.37
10,000	228.8		506	419	416	9.76
15,000	200		61	440	346	8.11
			I–II			
18,000	170		−.196	−.00480	108	2.53
19,000	150		−.196	485	104	2.44
24,100	50		−.196	475	78	1.83
29,200	−50		−.196	455	51	1.20
			II–III			
22,800	170		−.298	−.00300	44_5	1.04
23,600	150		−.298	.00310	44	1.03
26,900	50		−.298	.00310	33	.77
30,300	−50		−.298	.00275	20	.47
			III–IV			
43,000	−100		+.3(?)	−.0003(?)	−.2(?)	−.0047(?)
43,500	+ 50		+.3(?)	.0004(?)	.4(?)	−.0094(?)
			APPROXIMATE TRIPLE POINTS			
			L–I–II			
17.300	183	L–I	−.0066	.0045	−310	−7.27
		I–II	−.196	−.0047	110	2.58
		L–II	+.00046	−.0002	−200	−4.69
			L–II–III			
22,400	185	L–II	+.0004(?)	−.0002(?)	−200(?)	−4.69(?)
		II–III	−.298	−.0029	45	1.05
		L–III	+.0091(?)	−.0031(?)	−155(?)	−3.64(?)
			I–II–III			
32,300	−110	I–II	−.196	.0043	36	.84
		II–III	−.298	.0025	14	.33
		I–III	−.221	.0068	50	1.17

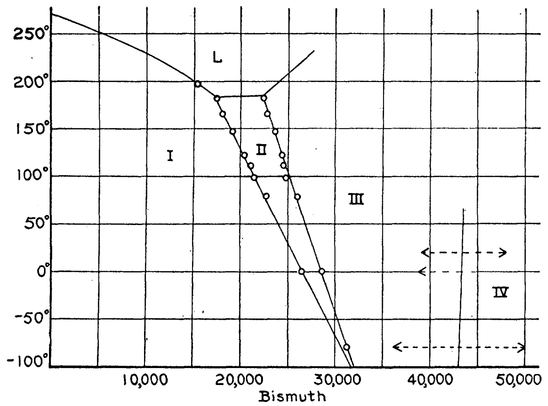

FIG. 3. The phase diagram of bismuth, pressure in kg/cm² as abscissa against temperature in degrees Centigrade as ordinate. The arrows on the transition line III–IV mark the limits of indifference.

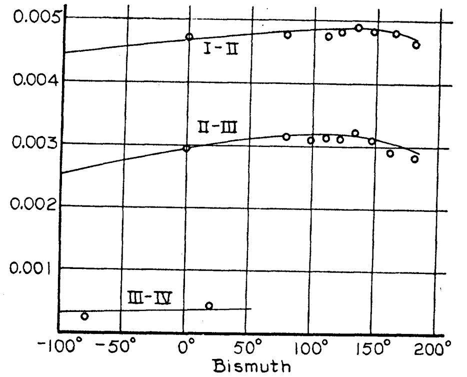

FIG. 4. The volume changes for the various transitions of bismuth, temperature in degrees Centigrade as abscissa against volume change in cm³/g as ordinate.

TABLE II. *Transition parameters of mercury.*

PRESSURE (kg/cm²)	TEMPERATURE (°C)	$\frac{d\tau}{dp}$	Δv (cm³/g)	LATENT HEAT (kg cm/g)	(g cal./g)
10,000	−109	0.0077	0.00104	22.1	0.518
15,000	− 73	67	.00071	21.1	.495
20,000	− 43	57	51	20.6	.483
25,000	− 17	48	41	21.8	.511
30,000	+ 5	40	36	25.0	.586
35,000	+ 23	32	32	29.6	.694

was frozen directly into the apparatus without protecting sheath. Determinations at this temperature were made with increasing pressure, decreasing pressure, and then with increasing pressure again. Temperature was then raised to 0°C and the pressure to about 36,000 to maintain the mercury solid, and the transition located with decreasing pressure. The run was terminated by leak of liquid mercury past the piston due to melting, in spite of the fact that the pressure in the apparatus was well above the melting pressure at this temperature. The change of volume of the transition was moderately large, corresponding to the total volume decrement produced by an increase of pressure of about 2000 kg, but nevertheless it was not sufficiently large. In conjunction with the super- and subpressing which the transition will support, it was not found possible to land exactly on the equilibrium pressure, but the transition, when it started, always ran to completion. The apparatus was then set up again, and the measurements at −79° repeated, with good checks for both pressure and change of volume. Temperature was then raised to −43°, where it was maintained constant by continual manual manipulation by two assistants. After determination of the transition parameters from above and below, temperature was raised to +22°, and again two determinations made. No attempt was made for higher pressures because there was slight leak due to melting at +22°. At room temperature no other transition was found up to 45,000. A notable feature was the very markedly lower compressibility of the high pressure modification. The transition parameters are given in Table II, and the experimental points are shown in Fig. 5.

Extrapolation of the transition curve to atmospheric pressure suggests that the transition should run in the neighborhood of liquid-air temperature. Such a transition has not been reported, but should now be searched for. There are measurements of the x-ray structure down to liquid-air temperature; the best recent work is in accord about the structure and finds no change with temperature. There was an early determination that gave a discordant structure, but apparently even this cannot be explained in terms of a transition. In all these x-ray determinations the mercury was, of course, frozen at a higher temperature and then cooled to liquid-air temperature; under these conditions the transitions may have been suppressed, even if the temperature of the transition had been slightly exceeded, because of viscous resistance to the transition at low temperatures. If the mercury is cooled sufficiently beyond this temperature, however, the transition should run. There are

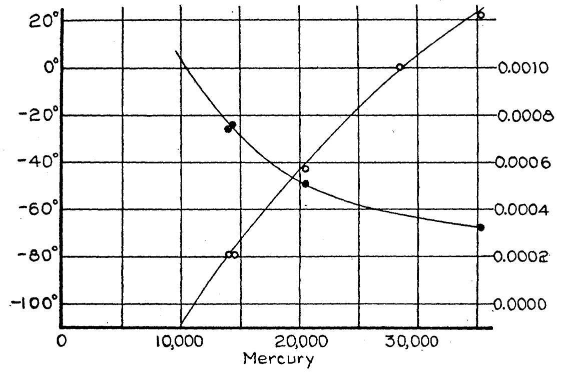

FIG. 5. The phase diagram and the volume change of the transition of mercury. Pressure in kg/cm² as abscissa, against temperature in degrees Centigrade as left-hand ordinate scale, and volume change in cm³/g as right-hand ordinate scale. The pressure-temperature points are shown as open circles, and the volume changes as filled-in circles.

measurements of the specific heat and the electrical resistance of mercury all the way from hydrogen temperatures. For the specific heat there are measurements by Simon[4] and by Pollitzer.[5] The measurements of Simon are very much the smoother; if these are plotted against temperature a very distinct break in the tangent will be found between 53° and 68°K. Simon does not comment on this, but it seems to me too pronounced to be spurious, and may perhaps be evidence of the transition. The resistance of mercury has been carefully measured at Leiden;[6] there is a gap in the temperature range from −156° to −183°. If the deviations from linearity of resistance as a function of temperature are plotted, a break will be found in this temperature interval, which again appears to be beyond experimental error. However, I do not regard this as definite as the specific heat evidence.

There is another consideration; it is possible that the transition curve found above does not extend all the way to atmospheric pressure, but it might be terminated by a triple point with still another modification somewhere below −79°, and with a low temperature transition line running steeply enough not to cut the temperature axis at atmospheric pressure. Such a state of affairs would demand the existence of yet another transition line, with a transition pressure at room temperature somewhere between 35,000 and the melting pressure, 12,000. Such a transition could not be observed at room temperature with the 50,000 apparatus because of leak, and certainly has not been observed with my other pressure apparatus. But at lower temperatures such a transition should be observable with the former apparatus. Accordingly a special examination was made for a new transition at −79° with the regular 12,000 apparatus. Pressure was now transmitted with a true liquid, and the indications were very much more sensitive than with the 50,000 apparatus. No transition was found up to 10,000 kg/cm². It therefore seems to me highly probable that the transition curve discussed above extrapolates to atmospheric pressure, and if the transition is not entirely suppressed by viscosity it will be found at atmospheric pressure not far from liquid-air temperature.

Thallium

The material was some which I had inherited from the late Professor T. W. Richards, and had been highly purified. Four different set-ups were used. In the first two the thallium was allowed to come directly in contact with the steel. The first run gave successful readings at 0° and 35°, reaching at 0° a maximum pressure of 51,000. There is a high pressure transition; the band of indifference is fairly wide, and although it was possible to locate the beginning of the transition with increasing pressure it was not possible to get a good value for Δv with increasing pressure, because it is obscured by plastic yield in the cylinder. The second set-up gave good readings at CO_2 temperature, and again Δv only with decreasing pressure. At 0° the run was terminated by the thallium blowing out past the piston. The third set-up gave good readings at 0° and 75°, the transition having become so sharp at 75° as to give good values for Δv both with increasing and decreasing pressure. At 180° the cylinder broke, amalgamated by the thallium, at a pressure which later proved to be almost exactly a transition pressure. It has been my rather common experience that rupture due to the

---

[4] F. Simon. Ann. d. Physik **68**, 241 (1922).

[5] Pollitzer, Zeits. f. Elekchemie u. angew. physik. Chemie **19**, 513 (1913).

[6] Onnes and Holst, Comm. Phys. Lab. Leiden, No. 142a, 1914.

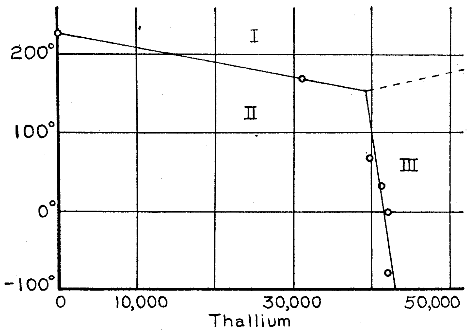

FIG. 6. The phase diagram of thallium, pressure in kg/cm² as abscissa against temperature in degrees Centigrade as ordinate.

amalgamation effect is quite likely to take place while a transition is in progress; perhaps there is greater mobility during the transition, or perhaps the new phase has an intrinsically greater penetrating effect. The fourth and last set-up was with the thallium completely surrounded with a copper capsule to protect the steel. With this set-up a point was successfully determined at 170°, which proved, however, on plotting to have both too low a pressure and too low a change of volume to fit in with the other points. Thallium is known to be polymorphic at atmospheric pressure, and the transition line has been followed by Werner[7] up to 3000 kg/cm². This transition is of the abnormal ice type, temperature falling with increasing pressure. My point at 170° fits almost exactly on a linear prolongation of Werner's curve, and there can be little doubt but that this is the transition I–II.

TABLE III. *Transition parameters of thallium.*

PRESSURE (kg/cm²)	TEMPERATURE (°C)	$\frac{d\tau}{dp}$	Δv (cm³/g)	LATENT HEAT (kg cm/g)	LATENT HEAT (g cal./g)
		I–II			
1	227	-0.00187_5	0.00004_4†		
39,000	153		.00024	−41.7	−0.98
		II–III			
43,000	−100	− .0632	−.00039	+ 1.1	+ .026
39,000	+153		−.00053	+ 2.7	+ .063
		I–III*			
39,000	153	+ .00242	−.00029	−39.0	− .91

* The parameters for I–III are at the triple point I- III and are calculated.
† Werner's value.

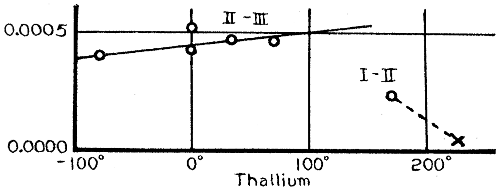

FIG. 7. The volume changes for the transitions of thallium, temperature in degrees Centigrade as abscissa against volume change in cm³/g as ordinate. The point at 227° for the transition of I–II is the value of Werner.

The phase diagram demanded by these considerations is shown in Fig. 6, and the changes of volume in Fig. 7. The II–III line, obtained by calculation from the thermodynamic parameters which are given in Table III, is shown dotted. At 170° the I–III transition was not found up to 45,000; this maximum at this temperature was set by plastic yield in the cylinder. It will be seen that this is consistent with the calculated I–III line.

Thallium was also examined by the shearing stress method at room temperature. The shearing strength curve has marked changes of direction in it, and there can be no doubt of the existence of other forms. It is not easy to determine from the shearing curve alone, however, whether the proper interpretation of it is one or two transitions. If the results of this volumetric analysis are accepted as meaning that there cannot be more than one transition, then the shearing experiments give 25,000 for the mean pressure of the transition. This is much lower than the value found above, and indicates an unusually large displacement of transition pressure by shearing stress.

Tellurium

The material was obtained from Kahlbaum; it was formed into a single crystal by my method of slow solidification, which should have effected an additional purification. This substance has a transition at room temperature in the neighborhood of 45,000 with a very large volume change, and at lower pressures probably another transition with volume change so much smaller that there is not complete certainty about it. Runs were made with three different set-ups. The first showed no transition to 52,000 at CO_2 temperature. A transition with unusually large volume

---

[7] M. Werner, Zeits. f. anorg. Chemie **83**, 275 (1913).

change was then located at 41,000 at 145°, but the volume change was not measured. The volume change was so large that it was easy to obtain pressure readings on the two-phase system. At 90° the experiment was terminated at 47,000 by fracture of the piston before the transition had put in an appearance. The second set-up gave at 171° an equilibrium point at 41,000. By cautious manipulation, what appeared to be a satisfactory value for the change of volume was also obtained at this temperature. The difficulty is that because of indifference and friction the transition runs to completion only at pressures very near the maximum attainable with the apparatus. At 142° a good value was obtained for the equilibrium pressure, but the indifference and friction were here so much greater that the piston was fractured in trying to force the reaction to run to completion in order to determine Δv. All the behavior at high pressure apparently indicates that we are here dealing with a transition much like that between ice I and III. That is, there is very little latent heat, and the transition may run with almost explosive rapidity at high temperatures, but there is an enormous temperature coefficient of transition velocity, so that at lower temperatures the transition will not run perceptibly under practical conditions.

After the measurements just described, explorations were made with the shearing apparatus at room temperature; this gave large and striking breaks, the only interpretation of which seemed to be two transitions. It is highly probable that the transition at the higher pressure, near 50,000, is the transition described above, the viscous resistance at room temperature being overcome by the shearing forces, as is not unusual. The transition at lower pressures seemed new. The volumetric apparatus was accordingly set up again, this time with the tellurium enclosed in a tin sheath, not to protect the steel, which was not necessary because there seems to be no chemical attack, but to reduce friction, which is unusually great with tellurium and makes the results somewhat irregular. At room temperature a doubtful transition with volume change near the limit of the detectible was found with increasing and decreasing pressure at a mean pressure of 36,000. At 85°, doubtful results were again obtained, the readings during increasing pressure being obscured by an effect which later proved to be due to slight leak of the tin. The results at 100° of the original set-up were now reexamined, and a slight break found at a pressure which extrapolates linearly from the two just found. I therefore think that the location of this transition is established sufficiently well to justify putting it in the phase diagram, but it must be remembered that it is not entirely free from doubt. The Δv values are too uncertain to more than estimate; they cannot be much larger than 0.0001 cm³/g.

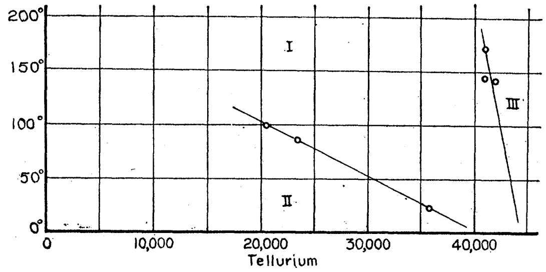

FIG. 8. The phase diagram of tellurium, pressure in kg/cm² as abscissa against temperature in degrees Centigrade as ordinate.

The transition parameters are indicated with sufficient accuracy in Fig. 8. In addition to the pressure-temperature values shown there, Δv II–III at 171° is 0.0058 cm³/g.

Gallium

A high pressure transition would be expected here for the same reason as for bismuth, namely, because the melting curve is of the ice type. The transition was at once found at CO_2 temperature at about 20,000; the change of volume is large, readings are easily made with the two phases present, and repetition gave good checks. Two other points were then obtained at −41° and −11°. No other transition was found to 46,000. The transition line is of the ice type and intersects the extrapolated melting line only slightly beyond the limit of my previous measurements.[8] It was tempting to try for points on the melting line of II; this was not possible with the 50,000 apparatus, but the pressures are so low as to be within the reach of previous types of apparatus. A special cylinder was therefore con-

---

[8] P. W. Bridgman, Proc. Am. Acad. **56**, 104 (1921).

structed, much like that used in my measurements on the alkali metals to 20,000, only somewhat smaller. I was fortunate to obtain from Dr. W. M. Craig a supply of 16.5 grams of highly purified gallium. With this, measurements were made with the new apparatus by the conventional piston displacement method, pressure being transmitted by isopentane, and measured by a manganin pressure gauge in the liquid, so that all frictional effects were eliminated.

A large number of readings were made with the special apparatus. At first there appeared to be certain very puzzling inconsistencies. The explanation was presently found to be that there is still another high pressure modification, II′, very much like II in its thermodynamic properties, but totally unstable with respect to it. Points were obtained on both transition lines I–II and I–II′, but only on the one melting line L–II′. The points on the melting line were obtained by the procedure of raising temperature at constant volume. The reason for this was that the preliminary, and as it later proved, incorrect values for the change of volume on melting led to the expectation that this melting line would be nearly horizontal, and in this case the ordinary procedure would have been useless. The procedure of changing temperature gives much less accurate values than the other. The values so obtained checked within the expected accuracy with the values calculated from the data for the other transitions, so that it did not seem worth while to repeat for the improvement in accuracy that could doubtless have been obtained by the other method. Although no points were obtained on the L–II line because of some caprice with which the phases appeared, the existence of a melting line lying higher than L–II′ was checked on one occasion by carrying the solid phase II a degree or more above the melting temperature of II′ without melting. In view of the fact that a solid practically never superheats, this constitutes almost a certain check of the explanation in terms of a third absolutely unstable phase.

Advantage was taken of the opportunity to measure the changes of volume on the melting line of I, thus making possible a calculation of its thermodynamic parameters. This had not been previously possible because the quantity of gallium then available was too small. Over the first 6000 kg the new determinations of the melting temperature of I as a function of pressure agree almost exactly with the former values, but above 6000 the new temperatures are somewhat lower, the maximum difference being 1° at 12,000.

The results are shown in Figs. 9 and 10, and the parameters of the transition are collected in Table IV. The value for Δv at atmospheric pressure shown in Fig. 10 is the value of Boyer, 0.00529 cm^3/g; it is seen to lie almost exactly on the curve with my high pressure values. No parameters are given in the table explicitly for the melting of II and II′ except at the triple points; experimental accuracy did not justify the attempt to estimate the variation of these parameters along the melting lines. The initial calculated slopes of these lines are indicated with sufficient accuracy in the figure.

Gallium is only the second example I have encountered in which a totally unstable phase appears at high pressures. The other example is water (both H_2O and D_2O). Perhaps it is significant that in both these cases the ordinary melting curve is of the ice type.

TABLE IV. *Transition parameters of gallium.*

PRESSURE (kg/cm²)	TEMPERATURE (°C)		$\frac{d\tau}{dp}$	Δv (cm³/g)	LATENT HEAT (kg cm/g)	LATENT HEAT (g cal./g)
			L–I			
1	29.85		−0.00205	0.00529	−782	−18.3
2,000	25.7		210	555	790	18.5
4,000	21.5		215	585	803	18.8
6,000	17.1		221	625	822	19.2
8,000	12.6		234	665	813	19.0
10,000	7.7		252	705	785	18.4
12,000	2.5		270	740	755	17.7
			I–II			
12,230	0		− .0085	− .0098	+314	7.4
14,580	−20		− .0088	98	281	6.8
16,800	−40		− .0095	98	240	5.6
18,800	−60		− .0108	98	193	4.5
20,500	−80		− .0130	98	145	3.4
			I–II′			
12,800	0			− .0098	+314	7.4
			− 0.0852			
13,390	− 5.0			—	—	
			TRIPLE POINTS			
			L–I–II			
12,050	2.4	L–I	− .00270	.00740	−755	−17.7
		I–II	− .00852	− .0098	+317	+ 7.4
		L–II	+ .00151	− .0024	−438	−10.3
			L–I–II′			
12,750	0.4	L–I	− .00277	.0075	−740	−17.3
		I–II′	− .00852	− .0098	+314	+ 7.4
		L–II′	+ .00137	− .0023	−426	− 9.9

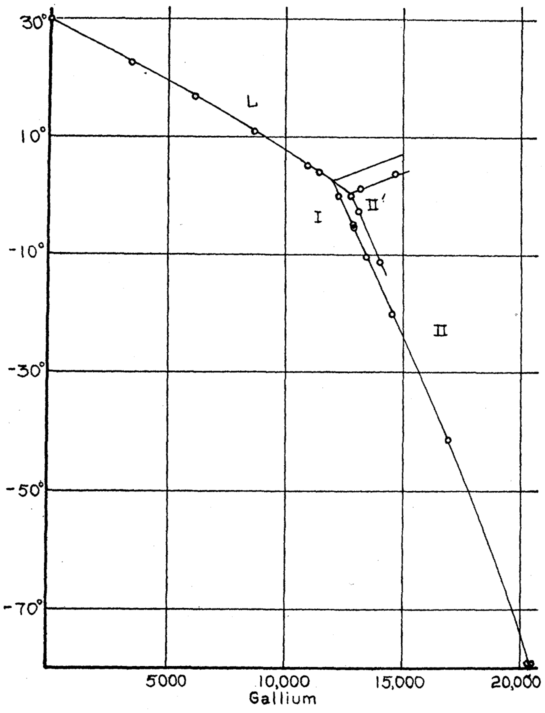

FIG. 9. The phase diagram of gallium, pressure in kg/cm² as abscissa against temperature in degrees Centigrade as ordinate.

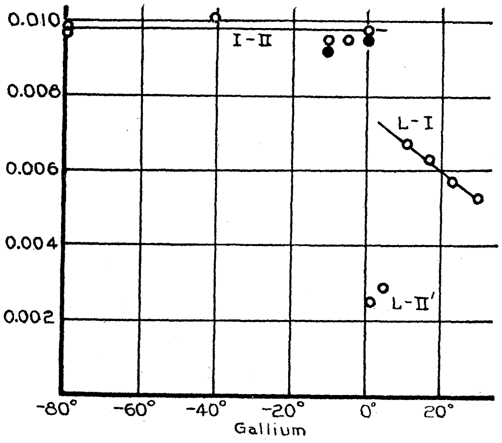

FIG. 10. The volume changes for the transitions of gallium, temperature in degrees Centigrade as abscissa against volume change in cm^3/g as ordinate. The filled-in circles are for the transition I–II′.

Iodine

This was found to have a transition at CO_2 temperature with small but unmistakable change of volume. The pressure limits of the transition are unusually wide; the transition runs to completion at once with increasing pressure at 20,600 kg/cm², and on decreasing pressure the transition runs at once to completion on reaching 10,800. The run was repeated with complete check both for the pressure limits and for the volume change, which is between 0.004 and 0.005 cm^3/g. A run was then made at 40°, and no perceptible difference was found in the pressure limits or in the change of volume. No other transition was found up to 53,000 at either temperature. A second set-up was then made, and readings made on a time schedule twice as long as on the first set-up, two minutes between readings instead of one, in the endeavor to narrow the pressure range. This was moderately successful, the pressure range now being 6000 instead of 9800, and the mean pressure 12,500 instead of 15,700. The volume change was essentially the same as before. It is therefore probable that the transition line of iodine runs nearly vertically, that is, with small latent heat, at a pressure not far from 13,000, and a volume change not far from 0.0045 cm^3/g.

The shearing apparatus gave both on the first trial and on repetition an unmistakable discontinuity with increasing pressure at about 20,000, which is doubtless the transition just described. But a second set-up showed practically nothing with increasing pressure and only a minor break with decreasing pressure. This emphasizes the fact that the shearing measurements give only qualitative indications of transitions.

SUMMARY OF EXPLORATIONS FOR THE ELEMENTS GIVING NEGATIVE RESULTS

There follows now a brief summary of these elements for which negative results were obtained by the volumetric method. It must be again emphasized that the sensitiveness is not as great as is possible at low pressures with the former apparatus, in which the pressure is transmitted by a true liquid. The greatest difficulty arises from friction; this results in irregularity of the readings, the motion of the piston having a tendency to take place in jumps. These jumps simulate small transitions. What is more, sometimes the jumps repeat themselves both with increasing and decreasing pressure. In these cases it is particularly difficult to be sure that small transitions have not been missed. However, I do not believe that on the average any transition with volume change much larger than 0.001 cm^3/g would have escaped detection.

The arrangement in the following is by columns in the periodic table.

Lithium. Nothing to 46,000 at CO_2 temperature.

Potassium. Nothing to 52,000 at CO_2 temperature.

Caesium. Probably nothing to 52,000 at 0°. This is more doubtful; there is some evidence for a transition at 25,000. Discontinuities were found four times both with increasing and decreasing pressure, but the uncertainty is particularly large here because of the very great compressibility of caesium, and I am inclined to think that the discontinuities were the result of friction.

Gold. Nothing to 51,500 at room temperature. The compressibility of gold stands strikingly out of line with that of copper and silver, and it therefore seemed to me not unlikely that a transition might be found.

Magnesium. Nothing to 51,000 at CO_2 temperature nor to 39,000 at 150°C.

Calcium. Nothing to 51,000 at CO_2 temperature.

Cadmium. This is known to have two new modifications at room temperature with very small volume change.[9] The transitions are very hard to detect, and up to now have been found only with single crystal material; the pressure of the two transitions is nearly the same, and in the neighborhood of 5000. Runs with the new volumetric apparatus were made at CO_2 temperature. It is fairly certain that there was a transition with increasing pressure near 20,000. The same result was found on repetition, but the transition could not be found with decreasing pressure. It is not unlikely that this is the transition already found at room temperature, made highly viscous by the low temperature. If this is the explanation it means that the reverse transition ran so close to atmospheric pressure that it could not be disentangled from the various creep effects always present at the zero on release of pressure. No other transition was found to 44,000 at CO_2 temperature. It would probably pay to examine this metal further at other temperatures.

Barium. Nothing to 51,000 at CO_2 temperature nor +150°.

Indium. Nothing to 50,000 at room temperature. The crystalline structure of indium is tetragonal, rather unusual in a metal; a transition would not have been surprising.

Carbon, graphite. Nothing to 52,000 at CO_2 temperature nor 155°.

Germanium. Nothing to 52,000 at room temperature; the friction was unusually high.

Tin. Probably nothing to 51,000 at CO_2 and room temperature; the shearing experiments suggest a transition.

Lead. Nothing to 52,000 at CO_2 temperature nor at 150°.

Phosphorus, dense variety of black phosphorus. At CO_2 temperature nothing was found to 52,000; the cylinder broke at the maximum. The second set-up gave nothing at 150° to 36,000, where the cylinder broke. In both cases the break was evidently due to chemical attack.

Arsenic. Two independent set-ups were used. The first gave nothing to 50,000 at 140° and the second nothing to 52,000 at 20° and 100°. A transition was expected because of the similarity of the crystal structure to that of bismuth.

Antimony. Nothing was found to 52,000 at room temperature or at 125°. A transition was expected because of the similarity of bismuth and antimony. However, it was found in the shearing experiments that there is very probably a transition near 50,000, which may have been suppressed in these volumetric experiments by viscosity.

Sulfur, amorphous modification. This showed nothing to 40,000 at room temperature, where the cylinder broke, doubtless by chemical attack, since the sulfur was directly in contact with the steel.

Selenium. The amorphous variety was examined at CO_2 temperature to 44,000. There were two rather large jumps during increasing pressure between 25,000 and 30,000 in the direction of increasing density, and one would therefore suspect an irreversible transition to the metallic form. However, a direct determination of the density after the run showed no permanent change. The matter should be examined further.

The metallic form showed nothing to 46,000 at CO_2 temperature nor at +155°.

---

[9] P. W. Bridgman, Proc. Am. Acad. **60**, 346 (1925).

OTHER ELEMENTS PROBABLY POLYMORPHIC AT HIGH PRESSURE

There is repeated here for the sake of completeness a list of elements which the method of shearing described in a previous paper has shown to be probably polymorphic at high pressure, namely: lithium, calcium, vanadium, manganese, zinc, strontium, yttrium, antimony, barium, lanthanum, cerium, praseodymium, erbium, and thorium.

Some of these elements appear in the list which have given negative results by the volumetric method of this paper. It is probable that in such cases the volume change may be too small to detect. The other elements which have given positive indications by the shearing method have not yet been investigated by the volumetric method.

RESULTS FOR COMPOUNDS

We now pass from the elements to consider a few simple compounds. The systematic investigation of polymorphism among the compounds will evidently be very time consuming; I am planning to take up this investigation in the near future. Most of my activity in this preliminary investigation was confined to the alkali halides. One or another of these salts was investigated a good many times in the course of the development of the apparatus. One would suspect that by the application of sufficient pressure the potassium, sodium, and lithium salts could be made to undergo transition from the simple cubic NaCl structure to the body-centered CsCl structure, since this transition has already been found in the rubidium halides at moderate pressures. The expected transition was found almost at once with the potassium salts at pressures in the neighborhood of 20,000, but apparently pressures higher than 50,000 will be required for the transitions of the sodium and lithium salts.

KCl. Clear single crystal material was used. Measurements have been made on this substance with five different set-ups, and in spite of this the data are not as complete as for the other two potassium halides. Three cylinders ruptured during the measurements; the rupture of one was almost certainly due to the chemical action of the metallic sodium in which the NaCl was embedded in order to make pressure more nearly hydrostatic. The other ruptures I think were probably just bad luck, due to damage received in previous exposures. One cylinder ruptured in which the KCl was protected from contact with the steel with a sheath of lead, and in the other no protection was used. Four of the five set-ups were made with the same type of cylinder as that used for the first measurements with bismuth; the fifth was an early form of the small (6 mm piston) apparatus, from which the stopper shaped cylinder later evolved.

The experimental results are shown in Fig. 11.

KBr. Clear single crystal material was used. Two independent sets of measurements were made, at six temperatures altogether, with the same cylinder, of the double piston bismuth type, with no accident. The results are shown in Fig. 12. The regularity of the results is, I think, surprising, in view of the very great difference between the readings obtained with increasing and decreasing pressure, due both to the friction of the pistons, and the intrinsic width of the region of indifference itself. This latter, judging from comparison with other transitions, must be very much the more important factor at low temperatures. At room temperature there was a difference in the transition pressures of 13,600 kg/cm^2 when approached from above and below. This decreases irregularly with increasing temperature; at 235° it had dropped to about 3000.

KI. In addition to the first exploratory runs, when the existence of transitions in this series of compounds was first found, runs were made at four temperatures with the double piston bismuth apparatus, and at room temperature with the same early form of the 6 mm piston apparatus as used with KCl. The results are shown in Fig. 13. The pressure difference between increasing and decreasing readings is about the same as for KBr, being 13,400 at room temperature, and dropping off with increasing temperature, but perhaps not as rapidly as for KBr. The great width of the band of indifference explains why the transition was not found before at room temperature in an exploration up to 20,000.[10]

Comparison of the results for the six rubidium

---

[10] P. W. Bridgman, Zeits. f. Krist. **67**, 371 (1928).

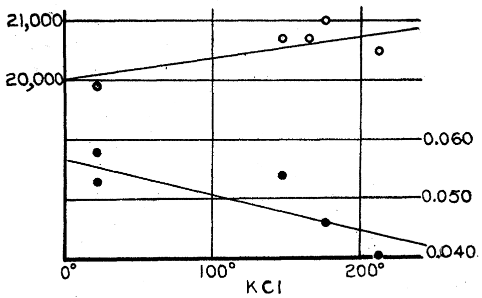

FIG. 11. The transition parameters of KCl. Temperature in degrees Centigrade as abscissa against pressure in kg/cm² as left-hand ordinate, with the corresponding points shown as open circles, and volume change in cm³/g as right-hand ordinate, with the corresponding points as filled-in circles. Notice that the usual order of the pressure-temperature coordinates is here reversed.

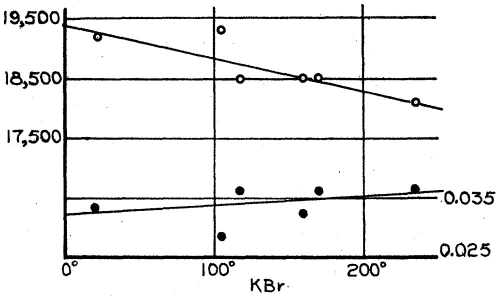

FIG. 12. The transition parameters of KBr. Temperature in degrees Centigrade as abscissa, against pressure in kg/cm² as left-hand ordinate, with the corresponding points shown as open circles, and volume change in cm³/g as right-hand ordinate, with the corresponding points as filled-in circles. Notice that the usual order of the pressure-temperature coordinates is reversed.

and potassium salts shows some interesting resemblances. At temperatures below 200° the order of the transition pressures is the same in the potassium and the rubidium series, the transition pressure increasing from the iodide to bromide to chloride. This is the reverse of the order in the series NH_4Cl, NH_4Br, NH_4I. At 0° the pressure difference between iodide and chloride is not dissimilar in the potassium and rubidium series. Above 200° the transition curves for potassium iodide and bromide cross; in the rubidium series there will probably also be crossing, but at higher temperatures.

The important thermodynamic parameters of the transitions at 130° are collected in Table V.

TABLE V. *Transition parameters of the potassium halides at 130°C.*

Salt	Pressure (kg/cm²)	ΔV (cm³/g)	Fractional Decrease of Volume	$\frac{d\tau}{dp}$	Latent Heat (kg cm/g)	Latent Heat (g cal./g)	Change of Internal Energy (kg cm/g)
KCl	19,900	0.055	0.108	+0.200	−84	−1.97	+1006
KBr	19,300	$.032_5$	.102	−0.188	+52	+1.22	680
KI	17,850	$.026_5$	.087	+0.430	−18	− .42	472

The density of the ordinary modification at the pressure of transition was obtained by extrapolating the second degree formulas which have been found for the compressibility in the range up to 12,000.[11] The corresponding fractional changes of volume at the transition in the rubidium series, from chloride to iodide was: 14.6, 11.3 and 10.7 percent. The order is thus seen to be the same in the rubidium and potassium series. The numerical magnitudes are somewhat less in the potassium series; this is to be expected because of the much higher pressure of the transition.

The latent heats are seen to be only a small part of the total energy change during the transition. The order of energy change is the same in the potassium and rubidium series; the absolute magnitudes are several-fold greater in the potassium series, as is also the range from chloride to iodide.

Other compounds. This covers the compounds the transitions of which have been measured up to the present with the 50,000 apparatus. In

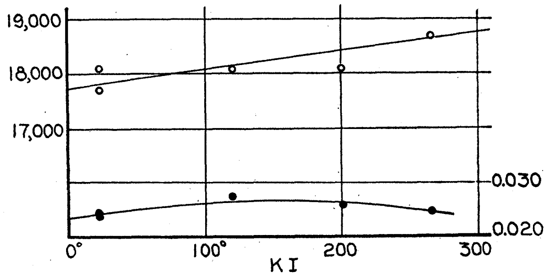

FIG. 13. The transition parameters of KI. Temperature in degrees Centigrade as abscissa, against pressure in kg/cm² as left-hand ordinate, with the corresponding points as open circles, and volume change in cm³/g as right-hand ordinate, with the corresponding points as filled-in circles. Notice that the usual order of the pressure-temperature coordinates is reversed.

---

[11] J. C. Slater, Proc. Am. Acad. 61, 135 (1926).

addition, a number of explorations have been made with negative results. Naturally the greatest amount of effort was spent in trying to find the transition in the sodium series. NaCl gave nothing at room temperature with two different set-ups, the first to 32,000 and the second to 50,000. NaI is the member of the series that would be expected to show the transition most readily; this gave negative results at room temperature with four different set-ups, to 46,000, 49,000, 48,000, and 57,000, respectively. However, it has already been mentioned in the previous paper that the shearing curve of NaI begins to bend over at 50,000, and I believe the transition is not far away.

Another interesting salt of the alkali halides series is CsF; this crystallizes with the NaCl structure, although all the other caesium salts are body-centered cubic. One might expect to be able to force the transition to the body-centered structure by high pressure. Two separate set-ups with CsF, for which I am again indebted to Dr. R. W. G. Wyckoff, gave negative results, the first to 42,000 at room temperature, and the second to 56,000 at 137°. It would thus appear that the fluorides are qualitatively different from the other halides. In view of the failure to obtain the transition with CsF, it seemed hardly worth while to explore the fluorides of any of the other alkali metals.

In addition to these, sugar gave negative results to 40,000 at room temperature, and BaS to 39,000 at room temperature. PbTe, on the other hand, probably has a small transition at a mean temperature of 18,000, but this is not certain; there is no further transition up to 39,000. The explorations mentioned in this paragraph were made with a preliminary form of apparatus, only one-third as sensitive as the final form.

I am indebted to the Rumford Fund of the American Academy of Arts and Sciences for financial assistance in purchasing some of the supplies.

DECEMBER 1, 1935 PHYSICAL REVIEW VOLUME 48

Intranuclear Forces

Eugene Feenberg* and Julian K. Knipp, *Research Laboratory of Physics, Harvard University*

(Received August 16, 1935)

Quantitative information as to the nature of intranuclear forces has been obtained by considering the hydrogen and helium isotopes, using a Hamiltonian of the exchange type based on the neutron-proton model with interactions between all the particles. The interactions between like particles are taken to be the same for protons and for neutrons except for the small Coulomb force between protons which accounts for at least half of the difference in the binding energies of He^3 and H^3. It is not inconsistent with existing experimental evidence to assume the range of such forces to be about the same as the range of neutron-proton forces. By making these assumptions and by using simple attractive potentials, it is found that the forces between like particles are given by a potential with depth not greater than 30 mc^2 and with an effective radius of action which must be less than 2.8×10^{-13} cm to be consistent with experimental data for the binding energies. A more accurate determination of the constants based on assuming a close correlation of the three- and four-body problems with "equivalent" two-body problems gives the depth of the proton-neutron potential as 74 mc^2 and of the like-particle potentials as 26 mc^2 and a range of 2.2×10^{-13} cm for the forces. Reasons for believing in the reliability of the "equivalent" two-body method for determining approximate binding energies for three- and four-body problems are discussed. It is shown furthermore that if the exchange operators multiplying the neutron-proton interaction potentials are assumed to be linear combinations of the Majorana and Heisenberg types, it is possible to explain the large scattering of neutrons on protons at low velocities. The proportion of the Heisenberg to the Majorana operator in the linear combination necessary to obtain the correct scattering is about one-fifth. It is then shown that in the three- and four-body problems such an operator can to a good approximation be represented by an equivalent Majorana operator and that because of this fact the results obtained for nuclear energies and for the magnitude and range of the forces (in which Majorana operators were used) remain the same except that the depth of the potential for like particles is increased from 26 to 41 mc^2. The latter value yields a scattering intensity for protons in hydrogen which agrees qualitatively with the experimental results.

---

* Now at University of Wisconsin.