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Phase changes

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CONDENSED SYSTEMS AT HIGH PRESSURES AND TEMPERATURES

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SCHENECTADY, NEW YORK

[Reprinted from the Journal of Physical Chemistry, **63**, 1934 (1959).]

CONDENSED SYSTEMS AT HIGH PRESSURES AND TEMPERATURES

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Received June 3, 1959

Considerations of the internal pressures of solids indicate that tangible products of superpressure processes will be hard, strong, refractory materials. A brief study showed that boron nitride melts at about 3500° at 80,000 atmospheres and is a good electrical conductor while molten. Some of the minerals associated with natural diamond (quartz, garnet, olivine) indicate that some natural diamonds probably formed at pressures of at least about 55,000 atmospheres and temperatures of at least about 1300°. It is expected that future studies of diamonds and their inclusions will yield information about the deeper layers of the earth's crust.

This paper will treat briefly three subjects which are united by virtue of their common connection with high pressure: first, a few remarks on the rules for recovering unchanged any new substances which may be prepared at high pressure; second, some recent exploratory work on the high temperature, high pressure behavior of boron nitride and carbon; third, some comments on the geological applications of the laboratory studies of high pressure minerals.

As you know, the field of high pressure has been receiving increasing attention during the past few years, a state of affairs which must be gratifying to Professor P. W. Bridgman and other pioneers in this field. Much of this new interest rests upon the preparation of interesting or valuable substances at high pressure and the subsequent recovery and use of these substances at low pressure. Of these substances, diamond, and coesite, a dense form of silica, are probably the best known, although many others have been prepared. Before very long many more undoubtedly will be discovered, and it is interesting to try to see what these substances will be like.

In Fig. 1 one can see the phase diagram of bismuth as determined by Dr. Francis Bundy of our laboratory.[1] Let one begin with bismuth at room temperature and compress it. At first it merely becomes denser, but at about 24,800 atmospheres, it changes abruptly into another allotropic crystalline form, known as "Bismuth II." This change is easily detected by the sudden increase in density or by the sudden increase in electrical conductivity. As the bismuth is compressed further, it changes into a third crystalline form, and so on. At about 125,000 atmospheres one reaches the most recently discovered form, and by then it is time to turn back. As one reduces the pressure the bismuth steadily expands, transforming from one form into another, until by the time we have reduced the pressure on it to one atmosphere we again have the ordinary kind of bismuth. Too bad. All that squeezing for nothing. Yet the majority of substances, when subjected to pressure, behave in a similar fashion. They may change into new, interesting forms willingly enough, but they carelessly revert to their ordinary forms as soon as the pressure is reduced, long before one can get a good look at them. Diamond, on the other hand, is a much more friendly crystal, at least to scientists, and it faithfully preserves at one atmosphere the crystalline form which it acquired at a high pressure.

As a beginning toward understanding why some high pressure phases can be recovered at one atmosphere, let us consider the internal pressures of substances. By "internal pressure" one refers to the cohesive or attractive pressures which hold substances together in the solid or liquid form against the disruptive forces of thermal agitation and mechanical tearing.

The notion of internal pressure can be given more precise form if one defines it as $(\partial E/\partial V)_T$, where E is the internal energy, V is volume and T is the absolute temperature. Thus the internal pressure of a perfect gas is zero at any pressure. If one evaporates a liquid at constant temperature, one overcomes the internal pressure of the liquid by thermal agitation so that the energy of evaporation divided by the volume change gives one a measure of the internal pressure of the liquid. The internal pressures of most liquids are surprisingly high, between 2000 and 6000 atmospheres—perhaps good glues have even higher internal pressures. The internal pressure inside a crystal is probably not the same in all directions but varies with direction. However, a suitable averaging process could always yield a value for the internal pressure which had thermodynamic significance.

A few more remarks on the nature of internal pressure are worthwhile. From the definition of internal pressure as $(\partial E/\partial V)_T$ it follows that it can be expressed in terms of other thermodynamic quantities as

$$P_\text{i} = \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

where P, T and V are connected by the equation of state of the substance. If the equation of state has the general form

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(1) F. P. Bundy, *Phys. Rev.*, **110**, 314 (1958).

$$P = \frac{RT}{V + b(v)} - a(v)$$

so that the pressure exerted by the substance is regarded as the sum of thermal agitation plus the interatomic forces of attraction and repulsion, then it follows that

$$\left(\frac{\partial E}{\partial V}\right)_T = a(v)$$

The term $a(v)$ is a function of volume and is positive for attraction and negative for repulsion. Clearly substances can have negative internal pressures, but the sum of the internal and external pressure can never be less than zero, since this would correspond to an explosion.

If one compresses a liquid or solid at constant temperature, its internal pressure would be expected to fall as the external pressure increases, for the atoms of the substance tend to repel each other more strongly as they are moved closer together from the equilibrium separations which they had at low external pressures.

In Fig. 2 the internal pressure of a substance is plotted as a function of the external pressure to which it is exposed. Because the internal pressure of a substance decreases with external pressure, but can never fall so low that the internal repulsion exceeds the external pressure, the internal pressure approaches the negative of the external pressure asymptotically. At a very, very high pressure the internal pressure must very nearly equal the negative of the external pressure. This implies that in the absence of phase changes the curve of internal pressure *versus* external pressure is concave upward or, in other words, the change of internal pressure with external pressure becomes less negative as the density of the substance increases. This is physically reasonable and corresponds to a decrease of compressibility with increasing pressure or density.

Suppose now that the substance undergoes a phase change at high pressure. The density of the new phase will certainly not be lower than that of the original phase, and in most cases the new, high pressure phase will have a higher density. Hence the rate of change of internal pressure with external pressure will be less negative for the new phase than for the old. Because the internal pressure must approach the negative of the external pressure at very, very high pressures, we can conclude that the internal pressure of the newly formed high pressure phase is less than the internal pressure of the old phase from which it was formed.

This seems reasonable, because one would expect the atoms of a substance to repel each other more strongly in a denser phase produced by the application of external pressure.

not necessarily

If the new phase is compressed further, its internal pressure will of course decrease, and perhaps other new phase changes will occur, each accompanied by a decrease in internal pressure. The shape of the curve suggests that phase changes would be more numerous at lower external pressures, because there is a larger internal pressure change available there. This seems borne out by experience; phase changes become relatively scarcer at higher pressures, both for substances in general and for any one substance in particular.

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If starting from a high pressure, one reduces the

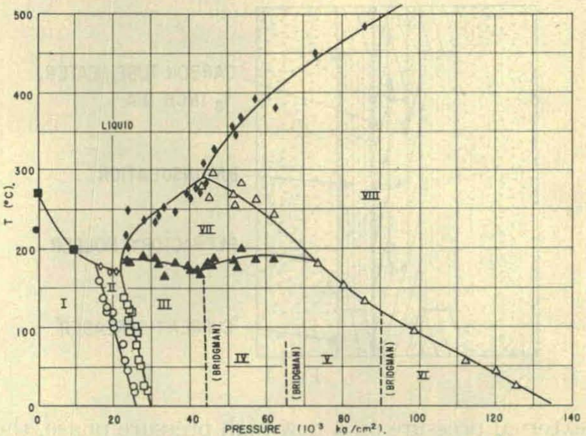

Fig. 1.—Phase diagram for ~~BN~~. Bi

$$\left(\frac{\delta P_{IN}}{\delta P}\right)_T = T\left[\frac{\delta}{\delta P}\left(\frac{\delta P}{\delta T}\right)_V\right]_T - 1$$

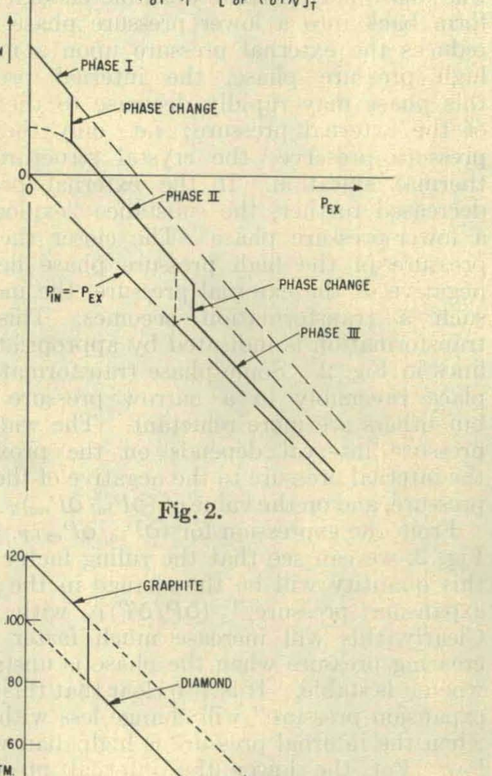

Fig. 2.

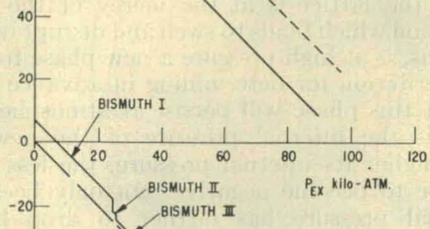

Fig. 3.

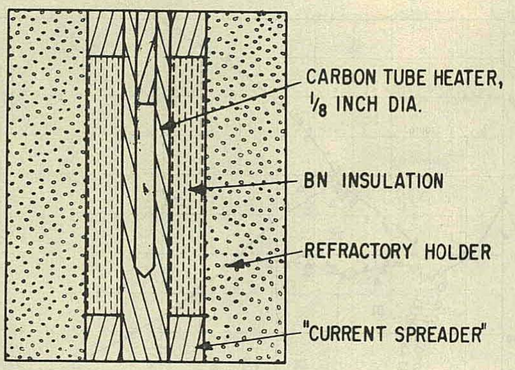

Fig. 4.

external pressure on a new high pressure phase, the internal pressure of this phase will increase. However, as the external pressure approaches the pressure at which this new phase first formed, this phase may become unstable enough to transform back into a lower pressure phase. As one reduces the external pressure upon a metastable high pressure phase, the internal pressure of this phase may rapidly decrease to the negative of the external pressure; *i.e.*, only the external pressure preserves the crystal structure against thermal agitation. If the external pressure is decreased further, the substance "explodes" into a lower-pressure phase. The closer the internal pressure of the high pressure phase lies to the negative of the external pressure, the more likely such a transformation becomes. This reverse transformation is indicated by appropriate dashed lines in Fig. 2. Some phase transformations take place reversibly in a narrow pressure interval, but others are more reluctant. The width of the pressure interval depends on the proximity of the internal pressure to the negative of the external pressure, and on the value of $(\partial P_{\text{in}}/\partial P_{\text{ex}})_T$.

what about rate processes?

From the expression for $(\partial P_{\text{in}}/\partial P_{\text{ex}})_T$, shown in Fig. 2, we can see that the ruling factor affecting this quantity will be the change in the "thermal expansion pressure," $(\partial P/\partial T)_V$, with pressure. Clearly this will increase much faster with decreasing pressure when the phase is unstable than when it is stable. It is also clear that this "thermal expansion pressure" will change less with pressure when the internal pressure is high than when it is low. For the lower the internal pressure, the more the lattice is at the mercy of the thermal agitation which tends to swell and disrupt it.

Thus, if at high pressure a new phase forms, the best criterion for determining in advance whether or not this phase will persist at atmospheric pressure is the internal pressure of the new phase. The higher its internal pressure, the less likely it will be to become negative, not only because the internal pressure has farther to drop before it can become negative, but also because the internal pressure falls less rapidly with decreasing external pressure when the internal pressure is high.

Since the internal pressure invariably falls as the external pressure increases, the best way to have a high pressure phase with a high internal pressure is to start at a low pressure with a parent phase which has a high internal pressure, and then quench the high pressure phase before reducing the pressure upon it. Of course the higher the pressure at which the phase change takes place, the more important it will be to have a parent phase which has a high internal pressure.

Ignores energy barriers, rate processes and possibility of new bond orbitals!!

Thus if we compare the internal pressures of bismuth and carbon as a function of the external pressure at room temperature, we would have something similar to that shown in Fig. 3. The values given for internal pressures are only approximate and were estimated from the mechanical properties of these solids. But it is clear why the two substances respond to pressure as they do. The internal pressure of carbon is quite high—some graphite "whiskers" have measured tensile strengths[2] of 200,000 atmospheres. Thus at the room temperature hypothetical transformation of graphite to diamond at 20,000 atmospheres, the internal pressure of diamond is still in no danger of becoming negative. However, the internal pressure of bismuth is already so low at one atmosphere, that when it changes into the bismuth II form its internal pressure is already negative. Naturally by heating a diamond one can reduce its internal pressure until the diamond changes to graphite.

The internal pressure of a substance increases as its temperature is decreased, but not indefinitely. Thus even at 0.1°K. the internal pressure of a high pressure phase might become negative as the external pressure is reduced. If the reversion to the low pressure phase involved an increase of entropy or volume, which seems possible, then the process might be useful as an adjunct to other cooling methods used to reach low temperatures.

From these considerations it seems to the author that most of the new substances which will be found as the products of high pressure, high temperature processes will be fairly hard, strong substances, whose parents are refractory materials which have high internal pressures at one atmosphere. Probably carbon has the highest internal pressure of any substance known today, so that the synthesis of a new substance substantially harder than diamond would be important not only for industrial reasons but also because its existence would substantially increase the range of both pressures and substances which might be expected to yield interesting new high pressure phases which could be quenched and recovered at low pressure. The internal pressure of carbon being what it is, about 200,000 atmospheres, it probably would not be worthwhile at this time to attempt to prepare substances at pressures much higher than about 400,000 atmospheres, for the new substances probably would not survive the decompression to one atmosphere. Fortunately this pressure is well above the static pressures currently available for high temperature synthesis, and we still have much to look forward to. Of course, the study of matter while it is under high pressure will continue to be fascinating.

The next topic is a brief description of some recent exploratory work on the high temperature, high pressure behavior of boron nitride and carbon,

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(2) R. Bacon, *Nature*, **182**, 297 (1958).

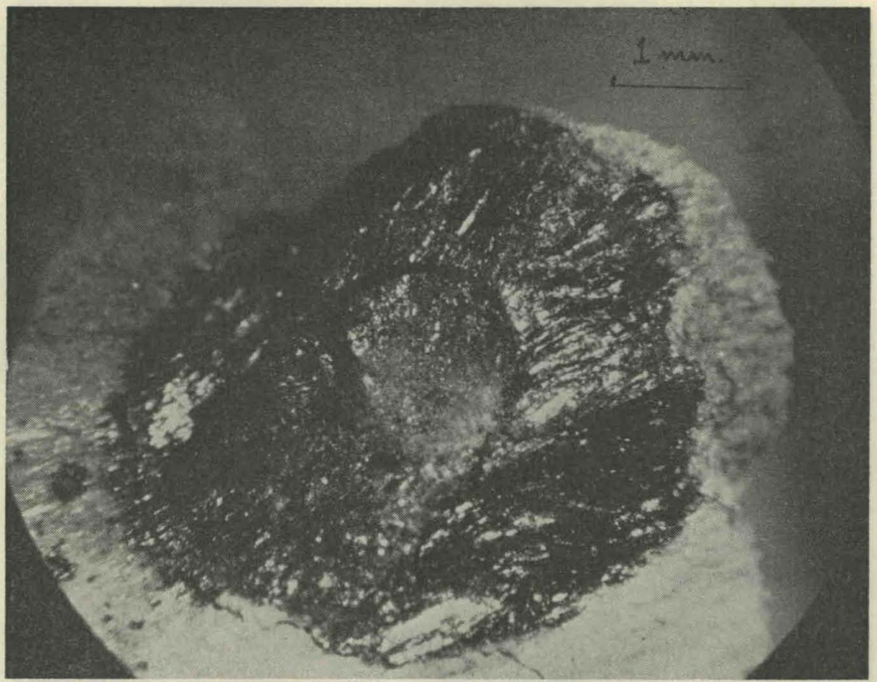

Fig. 5.—Photograph of zirconia melted at 65,000 atm. in a carbon tube.

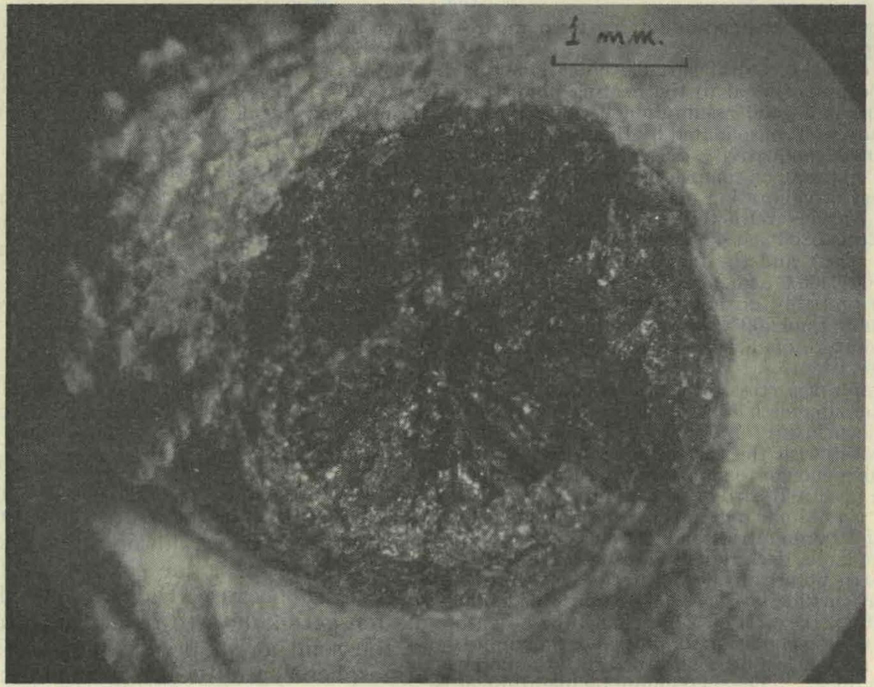

Fig. 6.—Photograph of boron nitride melted at 65,000 atm. in a carbon tube.

two very refractory substances. As one might expect, there are certain advantages in using high pressure for some high temperature studies. The main advantage is that many chemical reactions are more or less suppressed, particularly those in which a gas is ordinarily a product.

A typical reaction chamber arrangement for these high temperature studies is shown in Fig. 4. The zone of highest temperature is at the mid-length of the carbon heater tube. Various materials may be placed inside the tube. An electric current heats the tube, and the ends of the tube fit into carbon rings to reduce the current density and heat generation at the ends. The tube is electrically and thermally insulated by a shell of rammed boron nitride powder, which is in turn contained within a refractory cylinder of lower thermal conductivity than the boron nitride. When the heater tube is at its hottest, the refractory next to the boron nitride does not quite melt and its electrical conductivity remains very low. Solid boron nitride is also a very poor conductor of electricity. As long as the carbon heater tube carries 99% of the current, one can obtain a fairly good measure of its temperature from the electric power dissipated in it.

Such a reaction chamber was subjected to high pressure in a suitable apparatus and then heated and cooled under pressure. Any changes in electrical resistance during the course of the experiment were noted as useful indicators of changes occurring in the high temperature zone. The re-

Fig. 7.—Photograph of boron nitride which melted at 80,000 atm.

action chamber could be examined in detail after it was removed from the apparatus.

The temperature of the central part of the carbon tube was assumed to be proportional to the heating power dissipated in it. This is a good assumption because the refractories are already well consolidated by the high pressure, and so their thermal conductivity does not change much because of further sintering or compacting at high temperature. For purposes of calibration one observed the power required to melt various refractories, such as magnesia (melting temperature 2800° at one atmosphere), zirconia (m.p. 2600° at 1 atm.) and the tantalum carbide–carbon eutectic (m.p. 3300° at 1 atm.). The pressures used in these experiments probably do not increase these melting temperatures by more than 200°, Strong having found that the melting temperature of nickel is increased by 150° at 80,000 atmospheres.[3]

A photomicrograph of a cross section of the hottest part of the chamber after zirconia had been melted in it at 65,000 atmospheres is shown in Fig. 5. It is interesting that the zirconia did not react with the carbon tube. Presumably the pressure was high enough to suppress any such reaction, which would have produced carbon monoxide.

Figure 6 shows a photomicrograph of a cross section of the chamber in which boron nitride had just melted at 65,000 atmospheres. The large, dark radially arranged crystals in the center are frozen boron nitride. Surrounding them is the wall of the carbon tube heater. The boron nitride did not extensively attack the wall of the carbon tube because it was held in this molten condition for only about a minute. However, enough carbon has been absorbed into the boron nitride to color it black. The maximum temperature of the boron nitride was estimated to be about 3400° in this experiment.

Figure 7 shows a photomicrograph of a cross section of the chamber in which boron nitride has melted and attacked all the nearby carbon heater. This experiment was done at 80,000 atmospheres and the temperature was estimated to be about 3500°. One can see the large flakes of the frozen melt. These large flakes sharply indicate the extent of the molten zone. Their radial arrangement is the result of the radial temperature gradient which existed as the melt froze. The outer portions of the melt were the coolest and were the first to freeze. The inner portions were the last to freeze, and were often visibly richer in boron nitride than the outer parts. A Debye–Scherrer pattern of part of the melted zone showed the presence of graphite, hexagonal boron nitride and a trace of boron carbide. No diamond or cubic boron nitride was detected, which indicates that these substances probably are not stable at 80,000 atmospheres and 3500°. There was no strong evidence for a mixed crystal of boron nitride and carbon in either the hexagonal or cubic form.

Experiments similar to this one, but carried out at different temperatures, showed that solid boron nitride is a good electrical insulator but that molten boron nitride conducts electricity about as well as graphite.

The melting temperature of boron nitride increases with pressure, as shown in Fig. 8, and is estimated to be 3200° at 30,000 atmospheres, 3400° at 65,000 atmospheres and 3500° at 80,000 atmospheres. The uncertainty in these temperatures is probably 100°. The literature value for the melting temperature of boron nitride at low pressure is 2730°. The increase of its melting temperature with pressure implies that molten boron nitride has a lower density than the solid hexagonal form or the solid cubic form. This is interesting because Hall[4] found the density of molten germanium to be greater than the density of the solid at all pressures up to about 180,000 atmospheres, and solid germanium has a cubic structure like diamond or cubic boron nitride.

It would be interesting to determine the melting curve for carbon at high pressures, but there does not seem to be any material which can hold molten carbon without reacting with it or contaminating it. Perhaps this problem can be solved during the next several years.

The third and last portion of this paper has to do with some studies carried out in our laboratory on certain so-called "high pressure minerals."

The best known and most studied of these naturally occurring minerals is diamond, but plain

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(3) H. M. Strong, *Phys. Rev.*, *J. Geophys. Res.*, in press.

(4) H. T. Hall, THIS JOURNAL, **59**, 1144 (1955).

diamonds are not nearly as interesting as the diamonds which contain inclusions of other minerals. These minerals can be olivine, diopside, magnetite, zircon and certain types of garnet, as well as less common minerals.[5,6] Quartz has been reported occasionally as an inclusion in diamonds, particularly in some from Brazil,[5] but a careful investigation by us has so far shown that all such diamonds do not carry quartz entirely surrounded by diamond, but instead the quartz merely adheres to or has been deposited in fissures in these diamonds. This is an interesting point which bears on the synthesis of natural diamond, because we have found that in the range of pressure and temperature at which it is now possible to form diamond, quartz is not stable. A piece of quartz next to a growing diamond invariably changes into a denser form of silica known as coesite. If natural diamonds could form where quartz was stable, then they could have formed at pressures and temperatures far below those now found necessary in the Laboratory. This does not appear likely, so that the role of diamond as a high pressure mineral seems better established than ever. Incidentally, to my knowledge, no one has ever yet found coesite included in diamond.

In Fig. 9 we see a tentative phase diagram for carbon as a function of pressure and temperature. The chain line encloses the region reached experimentally by Bridgman and by Basset. The diamond–graphite equilibrium line is fairly well known at low temperatures and pressures by calculation from thermodynamic data, according to Rossini and Jessup.[7] At higher pressures and temperatures there is indicated a broad band which corresponds to the uncertainty of the position of the equilibrium line. We have studied the growth and destruction of diamond seeds in this region from 50,000 to 110,000 atmospheres, but so far the measurement of the pressure has proved difficult enough to leave some uncertainty in the position of the line, and we seek more precise measurements before publishing our results.

Although it may be true that there is a low pressure limit below which diamond cannot be formed, even metastably, the phase diagram does not indicate any upper limit to the pressure at which diamond could be formed except that it would have to be less than the pressure at the center of the earth, some 3.6 million atmospheres.

However, some diamonds contain olivine, a basic magnesium–iron silicate. Presumably this is a very common mineral deeper in the earth. Recently Ringwood[8] has discovered that the iron-rich form of olivine, called fayalite, can be transformed into a spinel crystal form at 55,000 atmospheres and 600° and that this spinel form can be recovered at one atmosphere. Experiments in our laboratory have confirmed this discovery, and in addition we attempted to change the magnesium-rich olivine called forsterite into a spinel form. But no spinel form was obtained at pressures as high as 130,000 atmospheres. When the phase diagram for the olivine–spinel system has been extended to higher pressures, we shall probably be able to set a maximum pressure limit or maximum depth of formation on those diamonds which contain inclusions of olivine. At present it is only possible to say that these diamonds could have formed at pressures as high as 130,000 atmospheres. This would correspond to a depth in the earth of about 400 km.

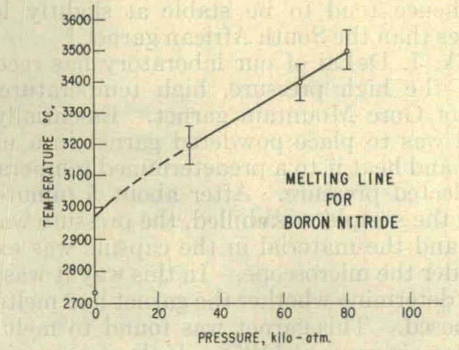

Fig. 8.

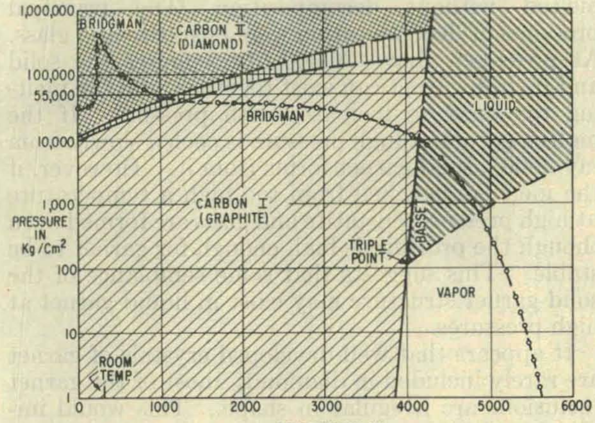

Fig. 9.

As mentioned earlier, certain types of garnet can occur as inclusions in diamond. The pyrope–almandine garnets are the most common of these, and such garnets are also found in the diamond-bearing blue ground of the South African diamond fields. Coes[9] and Yoder,[10] among others, have shown that many garnets require high pressure for their formation, and the pyrope–almandine garnets are among them. Thus a study of the behavior of such garnet at high pressures and temperatures might tell us more about the genesis of natural diamond and the deeper layers of the earth's crust.

A garnet which is very similar to this South African garnet is found in Gore Mountain, New York. The Gore Mountain garnet contains a little more iron and a little less magnesium than the South African garnet. The experience with garnet would indicate that the Gore Mountain garnet

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(5) E. Gubelin, *J. Gemmology*, **III**, No. 5 (1952).

(6) A. F. Williams, "The Genesis of the Diamond," Ernest Benn, London, 1932.

(7) F. D. Rossini and R. S. Jessup, *J. Research Natl. Bur. Standards*, **21**, 491 (1938).

(8) A. E. Ringwood, *Nature*, **178**, 1303 (1956).

(9) L. Coes, Jr., *J. Am. Ceramic Soc.*, (1955).

(10) H. S. Yoder, Jr., *Am. Min.*, **XL**, 342 (1955).

would hence tend to be stable at slightly lower pressures than the South African garnet.[9]

Mr. A. J. DeLai of our laboratory has recently studied the high pressure, high temperature behavior of Gore Mountain garnet. Essentially his method was to place powdered garnet in a nickel capsule and heat it to a predetermined temperature at a selected pressure. After about 5 minutes of heating the sample was chilled, the pressure was reduced, and the material in the capsule was examined under the microscope. In this way it was possible to determine whether the garnet had melted or decomposed. This garnet was found to melt and decompose *in vacuo* at 1185°. If the pressure is less than 26,000 atmospheres, this garnet cannot be melted without decomposition. The principal products of decomposition were enstatite and glass. At pressures above 26,000 atmospheres the solid and molten garnet can exist together, and the melting temperature increases with pressure. If the molten garnet at high pressure is cooled slowly from say 2000°, solid garnet forms from it. However, if the melt is quenched from too high a temperature at high pressure, enstatite and glass are formed even though the pressure is high enough for garnet to be stable. This suggests that some semblance of the solid garnet structure may exist in liquid garnet at high pressures.

It appears that well-developed crystals of garnet are rarely included in diamond; most of the garnet inclusions are irregular in shape. This would imply that the garnet was molten or nearly molten as the diamond formed around it.

In any event, the diamonds which contain garnet inclusions probably did not form at temperatures higher than about 2000°, or they would contain enstatite instead of garnet. Enstatite is a relatively rare inclusion in diamond. And because the garnet inclusions mostly appear to have been molten, the diamond often evidently formed at temperatures above about 1300°.

Now we have two high pressure minerals, garnet and diamond, one encased in the other. It is very unlikely that both were formed metastably, that is, at pressures below which either was stable. At least the garnet must have been stable. This implies that the diamonds containing garnet formed at pressures of at least 25,000 atmospheres. If in addition the diamond formed at a pressure where it was stable, then the lowest pressure possible would be about 55,000 atmospheres. Such a pressure would exist at a depth of about 150 km. beneath the surface of the earth.

Thus, it now seems even more likely that diamonds have been formed at considerable depths in the earth, and we are quite fortunate to have any of them at the surface.

The problems of the origin of natural diamonds are by no means completely solved. But you can see that we are making some progress toward understanding them. It is very likely that within a few years the diamond will prove to be a very valuable geological indicator from which we will be able to deduce much about the physical and chemical conditions which have existed and now exist in the deeper layers of the earth.

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