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**MAN-MADE DIAMONDS**

BY

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### MAN-MADE DIAMONDS

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In the 1920's it was quite widely believed that diamond had been made from carbon under conditions of high heat and great pressure. The story was indeed one to capture the imagination. It involved famous chemists, a thoroughly

the mass cooled from the outside. When the metal was dissolved from the solidified melt, there remained traces of transparent material having optical properties similar to those of diamond and giving some carbon dioxide upon

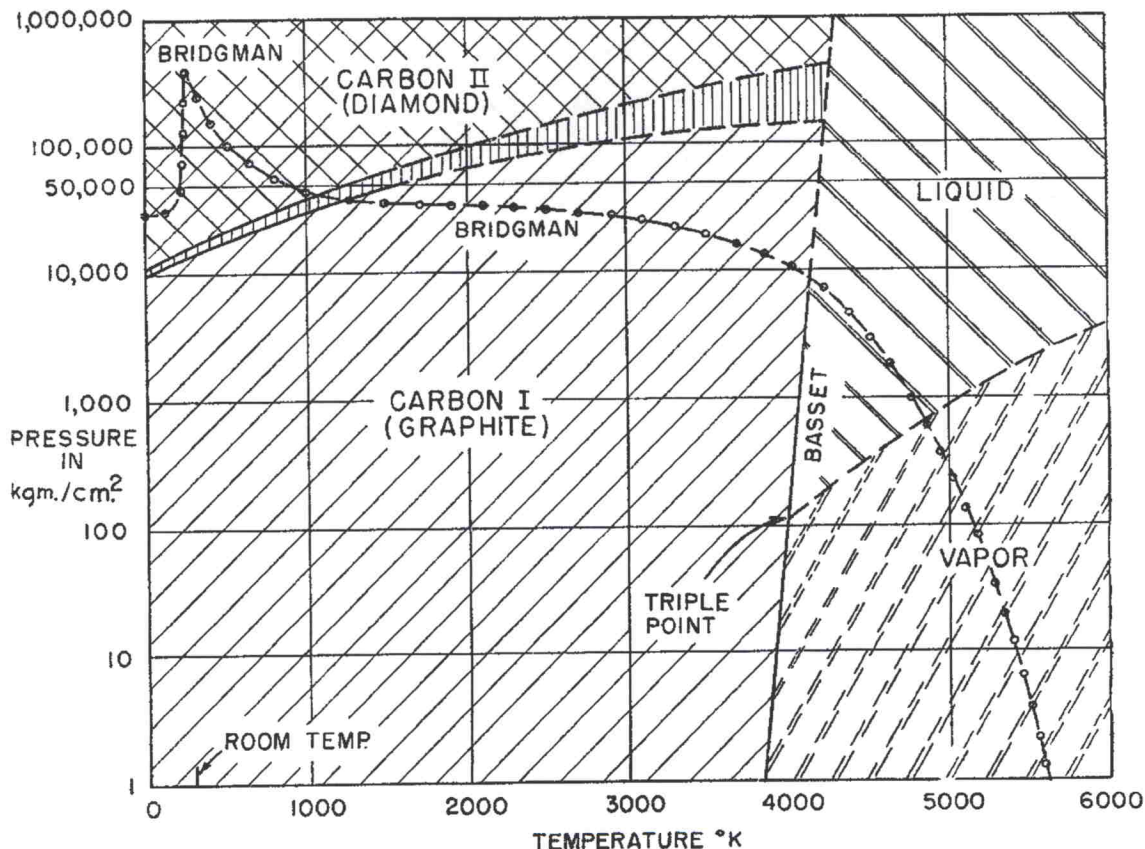


Fig. 1. Phase diagram of carbon

fascinating subject and very striking experimental techniques.

In the recent past, however, informed scientists soberly agree that there has been no certain example of diamond production in the laboratory. More than a century of claims and counterclaims for the synthesis of diamond attest to the fascination of the subject and the extreme difficulty of the experimental techniques. Henri Moissan dissolved sugar charcoal in molten iron and quenched the solution in cold water in order to crystallize the carbon under the great internal pressure supposedly generated by contraction as

combustion. Moissan therefore believed he had made diamond

In 1880, J.B. Hannay reported he had made diamonds by heating a mixture of hydrocarbons, bone oil and lithium at red heat in sealed wrought-iron tubes. The project was said to be fraught with great difficulty because of exploding tubes; only three out of eighty held. Hannay's identification of his diamonds seemed very conclusive, since it even included a density of 3.5 and a carbon analysis of 97.85 percent.

Sir Charles Parsons tried for thirty years to synthesize diamonds, including in his

experiments many attempts to duplicate the work of Moissan and Hannay. At first Parsons thought he had succeeded; but later, having some doubts, he scrupulously re-investigated all his work on the subject. Parson's new work clearly demonstrated how he had been misled into regarding as diamond various transparent, singly refracting minerals (spinel) which were very resistant to chemical reagents and would not burn. He finally concluded that neither he nor anyone else had ever succeeded in making diamonds in the laboratory.

The early claims to diamond synthesis were again reviewed by Prof. N. V. Sidgwick, of Oxford, in 1950, and Henry Eyring, of the University of Utah, in 1952. These authorities conclude that the synthesis of diamond in the

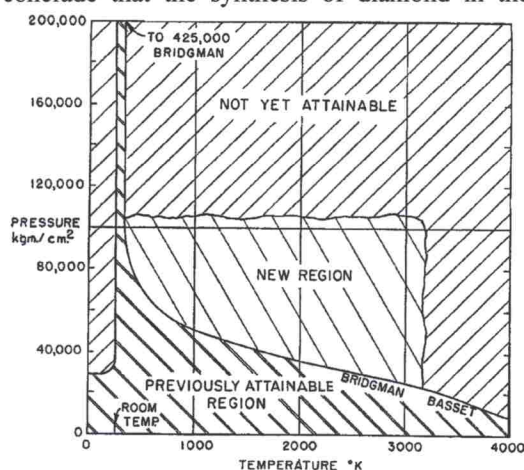


Fig. 2. New region of pressure and temperature available for research

laboratory has never been shown to be a success, and that thermodynamic considerations make it seem improbable that diamonds could have been formed under the conditions used in the experiments reported.

For a full account of the arguments the reader is referred to an extensive literature on the subject, a bibliography<sup>1</sup> for which is appended.

### Suggestions from Thermodynamics

The phase diagram for carbon as now understood is plotted in Fig. 1. Only the boundary between graphite and its vapour at low pressure is accurately established by experimental measurements. The boundaries at higher pressures between graphite, vapour and liquid are based on the work of Basset, and are not fully accepted.

The location of the boundary between the graphite and diamond-stable regions has very little direct experimental evidence at present.

The position of the lower temperature part of this boundary was calculated by thermodynamic methods by Rossini and Jessup<sup>ii</sup> of the U.S. Bureau of Standards in 1938. The higher temperature part of the boundary shown by broken lines is purely extrapolated from the other part, as the physical data have never been obtained.

The chain-line running across the diagram shows the upper limits of pressure and temperature that are known to have been reached in controlled experiments (this excludes atom bombs) according to the published literature. Prof. P. W. Bridgman, of Harvard University, is the outstanding investigator in this field, working up to more than 400,000 atmospheres at room temperature. He also held temperatures near 3,000° K. at 30,000 kgm./cm.<sup>2</sup> for very short intervals of time.

The diagram shows that Bridgman has operated well up into the diamond-stable region and has tried many times to synthesize diamonds but without success. He has stated in several of his papers that the reason for his lack of success is that at the relatively low temperatures at which his experiments were carried out the rates of reaction were negligible. He recognized the necessity of going to higher temperatures, but he had not developed apparatus capable of operating at these high pressures and temperatures simultaneously. The maximum conditions he has reported in this direction were 30,000 kgm./cm.<sup>2</sup> and 2,200°-3,000°K. for periods of one or two seconds.

Bridgman attempted to establish a point on the diamond-graphite equilibrium curve in a series of experiments in which diamonds were heated to about 2,500°K. for a few seconds at pressure which were increased until the diamonds failed to graphitize. This pressure was reached at 30,000 kgm./cm.<sup>2</sup>. He suggested in his paper that this point, 30,000 kgm./cm.<sup>2</sup> and 2,500°K., might lie near the diamond-graphite equilibrium curve.

In Bridgman's experiment the possibility that pressure reduced the rate of conversion of diamond to graphite cannot be ruled out. If so, the diamonds would fail to graphitize at 30,000 kgm./cm.<sup>2</sup> in the few seconds at high temperature available. If this be the case, the point 30,000 kgm./cm.<sup>2</sup> and 2,500°K. is still within the graphite region of stability.

The known evidence about the thermodynamic stability for diamond and graphite led us to believe that diamonds could be formed in the pressure region 30,000-100,000

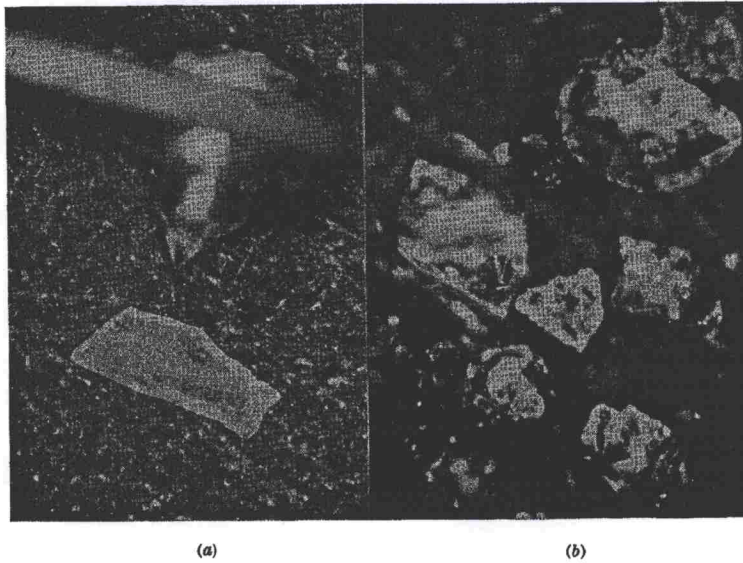


Fig. 3. Man-made diamonds. (a) 1-mm. diamond shown with phonograph needle.  
(b) 0.2-0.5-mm. octahedra

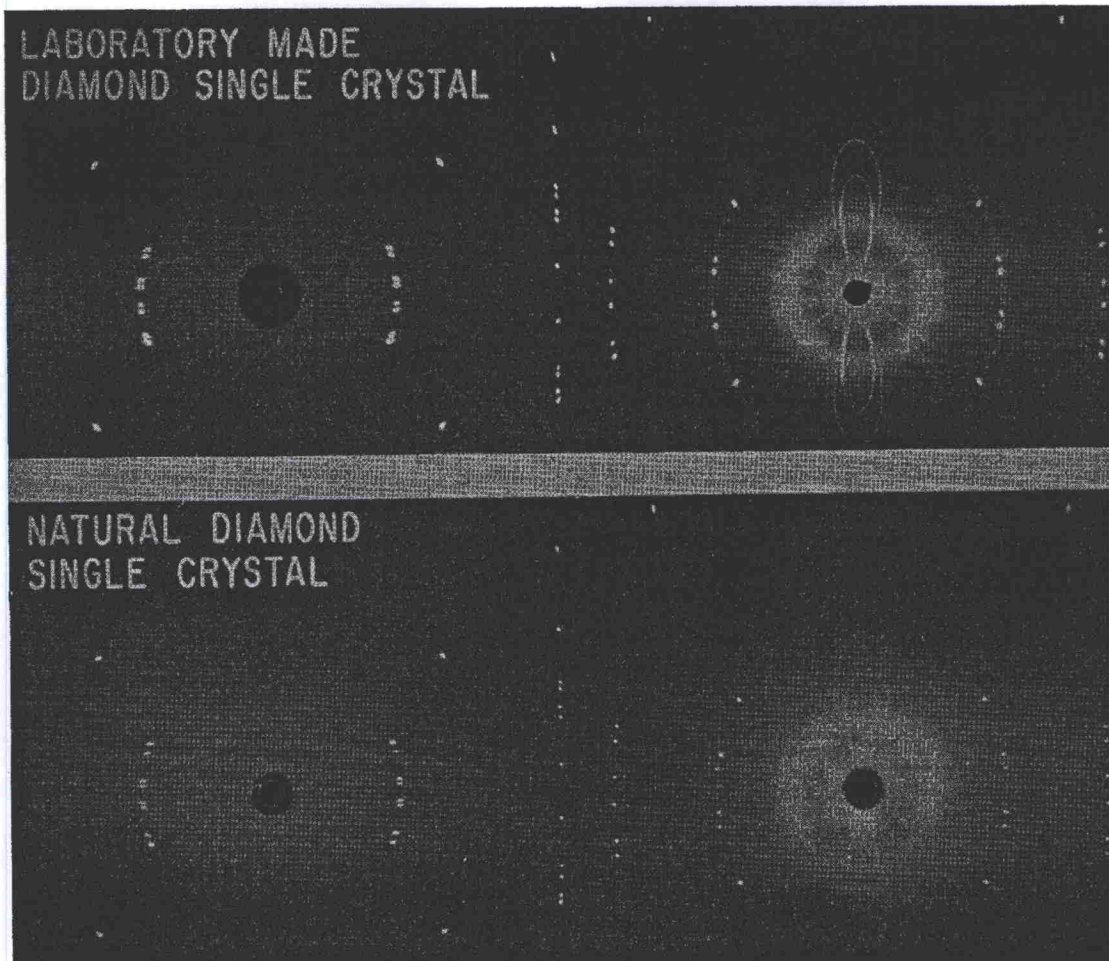


Fig. 4. X-ray diffraction patterns of man-made and natural diamond (powder camera photograph)

kgm./cm.<sup>2</sup> at temperatures somewhere in the range of 1,000°-3,000°K.

Practically all known ultra-high-pressure generators are based on the principle of pushing a piston into a cylinder that encloses the substance to be subjected to the pressure. The main factor which limits the maximum pressures that can be reached within vessels is the strength of materials. The strongest steels in the most favourable form and size (piano wire, for example) have ultimate tensile strengths of the order of 14,000-21,000 kgm./cm.<sup>2</sup>. Sintered carbides, such as 'Carboloy', have compressive strengths of the order of 50,000 kgm./cm.<sup>2</sup> or more. The pressure required for reasonably rapid synthesis of diamond was thought by our group to be above the compressive strength of 'Carboloy' in the range 50,000-100,000 kgm./cm.<sup>2</sup>.

Merely making the walls thicker on a pressure vessel contributes very little to its pressure-holding ability after a certain wall thickness is reached. By using multiple support bands on the cylinder part (a technique used years ago in making large gun barrels), and special sealing gasket devices between the piston

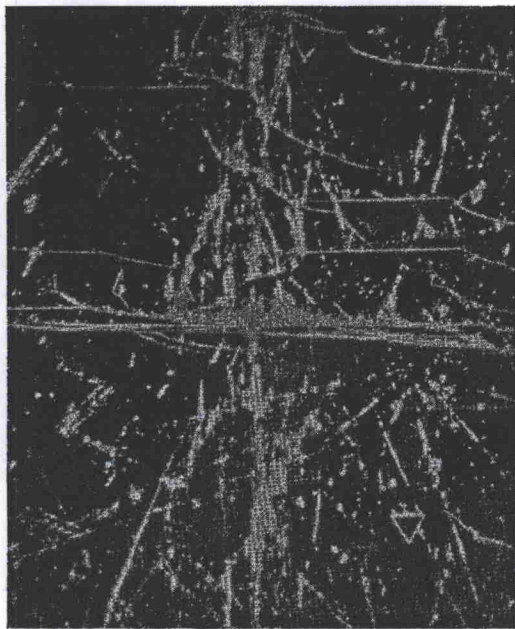


Fig. 5. Scratches made on natural diamond 111 face with man-made diamonds. A large number of scratches appear in a generally vertical direction down through the centre of the picture. The horizontal marks are growth steps on the crystal face. The triangular pit in the lower right-hand corner is also a typical growth mark found on diamond faces

and cylinder, Bridgman had developed pressure vessels good for 50,000 kgm./cm.<sup>2</sup> at room temperature. At high temperatures, materials get weaker and in general the attainable pressures are lower.

By developing some new ways of distributing stress and giving support to critical parts, our research group has succeeded in developing pressure vessels that operate at pressures up to at least 100,000 kgm./cm.<sup>2</sup> and temperature in excess of 2,300°K. for hours of continuous operation.

### Calibration of Pressures and Temperatures

Pressures of this magnitude are calibrated by making use of four of the electrical resistance transitions observed by P. W. Bridgman<sup>iii</sup> in the pressure region up to 80,000 kgm./cm.<sup>2</sup>. The transitions are bismuth 25,400, thallium 45,000, caesium 55,000 and barium at 80,000 kgm./cm.<sup>2</sup>. For pressures greater than 80,000 kgm./cm.<sup>2</sup>, the melting point of germanium as a function of pressure was used. It was found to decrease linearly with pressure to press loads corresponding to 100,000 kgm./cm.<sup>2</sup>.

Temperatures inside the pressure cells are measured by use of thermocouples, melting points of materials, change of electrical resistance of wires, Curie points of magnetic materials, thermocolour paints, etc.

### Region now Available for Research

In Fig. 2 appears a pressure-temperature diagram, with linear scales on both axes, showing the new region of exploratory research which has been opened up by the development of our new high-pressure and high-temperature apparatus. Note that the newly attainable region covers about as much area as does all the region previously attainable.

### Diamond Synthesis

The new region of attainable pressure and temperature extended well into the diamond-stable region as defined in Fig. 1. Under these supposed diamond-stable conditions, processes were discovered which yielded diamonds ranging in size from less than 100 microns to more than 1 mm. along an edge. The various processes have been independently repeated more than one hundred times by a number of workers in this Company. Each time crystals were grown which pass the critical tests for identification with diamond. The present chamber sizes permit the synthesis of up to about ¼ carat of diamond material.

It is not necessary to introduce diamond seeds. Nucleation and growth occur

spontaneously and profusely when diamond-stable conditions are reached. In some of the early successful work, diamond seeds were added; but growth occurred independently and apart from the added seed. In a few cases under special conditions, some growth has occurred on the seed crystals.

The man-made diamonds form in many of the different crystal habits found in Nature. These include octahedra, tetrahedra and dodecahedra. Some typical forms are shown in Fig. 3.

### Proof that Diamonds were Made

The proof that diamonds were made was based on the following conclusive tests:

- (1) Identity of crystal structure of man-made diamonds to natural diamonds as determined by X-ray diffraction patterns (Fig. 4).
- (2) Chemical analysis to show that crystals made were composed of carbon. Those analyzed were 86 percent carbon, 14 percent inorganic ash identified with the growing media.
- (3) Hardness tests. The laboratory-made diamonds were hard enough to scratch the hardest face, the 111 face, of natural diamond (Fig. 5).
- (4) Repeatability. The synthesis of diamond has been repeated, entirely independently, by a number of workers in the General Electric Company. The diamonds so made pass the above conclusive tests for diamonds.

In addition, it was shown that the index of refraction for the man-made crystals was within the range 2.40-2.50. Mineral compilations<sup>iv</sup> list five isotropic minerals having a refractive index near this range. Natural diamond is one of them and its value is 2.419. The other four are:

	Index of refraction	Moh's hardness
Franklinite, (Zn,Fe,Mn)O (Fe,Mn) <sub>2</sub> O <sub>3</sub>	2.36 ±	6
Perovskite, CaO TiO <sub>2</sub>	2.38 ±	5.5
Sphalerite, (Zn,Fe)S	2.428	3.5-4
Eglestonite, Hg <sub>2</sub> Cl <sub>2</sub> , Hg <sub>2</sub> O	2.49 ±	2.3

These four are ruled out as possibilities by the other critical tests.

The result of more than four years effort in this laboratory has been the development of equipment capable of holding pressures and temperatures in the diamond-stable region for hours at a time. Synthesis of diamond has been accomplished more than a hundred times. A number of people have independently repeated the various diamond-making processes

successfully. These laboratory-made diamonds can scratch natural diamonds and have a crystal structure identical with natural diamonds.

<sup>i</sup> Note. References centering about the claims of Hannay and of Moissan, which are the major ones, are dealt with chronologically. Earlier references extending back to 1828 are considered in J. W. Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 5 (Longmans, Green and Co., London, 1924).

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<sup>ii</sup> Rossini, F. D., and Jessup, R. S., *J. Res. Nat. Bur. Stand.*, **21**, 491 (1938).

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<sup>iii</sup> Bridgman, P. W., *Proc. Amer. Acad. Arts and Sci.*, **81**, 165 (1952).

<sup>iv</sup> Palache, Berman and Frondel, "Dana's System of Mineralogy" (J. Wiley, 1951).