OCT 3 1966

Reprinted from "The New Scientist," Volume 8, Pages 1660-1662

Materials for the Future—5

Making new materials at very high pressures

Diamond is so far the most important material synthesized by using very high-pressure techniques. But there are fascinating possibilities of creating a wide range of substances, including semi-conductors, harder steels and a new family of plastics

---

by Dr. H. A. GEBBIE
Basic Physics Division, National Physical Laboratory

FOR many people very high pressure technique is associated with the successful synthesis of diamond about five years ago. But for others it is associated with the lifelong work of the American Nobel Prize winner P. W. Bridgman. If they are physicists, it will almost certainly be the second. Now Bridgman did not himself achieve this synthesis, but it would be difficult to deny that his contributions to high-pressure physics in the design of apparatus, to pressure measurement and to the study of phase relations (the relations between physically different forms of the same material) were of the first importance to those who finally did. It seems likely, then, that progress in the relatively new field of high-pressure chemistry, by which new substances can certainly be created, will be closely connected with work on the physics of high pressure where measurements are made to study changes when pressure is the independent variable.

Pressure is a measure of the mechanical energy of a system. There is therefore the same kind of interest in subjecting matter to extreme pressures as there is to the use of high-energy accelerators, or extreme temperature devices. There is, however, a difference —that comparatively little effort has been put into finding ways to do it. This is particularly true of Great Britain, where there has never been a large school of ultra-high pressure research.

At present it is possible to maintain material at pressures up to about 200,000 atmospheres. The significance of pressures of this order is that the stresses produced are greater than binding forces between atoms of most solids, and atomic rearrangements take place which bring the material into equilibrium with the new conditions. In doing so, the solid completely changes its character and becomes a new substance. In some cases the new solid continues to exist when the pressure is removed even though it is not stable in the thermodynamic sense. By far the best example of such a solid is diamond. and its continuing value brings out the difference between stability in the material and the thermodynamic sense It is not the only one, however, and an account will be given later of other new solids which have been produced by very high pressure synthesis.

This almost certainly prompts the question, how are these pressures obtained when it is said that they reach the limiting stresses in solids? The first and obvious answer is that the very strongest materials, such as high-grade steels, cemented tungsten carbide (carboloy) and even diamond itself are used in the construction of high-pressure apparatus. Less obvious is the means by which, through careful design, the most highly stressed parts of very high pressure devices are "supported" by less-stressed members, and so on down the stress scale till the pressure can be held by the ordinary steel structure of a hydraulic press.

The clearest but most extreme example of "support" in this sense would be to have one pressure vessel completely enclosed in another containing a pressure-transmitting medium. If the second is at atmospheric pressure and is stressed close to the limiting value, then the inner vessel can contain a pressure which is increased by the limiting amount—and so in principle the pressure can be "cascaded" upwards even though the stress in any one vessel is limited. In practice this type of "support" is difficult to achieve, but the principle is used in all forms of extremely high-pressure apparatus

Many of these original designs were the work of P. W. Bridgman, and from them another American, H. Tracy Hall, has developed two new forms which have been particularly successful. The first of these is a conical carboloy piston device, with a cylindrical chamber supported by concentric steel binding rings from which the name "Belt" apparatus is taken. The second type of equipment which Hall invented is the tetrahedral design. In this, the sample is contained in a volume of that shape whose surfaces are defined by the plane faces of four carboloy anvils pushed by hydraulic rams. In both of these devices use is made of gaskets of pyrophyllite. a silicate mineral which, for this purpose, has a favourable combination of friction and high-pressure flow. The pyrophyllite allows the pistons or anvils to move and build up the pressure, while at the same time acting as a very viscous liquid transmitting the pressure and providing a seal. It is an electrical and thermal insulator, so that a specimen completely enclosed by it can be made considerably hotter than the carboloy components. This is very important because the strength of carboloy decreases rapidly with temperature. It is in this ability to produce simultaneous high pressure and high temperatures that the new forms of apparatus invented by Hall are particularly valuable, and where they have the greatest advance on Bridgman's apparatus.

Though it is not used for synthesis, another way of generating high pressures should be mentioned here. This is to make them last only a short time by having explosives drive into the sample —either projectiles or shock waves. It is by the latter that the very highest known pressures have been obtained. Only recently in *The New Scientist* (Notes and Comments, 15 September, 1960) it was reported that Russian physicists claimed to have reached pressures of five million atmospheres in this way by focusing shock waves. Their methods have not been described in detail, but full scientific publications have appeared from the United States on similar work giving evidence of pressures of two million atmospheres having been achieved.

Now what can a physicist study and why, when he has such pressures at his disposal? Most physical measurements are more difficult in high-pressure apparatus than in experiments when other quantities like temperature or magnetic field have to be varied, so the range of experiments is limited. What might seem to be the simplest experiment of measuring the volume changes with pressure, to determine compressibility, is in fact quite difficult because the changes are small and the containing apparatus may also be changing. Nevertheless a great deal has been done to determine, for different substances, the equations of state which describe the relations between pressure, volume and temperature. The study of changes of phase—from one form of the solid to the other—which can be found from the equations of state is particularly important.

Another quantity which has been measured for a large number of solids at high pressures is electrical resistance. It is useful for detecting phase changes because these are very often accompanied by sharp changes in resistance. Such changes are much used as fixed points in the scale of pressure above 10,000 atmospheres. Bridgman assigned values to the pressures at which these sharp changes took place by measuring them in apparatus where the pressure could be calculated from the known loading, dimensions and corrections for frictional loss. Resistance measurements in bismuth, thallium, caesium, barium and lead are particularly valuable in finding the relationship between specimen pressure and external loading with an apparatus where the frictional loss is unknown. Other physical measurements on specimens at high pressures include optical absorption spectra and X-ray patterns. The former, made particularly by H. G. Drickamer and his collaborators at University of Illinois, give valuable information about how the energy band structure varies with the separation of atoms in crystals, and has been applied extensively to the study of semiconductors. The latter have been made at Chicago by A. W. Lawson, and elsewhere, to get lattice parameters.

Now in what fields does the availability of such data add to our understanding? Geophysics is certainly the most obvious. To improve our understanding of the internal structure of the Earth, the physical characteristics of materials likely to be found there must be known. The pressure at the centre of the Earth is estimated at three million atmospheres, so if we include the recent advances made by shock wave techniques we can make some laboratory measurements over the entire pressure range to be found on this planet. But the contribution to geophysics is not limited to the extreme values. Inside the range to 200,000 atmospheres where static pressure can be maintained, and which corresponds to a depth on the Earth of 500 miles, the phase diagrams of a number of minerals have been studied to find the solids which can be expected to exist, and to measure their properties. It is hoped that information of this kind might help us to understand the famous Mohorovicic discontinuity in the Earth's crust. Conversely, when geological specimens are shown to be of a form which could have been made only under high pressures, the depth of their original site can be estimated and so extra information on Earth movements is obtained.

Now that something is known about the techniques for producing high pressures and what can be measured, we turn to their use in the synthesis of material. Diamond is by far the most important example to date, so its particular history is worth brief consideration. For the obvious prize of being able to make valuable gem diamonds, a number of people over the last 100 years have made considerable efforts to achieve the synthesis. In these efforts high pressures have always been used because diamond has a density of 3.5, while graphite, which is the stable form of carbon under ordinary conditions, has a density of 2.5. So it was felt that if only graphite were to be subjected to a sufficiently high pressure, diamonds would be formed. This was an illusion, because even after the study of the phase relationships between the different forms of carbon had established the temperatures and pressures at which diamond would be the stable form, the problem remained of finding the combination of these at which the reaction would go at a worth-while rate; that is, the kinetics of the reaction still had to be studied. These phase studies showed that at room temperature the pressure at which diamond was more stable than graphite was about 20,000 atmospheres and that this pressure increased with increasing temperature. This meant that in fact most of the early attempts had not been thermodynamically sound because the pressures were too low, quite apart from the matter of the kinetics. After the second World War the Research Laboratory of the General Electric Co. in the United States started experiments having thermodynamic data, or at least extrapolations from it, to guide them. H. Tracy Hall invented the "Belt" apparatus mentioned above. With this apparatus pressures up to 100,000 atmospheres could be realized simultaneously with temperatures of 2,000° C, and in it successful diamond synthesis was achieved. This was first reported in 1955, and in 1959 a much fuller account was given which showed the very important part played by metal catalysts in the kinetics of this process. Tantalum was quoted as being particularly effective, but several other metals could be used. Although gem quality diamonds have not yet been made, synthetic diamond is now an important article of commerce, competing with bort or natural commercial diamonds for use in abrasives. In 1959 General Electric in the United States manufactured about ½ ton of synthetic diamond with a value of £3,000,000.

Closely related to diamond is a cubic form of the compound boron nitride which normally is found in a hexagonal modification corresponding to graphite. This new material, which has been