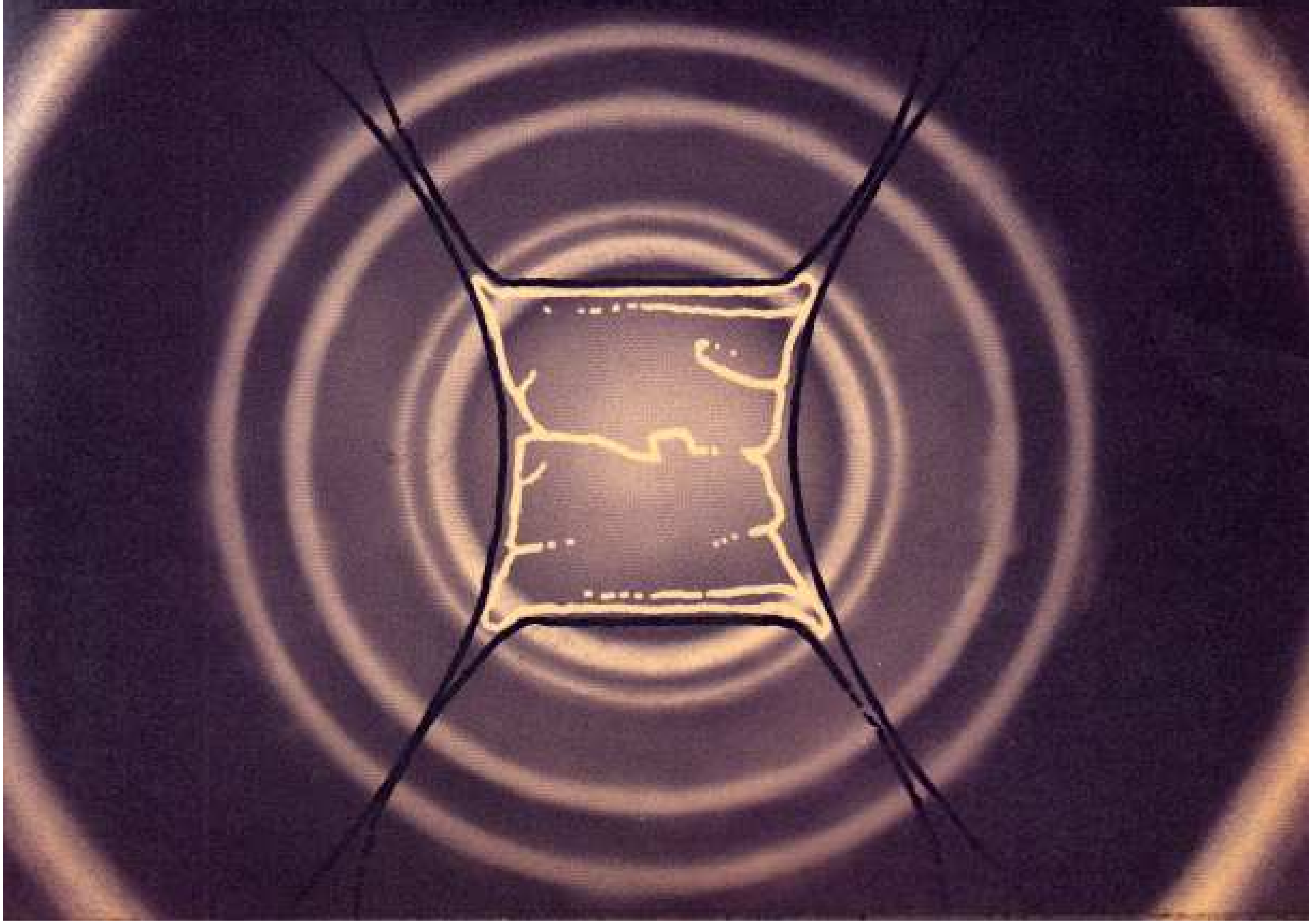
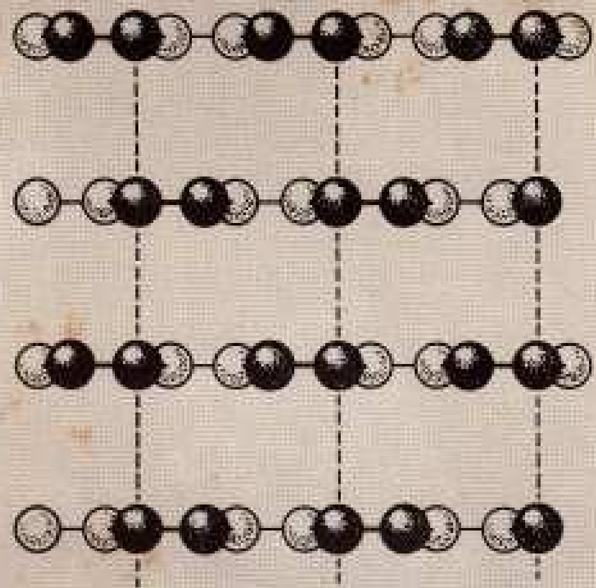
Chemistry Background Book

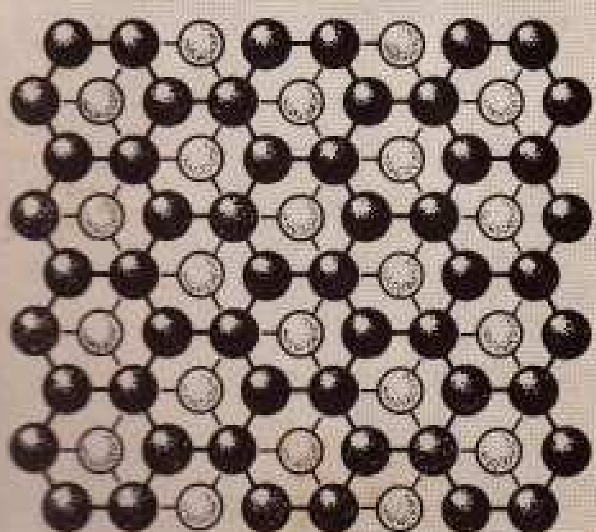
Making diamonds

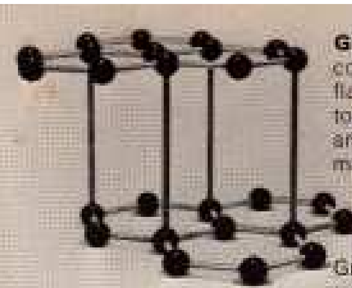


To transform graphite into diamond, the hexagonal rings have to be puckered and the layers brought much closer together. This requires very high pressures indeed.

Side view and top view of the structure of hexagonal graphite.



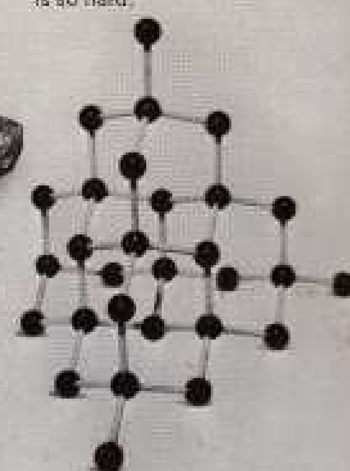




Graphite structure – interconnecting hexagonal rings in flat layers. The layers are held together only by weak forces, and hence graphite is a soft material.

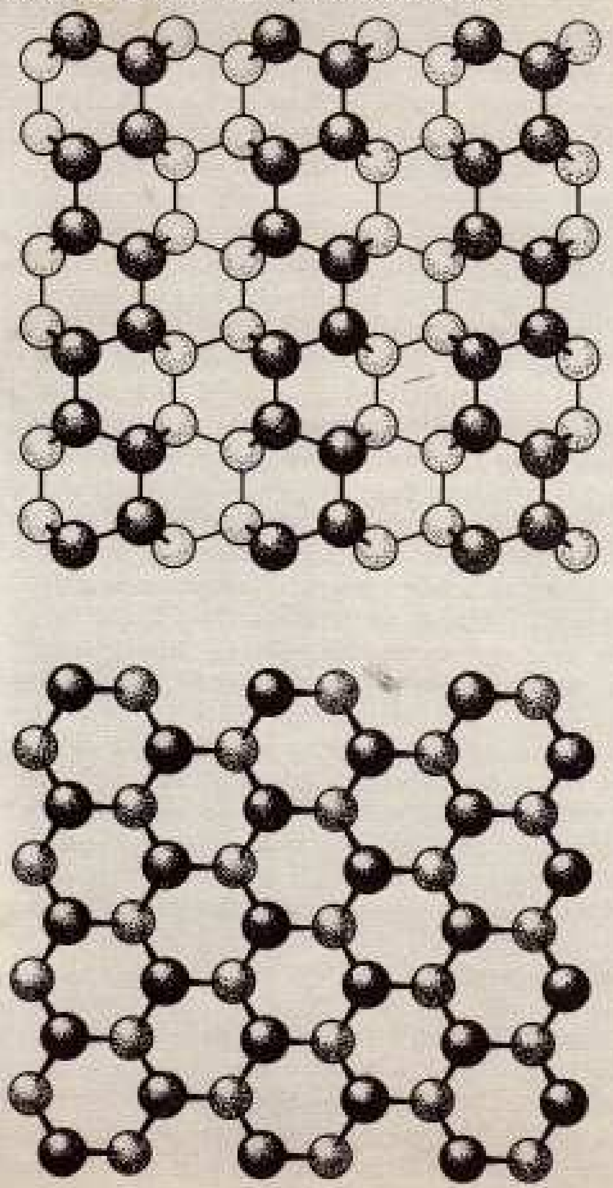
Graphite – a soft flaky substance.

Normal cubic diamond structure – puckered hexagonal rings such that all the atoms are equidistant. There are no layers in the diamond structure which is one of the reasons why diamond is so hard.



Natural diamonds, most of which will be cut to make gems.

Lonsdaleite – very small quantities of hexagonal diamond have recently been identified in meteorites and in diamonds made by an explosive process (see page 10). This new modification, now named lonsdaleite, after the British crystallographer Dame Kathleen Lonsdale, bears the same relation to cubic diamond as wurzite, the hexagonal form of zinc sulphide (ZnS), does to the common cubic form of zinc blende.
Its structure is shown here in top view and side view.



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Making diamonds

Diamonds have been known and valued for thousands of years. They are the epitome of indestructibility, and it has been suggested that the shape of the pyramids of Egypt was chosen to resemble that of a natural diamond. In the Middle Ages the strength of diamond was believed to keep the bearer safe from harm, and diamonds were often carried by travellers as amulets or charms in those uncertain times.

Diamonds have been found in many parts of the world: in India, Siberia, Australia, Russia, and America. But nowadays most diamonds come from Africa. Children like bright pebbles to play with and it was in 1867 that some children found the first diamond recorded in South Africa while they were playing by a stream. It was shown to Dr Guybon Atherstone in Grahamstown, and someone wrote with it on a window-pane to prove that it was indeed a diamond, for nobody expected to find one in South Africa in those days. The window-pane was still there when I studied at Rhodes University in Grahamstown some twenty years ago.

Over the ages there have been countless attempts to make diamonds and many of them make strange reading today. But I wonder how many people would know how to start, even now, when so much is known about chemistry and physics. Diamond is one form of the element carbon – the element which is much more familiar to most of us in the form of graphite, the soft black substance in pencils ambiguously called lead. Crystals of graphite are built up of layers of atoms in which the carbon atoms are joined together in flat hexagonal rings (see diagram). The layers of atoms are attached to one another by weak forces, and so are able to slide more or less freely over one another. This is why graphite is used for pencil leads: when the tip of the pencil is pressed on paper, the graphite layers flake off, leaving a mark on the paper. In diamond, the structure is different: the rings are puckered to form an interconnecting network (see diagram) and all the atoms are strongly bonded together. Consequently, diamond is the hardest substance in the world.

This difference in structure explains why two forms of the same element—carbon—are so unlike each other (see the Background Book *The Structure of Substances*). Indeed, many of the early experimenters did not even realize that diamond was made of carbon.

It is no surprise that the early experimenters failed in their attempts to make diamonds. If you want to make something you must at least know what substances to start with.

Finding the right conditions for making diamonds from carbon is a problem on its own. It was tempting to do this by trying to imitate the way in which natural diamonds are made, but the diamonds brought to Europe before about 1880 came from actual or ancient river beds, and people realized that the diamonds had been formed elsewhere and then carried away by the rivers. Not knowing what kind of minerals had been present when the diamonds originally grew, experimenters were unable to produce an artificial melt of the right kind in which to make them. Thus genuinely scientific attempts to make diamonds could really begin only in the last decades of the nineteenth century, when two separate facts were recognized at about the same time.

In the first place, as new diggings discovered at Kimberley in about 1870 got deeper and deeper, people began to realize that the rock formations were not alluvial (laid down by water) as had always been the case before, but were the tops of ancient volcanic pipes. They were filled with a bluish-green rock usually called *kimberlite*, and it seemed that the source rock of diamond had at last been found. It was studied very carefully by chemists and geologists, and a number of them reported that they had made small diamonds from melts of natural kimberlite, or from chemical mixtures approximating to it. However, since no recent worker has succeeded in repeating these experiments, and none of the supposed 'diamonds' seems to have been kept, we shall probably never know whether or not any of them were genuine.

Another way of making diamonds soon caught public attention, for in 1888 fragments of a nickel-iron meteorite from Siberia were found to contain diamond, and in 1893 diamond was also found in meteoritic iron from the Canyon Diablo crater in Arizona. In each case the diamond was a significant percentage of the whole fragment – very much richer than kimberlite, which contains at most about one part of diamond to every fifty million parts of rock.

The discovery of diamonds in association with meteoritic iron initiated some really vigorous attempts to make diamond. Most of the experimenters adopted much the same approach – trying to imitate the conditions that they thought were present in meteorites. This involved placing graphite in iron which was heated until it was molten, and then quenching the iron rapidly by putting it into cold oil or water. It was expected that the outer layers of the iron would contract on cooling, so that the centre of the lump, where the graphite was, would thereby be subjected to very great pressures while still at a high temperature.

A number of scientists, including Moissan in France and Sir William Crookes in England, claimed to have succeeded in making diamonds in this way. Sir William Crookes actually demonstrated his method during a Friday Evening Lecture at the Royal Institution in London, saying 'I now proceed to make diamonds before your very eyes'. But, as with the kimberlite experiences, later workers who have attempted to repeat these experiments have been less fortunate, or less gullible, according to your point of view. Here again, no diamond alleged to have been made by any of these people can be found today.

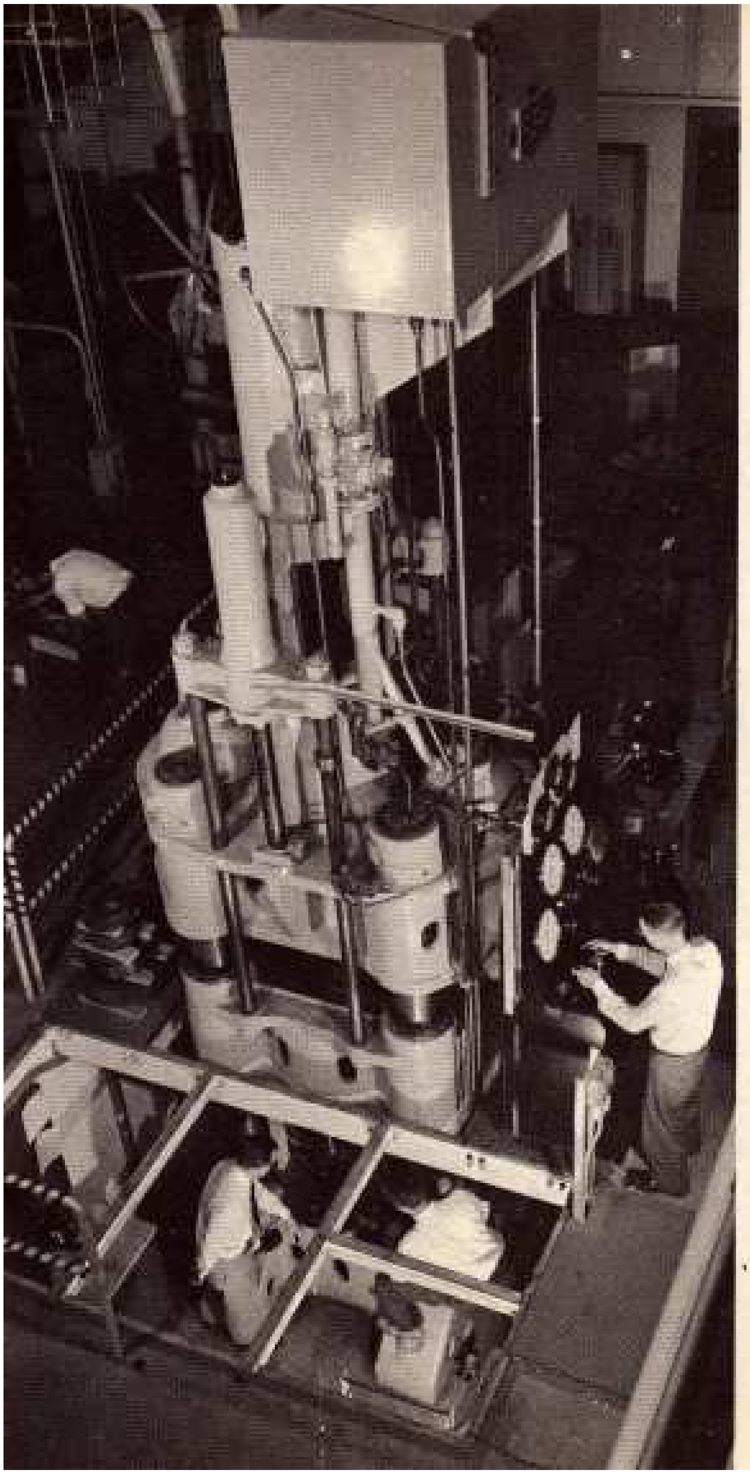
The only 'artificial diamonds' to have come down to us from that period were made by Richard Hannay, and there is a great deal of speculation about these. Hannay, working in Glasgow in the 1880s, subjected various 'carbonaceous mixtures' to high pressures and temperatures. He appears to have combined both ways of making diamonds so far described, by heating his mixtures in iron tubes. He claimed to have succeeded in only a few of his experiments, and he sent some of his diamonds to the British Museum to be tested. These tiny crystals are undoubtedly diamonds, so the questions to be answered are whether Hannay really made them, whether his assistants played a trick on him, or whether he knew that they were natural diamonds and pretended that he had made them. Nowadays many people are very interested in this question, because the processes by which synthetic diamonds are now made in large quantities can only be protected by patents if no one has used the same method before. My own conclusion is that Hannay's diamonds are probably natural, rather than artificial, but not everybody is in agreement.

However that may be, millions of carats (a carat = 0.2g) of synthetic diamonds are now being made by processes very similar to those tried by Moissan and Crookes and their contemporaries. Most of these diamonds are very tiny, like grains of sand. They are very satisfactory for making grinding wheels, which is one of the main industrial uses of diamonds.

Aerial photograph of the Canyon Diablo, a meteorite crater in Arizona, U.S.A., which is over 4000 feet across and 600 feet deep. In 1893, diamond was found in the meteoric iron in this crater.
J. S. Shelton

Large diamonds made by the United States General Electric Company. These diamonds are not good enough for cutting into gems, and at present there is little prospect of synthesizing gem diamonds.
U.S. General Electric Co.

The 1000 ton press (*right*) used by the U.S. General Electric Company to make their first synthetic diamonds.
U.S. General Electric Co.



The U.S. General Electric Company has grown larger diamonds (see opposite), some of which were exhibited at the World Fair in Seattle in 1962, but these were certainly not of gem quality, and at present there seems little prospect of making gem diamonds.

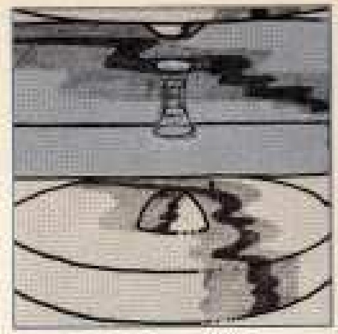
One of the reasons why synthetic diamonds are so small is that it is only possible to create the temperatures and pressures necessary to produce them in pressure vessels which are very small. The pressures used are about 50,000 atmospheres, and the temperatures around 1650°C. To produce such conditions, it is necessary to concentrate the pressure from a relatively large press on to a very small area, like a woman concentrating her weight on a stiletto heel and thereby creating a force large enough to damage a hard surface. In making diamonds the process takes several minutes.

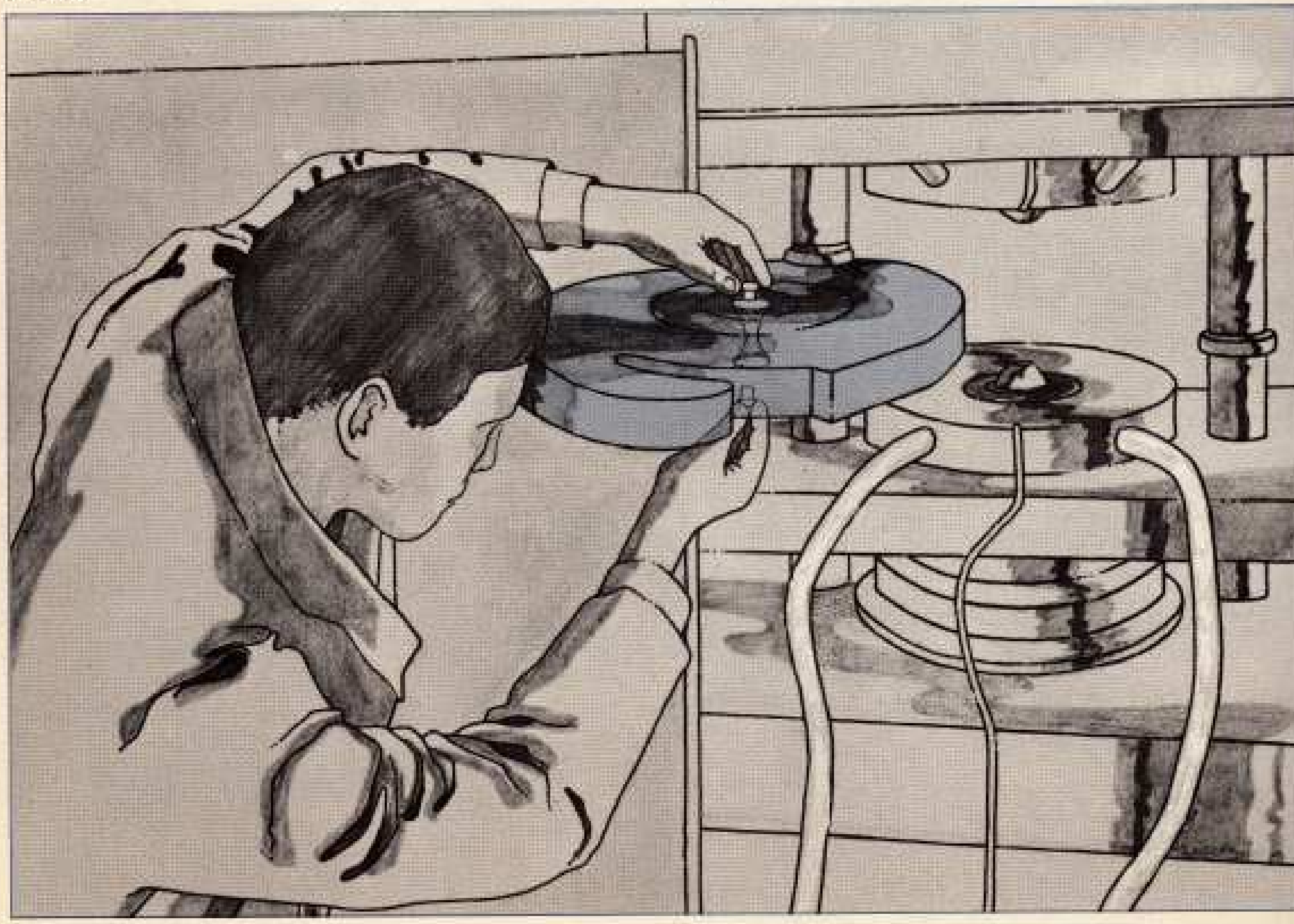
Since diamond is made from pure carbon and has a density of 3.5 g/cm^3, one might suppose that any other form of pure carbon (say graphite, which has a density of only about 2.2 gm/cm^3) could be squeezed in a huge press until it was dense enough to become diamond. It is very difficult indeed to do this, although not impossible; some scientists report that they have compressed pure graphite and formed diamond. However they had to use pressures approaching 200,000 atmospheres – much higher than those normally employed. Moreover it is not known how pure the graphite in these experiments was, though this may be critical. One of the difficulties in understanding the results of experiments at high pressure and high temperature is the very great importance of trace elements in promoting or inhibiting certain reactions. If the graphite contained some nitrogen, which is not at all unlikely, this may have played an important part in the experiment because it has recently been found that many natural diamonds contain appreciable amounts of nitrogen (up to 0.5 per cent); pure diamonds are rare. In practice synthetic diamonds are not made from pure carbon, but from mixtures of carbon and certain metals. A number of metals, including platinum, have been found to be suitable, but most synthetic diamonds produced in large quantities so far have been made with nickel. The origin of the carbon does not seem to matter: one group has demonstrated this rather nicely by making diamonds from toasted tea-cakes.

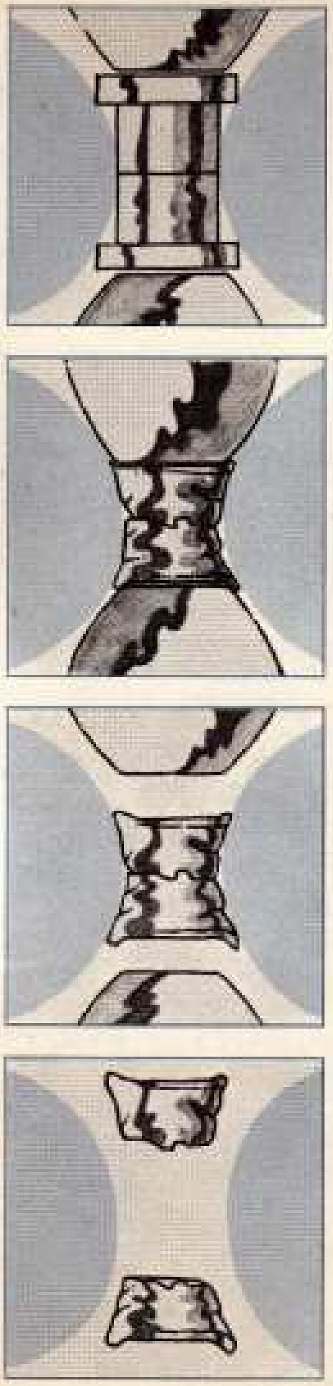
Stages in the manufacture of synthetic diamonds

A pyrophyllite capsule (*below*), containing the carbon from which the synthetic diamonds are to be made together with metal discs, is put into the die of a press.

The die (*right*), now holding the capsule, is swung into position between the two anvils of the press.

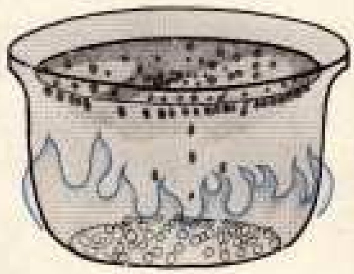






The capsule (*left*), is subjected to a continuous temperature of around 1,650°C and a pressure of around 50,000 atmospheres. Then the crushed capsule is removed from the press. The material recovered from the presses is first sorted by hand to remove the large pieces of metal and pyrophyllite. Then the remaining material is washed in hot nitric acid to get rid of any metal traces.

The material is put into a bath (*below*) containing a hot caustic solution, in which diamond sinks to the bottom, while the lighter carbon residue floats on the surface.

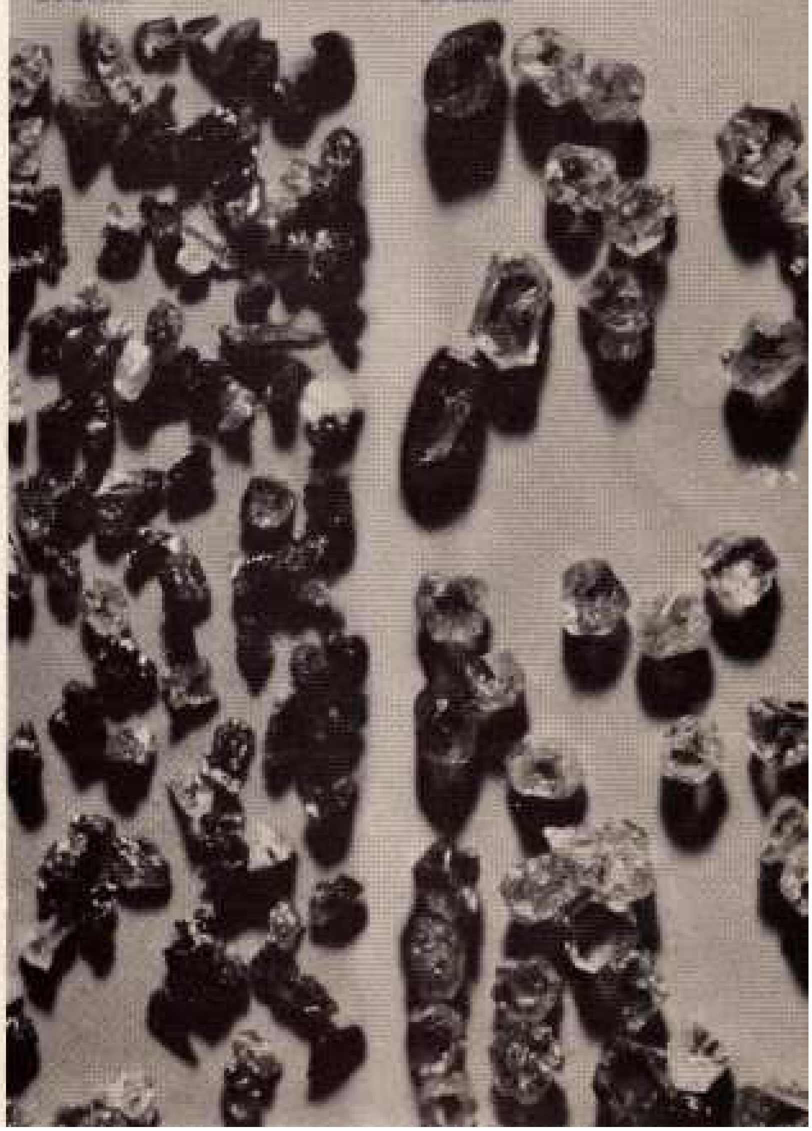


The end product – synthetic diamonds (*right*). The diamonds are now separated into different particle sizes using diamond sieves and mechanical vibrators. They are then graded into two main categories: splintery, spiky shapes for use in machining tungsten carbide, and other high speed metals and metal alloys; and chunky shapes which give a long working life to metal bonded saws used to machine concrete, stone, ceramics, and glass. The two categories are separated by feeding the material onto an inclined, vibrating table on which the chunky diamonds roll to the lower end and the flat or spiky particles slide to the top.

The end product ⋆ synthetic diamonds

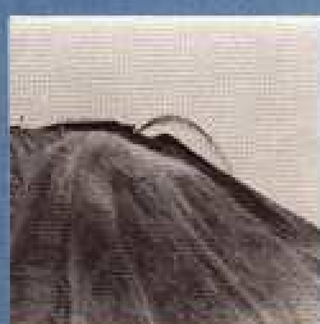
Rough splintery diamonds (x80) are for use with high speed hard metals and metal alloys.
De Beers

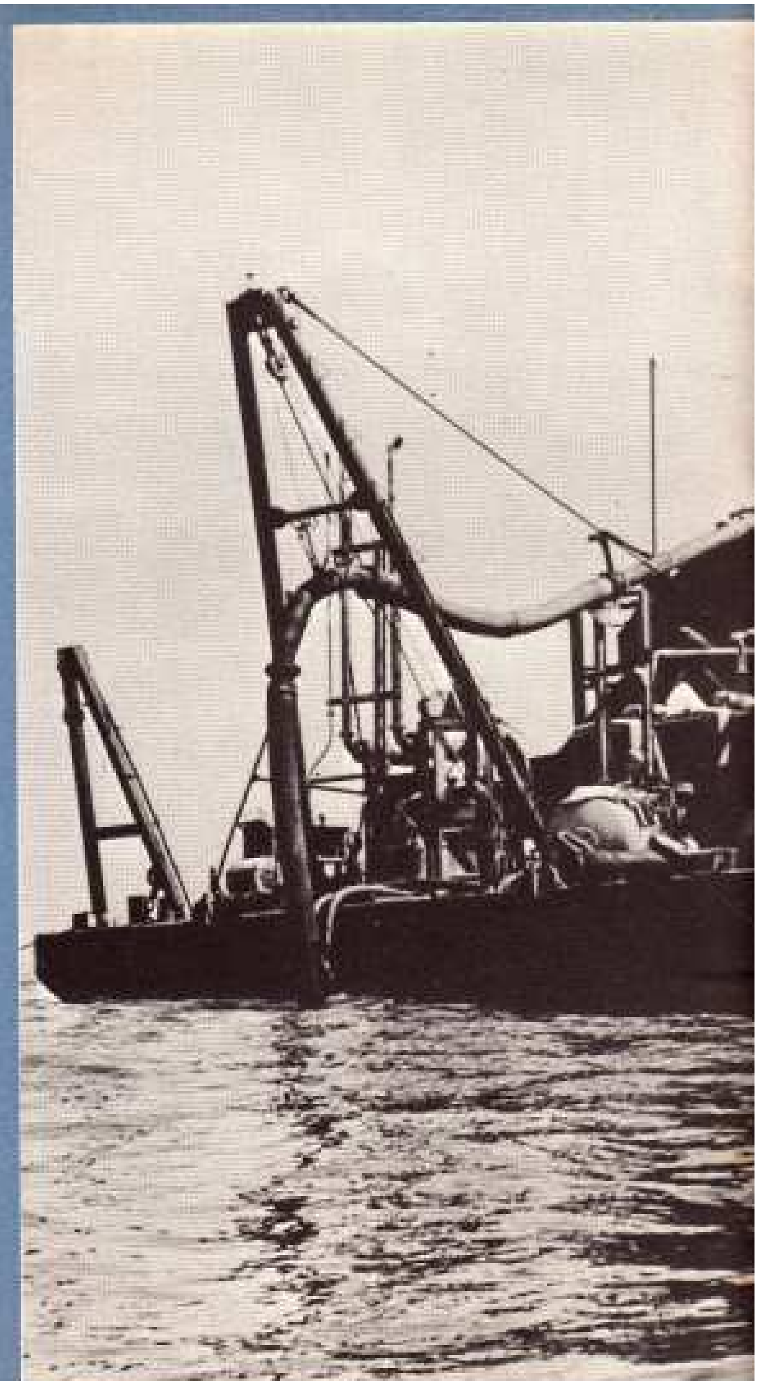
Chunky single crystal diamonds, many of them cubo-octahedral in form (x80) for use with stone, ceramics, and glass
De Beers



The extraction of natural diamonds a contrast to the way synthetic diamonds are made

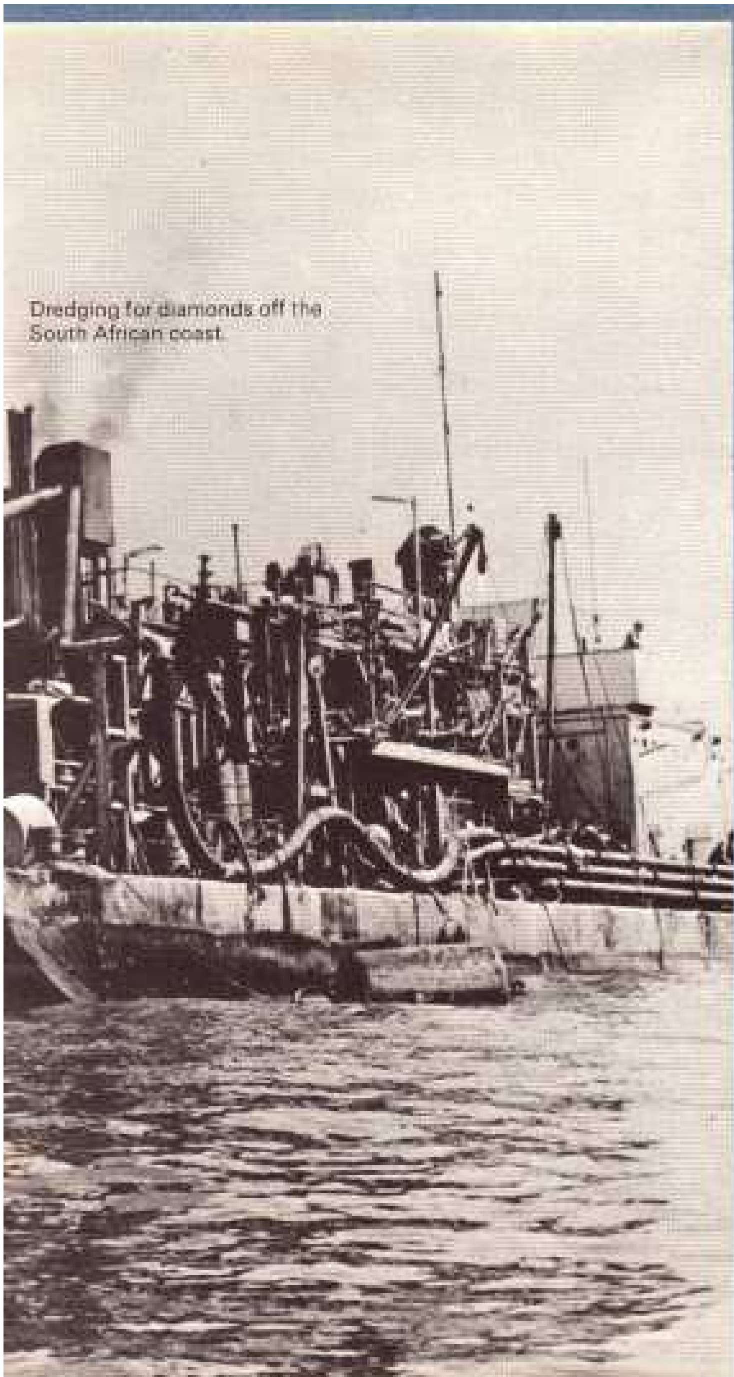
In a diamond mine:
this cone contains a chemical compound which floats off the lighter parts of the diamond-bearing material. The heavier minerals, including the diamonds, sink to the bottom where it is collected for further processing.
N. W. Ayer & Son, Inc.





Here can be seen the 'tailings', being deposited at the end of a conveyor system.

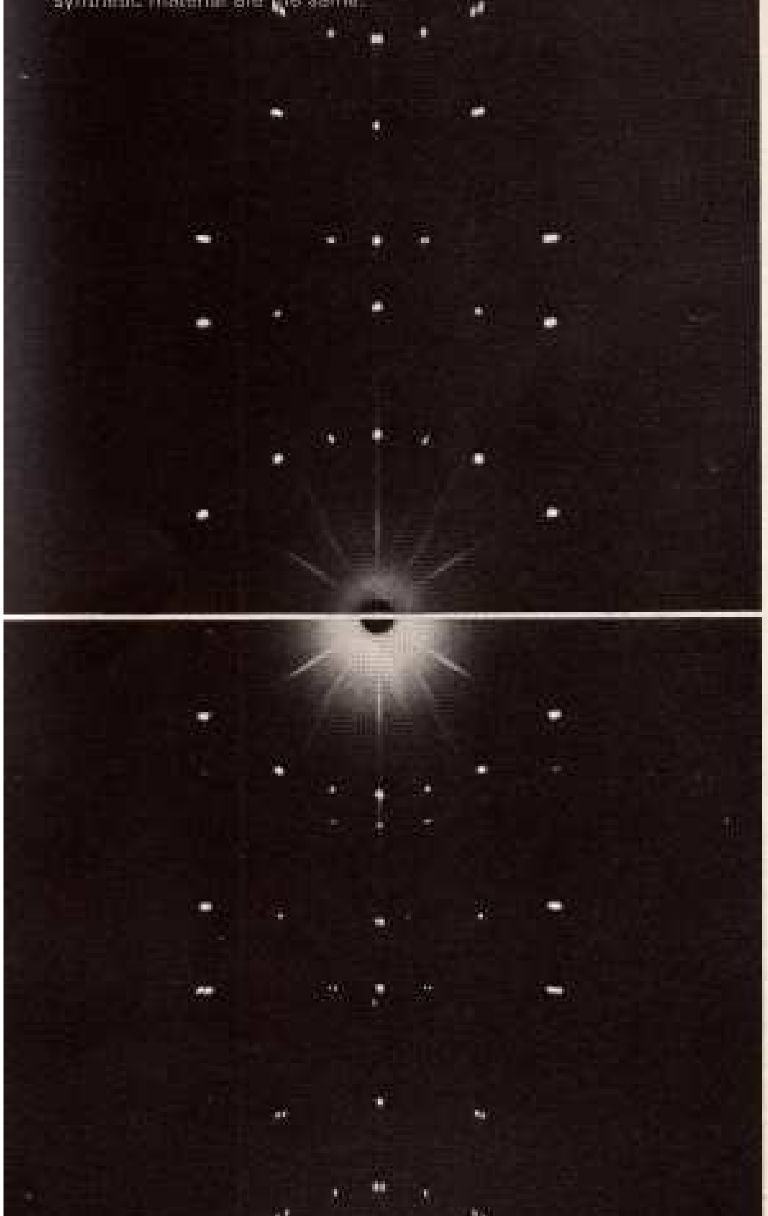
Dredging for diamonds off the South African coast.



Two ways of separating diamond from its ore in which it constitutes only about 1 part in 50 million.

The crushed ore is passed in a stream of water over a table covered with grease. Water does not wet the surface of diamond, and therefore the diamonds stick to the grease. The rock is washed away.

Electrostatic separation (dry ore) – this method depends on the fact that diamond is an insulator. When it is given an electrical charge it retains it long enough to be deflected from the gangue by a charged comb. The gangue falls directly downward from a roller while the charged diamonds are deflected away from the gangue by the comb.



X-ray diffraction photographs of natural diamond (top half) and synthetic diamond (bottom half). The similarity of the two photographs shows that the structure of the natural and synthetic material are the same.

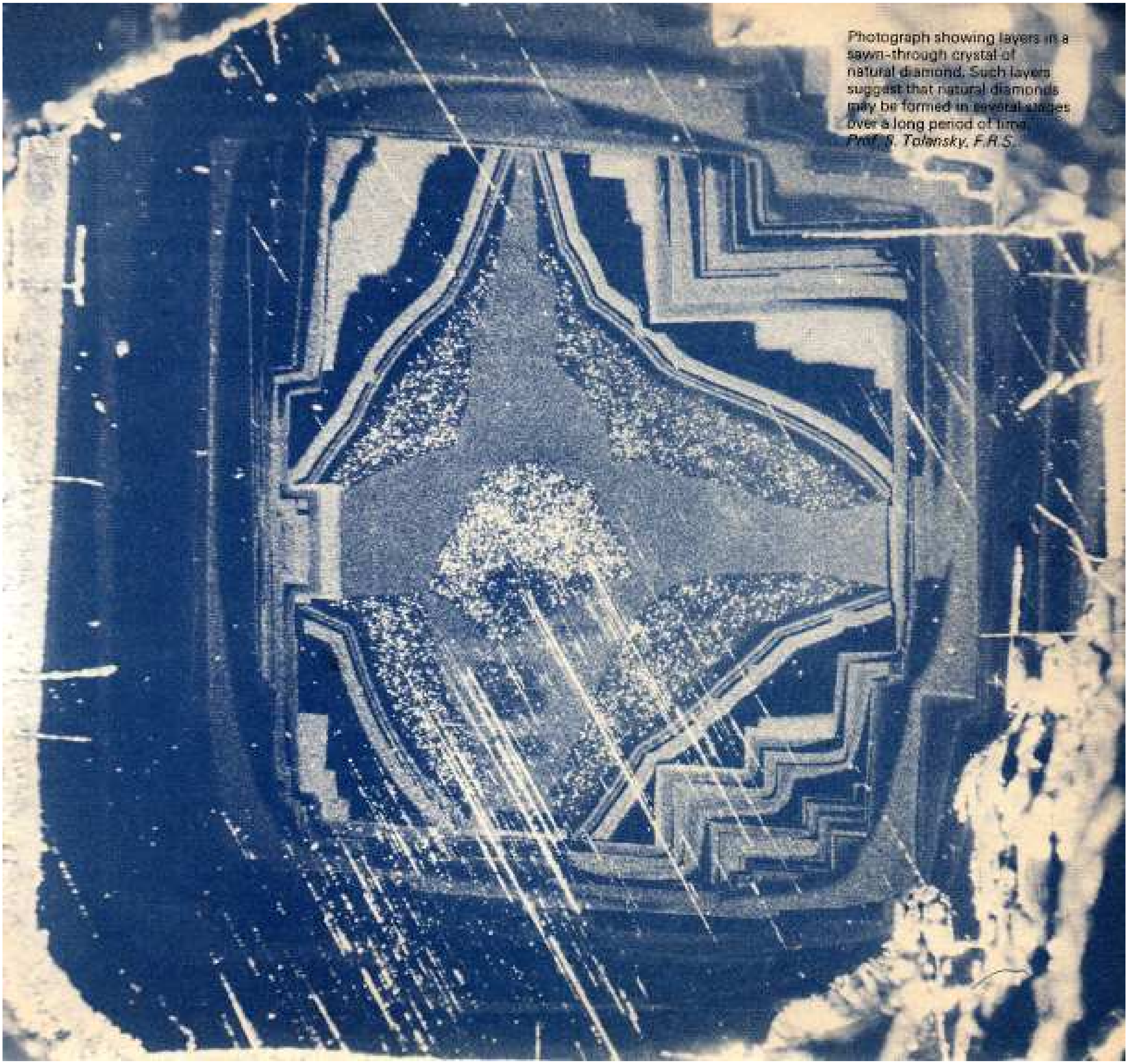
The extra reflections in the photograph of synthetic diamond are due to nickel carbide—nickel is frequently used in the manufacturing process.

What role does the metal play? Is it merely a solvent for carbon, so that diamond crystallizes instead of graphite under suitable conditions of temperature and pressure, or is the metal an essential ingredient of the diamond itself? This question is unexpectedly difficult to answer. The earliest synthetic diamonds contained appreciable amounts of nickel, probably in the form of a nickel carbide, but nowadays most of the crystals show hardly any traces of the metal used.

Manufacturers now understand the process well enough to exert some control over the colour and shape of the tiny diamonds, and can make different kinds for special purposes. This is a great achievement, because natural diamonds cannot as a rule be altered in any way, so a lot of time has to be spent sorting them into different shapes and sizes, or searching for the very rare diamonds which happen to be the only ones suitable for a particular job.

Methods of manufacturing diamonds suggest new ways in which diamonds may be used. For example, in electronics, miniaturization of components means that many transistors are now no larger than relatively inexpensive diamonds. But transistors are usually made from crystals of germanium and silicon – corresponding elements to diamond in the Periodic Table – and because they have a similar crystal structure, it is tempting to think it might be possible to make diamond transistors. As with germanium and silicon crystals, the diamond crystals would have to be doped with trace amounts of such elements as boron, nitrogen, and aluminium. This has been done both during and after growth, but the temperatures and pressures must be in the same range as those needed to make diamonds, and such work is still in an experimental stage.

So far we have been considering the process of making diamonds by holding the carbon at high temperatures and pressure for several minutes. But it is also possible to make very small diamonds (much smaller than the ones we have been discussing, but still recognizable as diamond by X-ray diffraction patterns) in properly arranged explosions. It has even been suggested that an atom bomb should be let off in a coal mine to make diamonds, but it is a good deal easier than that because small explosive charges produce enormous pressures for a small fraction of a second. The fact that diamonds can be made in this way has aroused a great deal of interest among scientists, because some people think that



Photograph showing layers in a sawn-through crystal of natural diamond. Such layers suggest that natural diamonds may be formed in several stages over a long period of time.
Prof. S. Tolansky, F.R.S.

diamonds in meteorites mentioned earlier might have been formed when the meteorites hit the Earth, so that they would not have been present in them beforehand. This would affect theories about the origin of meteorites, which would have had to be quite large to provide the pressures usually considered necessary to form single crystals of diamond.

Although people now know how to make diamonds from mixtures of carbon and metal, almost nothing certain has been learnt about the formation of natural diamonds. Kimberlite *seems* to be the source rock, but the diamonds constitute only a very small part of it, which implies that the process resulting in natural diamonds may not have been as efficient as that which produces diamonds in meteorites. Only one experiment, carried out by a group of scientists in Sweden, seems to have resulted in the formation of tiny diamonds in a silicate – that is, in a mixture anything like kimberlite. The question how large white gem diamonds are formed remains unanswered. Perhaps quite new methods will be needed if we are to make any artificially.

The largest cut diamond in the world; the 'Star of Africa', shown actual size in the Royal Sceptre, part of the Crown Jewels. *Crown Copyright. Reproduced by permission of the Controller of H. M. Stationery Office.*

Because the kimberlite pipes containing diamonds are ancient volcanoes, the diamonds may have originated in two quite different ways. They may have been formed very early in the history of the Earth, and at great depth, and perhaps subsequently thrown up by volcanic eruptions. Alternatively, they may have crystallized from the kimberlite as it cooled in the places at which it is now found. Even now it is not possible to decide definitely between these two theories, and, as so often happens in science, it may be that both of them are partly right, and that both origins are possible for diamonds. There is plenty of evidence that many diamonds have grown in several stages, with one layer over another – a crystallographic onion, as it were – though you often need a microscope to see the boundaries between the layers (see page 11). These different stages of growth may have been separated by millions of years.

If diamonds were formed in the depths of the Earth, then the present high-pressure/high-temperature industrial process could well be analogous to the natural one, and the most important differences would lie in the scale and the time taken to form large diamonds. The fact that we find the diamonds in a certain kind of rock is then an accident rather than a valuable clue, and will not help us very much.

A great many diamonds contain small crystals of other well-known minerals, and if the diamonds were formed in the depths of the Earth, the minerals must also have come from there. Most of them are much more easily altered than are diamonds during ordinary geological processes, but here we have small geological samples from great depths in the Earth which are neatly packaged in transparent containers of a strength and durability we cannot begin to imitate. These samples are being studied by several different techniques. Thus, at a time when we are beginning to understand the basis of life itself and to venture out into space, making and studying diamonds may help us to understand that most inaccessible place in the universe – the centre of our own planet.

Questions

1. Why is it so difficult to make large synthetic diamonds?
2. There is an old saying that it needs a diamond to cut a diamond. Why is this so and to what uses are diamonds put in industry?
3. There is still a great deal of speculation as to how natural diamonds are formed. From what you have read in this book, what do you think?

Some industrial applications of diamonds

Marble being cut with a diamond frame saw.

Turning a corneal contact lens with a diamond tool. Made of acrylic resin, the finished lens is only about 8 mm in diameter and 0.1 mm thick. Natural diamond is used here. *De Beers.*

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