

TRANSFORMATIONS IN SOLIDS AT HIGH PRESSURE

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INTRODUCTION

Apparatus is available today that will routinely produce pressures near 70,000 atmospheres simultaneously with temperatures of 1500°C on a sample of about 2 cc. volume. The limitation on the attainable pressure and volume is imposed by the compressive strength of cemented tungsten carbides. Present technology is unable to produce sound tungsten carbide parts (anvils, pistons, cylinders, etc.) of large size. By sacrificing tungsten carbide anvils it is possible to obtain pressures of about 135,000 atmospheres at 1500°C in a volume of approximately .02 cc. Apparatus used for simultaneous pressure, temperature work are primarily of the belt or multiple anvil type such as the tetrahedral or hexahedral press. By using small Bridgman anvils, pressures beyond 500 kilobar (at room temperature) have been reported in paper-thin samples about .001" thick by 1/16" in diameter.

The conditions listed above, obtainable in static pressure apparatus, are sufficient to induce a variety of changes in solids. As a matter of fact, pressure seems to be a more effective agent in creating new polymorphic forms of substances than does temperature. However, pressure and temperature combined are much more effective than either agent used alone. As an example of this situation, 53 metallic elements when subjected to high temperatures have produced a total of 21 new polymorphs, but the same metals subjected to high pressure at room temperature have yielded 40 new polymorphs. When ice is subjected to high or low temperature its crystal structure remains the same and no new polymorphs are produced. The action of high pressure at room temperature on ice produces one new polymorph. On the other hand, the combined action of high pressure and temperature has produced five new polymorphic modifications of ice.

Permanent and Reversible Transformations The transformations produced in solids by the effect of pressure (with or without temperature) may be classed as "permanent," or "reversible." The formation of diamond from graphite by the combined action of pressure and temperature can be classed as permanent or irreversible change. Pressure and temperature are applied to graphite in the presence of a solvent-catalyst such as nickel whereupon the graphite is transformed to diamond. After this transformation has taken place, the temperature is reduced to room temperature and, following this, the pressure is then reduced. This sequence of events allows the diamond to be "captured" in the permanent state even though diamond is thermodynamically unstable with respect to graphite under room conditions by about 500 small calories. The long term stability of diamond is brought about by the very large activation energy required for its transformation to graphite at room temperature.

An example of a reversible change taking place in a solid is given by the substance bismuth. As bismuth is compressed it transforms to new polymorphic modifications at 25,000 atmospheres, 27,500 atmospheres, and 75,000 atmospheres. As pressure is reduced, however, the bismuth reversibly transforms through the lower pressure phases until it returns to the normal atmospheric variety. Sometimes the reversible transformations are sluggish. A transformation from a face-centered-cubic to a body-centered-cubic phase occurs in the metal ytterbium near 40,000 atmospheres as pressure is increased. However, as pressure is decreased the reverse transformation occurs by as much as 25,000 atmospheres lower pressure and proceeds very slowly. It is quite likely that the high pressure body centered cubic form of ytterbium could be obtained in a "permanent" form by cooling to low temperature before pressure is released. This is the case with a high pressure form of indium antimonide that will be discussed later.

Transformations in solids may be further classified as follows:

1. Solid-solid
2. Solid-liquid
3. Isostructural transformation (Same crystal structure to same crystal structure of higher density)

4. Electronic transformation
5. Close-packed to non-close packed
6. Non-metal to metal
7. Metal to non-metal
8. Magnetic Transitions

Solid-Solid Transitions A considerable number of polymorphic transitions, of a permanent nature, have now been accomplished by high pressure, temperature means. Interest in these transformations stems from the synthesis of diamond at the General Electric Company in 1954. Diamond is still the only commercial product that has come from high pressure, temperature research. Most university research is concerned with the measurement of the properties of materials and very little work is directed toward the production of new permanent materials. It is supposed that there is considerable effort going on in industry to use heat and pressure to produce new materials; however, most of this work is proprietary and is not being published. The present state of high pressure technology dictates that a new substance, to be produced economically, must have a value of about \$5000 per pound. Diamonds meet this criteria. Classes of substances that could meet this value criteria are abrasives, semi-conductors and drugs. In order for a new abrasive to be worth \$5000 per pound, it would have to have a hardness and wear resistance, rivaling that of diamond. Any semi-conductor produced by high pressure, temperature means would have to have exceptional properties that have not been obtained in semi-conducting substances produced by ordinary means. Very high pressures have been effective in causing polymerization in some organic substances that have not been possible by any other means. For example, steric hindrance between the methyl groups in tetramethylethylene is so great that it has been impossible to break the double bond and cause polymerization to occur by the usual procedures. However, the application of very high pressures causes the methyl groups to bend away from their normal positions, allowing the double bond to polymerize, thus forming a polytetramethylethylene substance. It might be that there are instances of steric hindrance that prevent the synthesis of important drugs by conventional techniques. In this case high pressure might be effective and, if so, might prove to be a commercially feasible operation.

Many of the permanent materials that have been produced require either a solvent or a catalyst or both for their synthesis. The difference between a solvent and a catalyst can be a point for argument. However, the transition metals used in the synthesis of diamond appear to perform both functions, i.e., the transition metal acts as a solvent and also as a catalyst. Lead, silica, and silicate minerals will dissolve graphite under high pressure, temperature conditions. However, it has not been possible to

form diamond in these solvent systems under conditions where diamond is thought to be stable. Apparently nickel and other transition metals act as solvent to dissolve graphite and break up the crystalline graphite lattice. But, in addition, the mixture apparently forms a loose complex with the carbon and orients the extended carbon bonds in a proper spatial arrangement to join together in tetrahedral bonding. Of course diamond has now been synthesized directly from graphite without the use of a solvent-catalyst by utilizing higher pressures and temperatures than are necessary when the solvent-catalyst is used. This may also prove to be true with other polymorphic changes that have been produced in other substances. Other outstanding polymorphic, permanent transformations that have been brought about include the cubic form of boron nitride (an analog of diamond), the dense form of silica known as coesite and the yet more dense form known as stishovite. This latter material, Professor Vereshchagin of the Moscow institute of High Pressure Physics informs me, should be designated Popovavite inasmuch as Popova was the director of the student's (Stishov's) thesis when this discovery was made. At any rate, Stishovite is the first substance in which silicon has been found to have a coordination number of six rather than the usual four. Following the discovery of Coesite and Stishovite in the laboratory, these materials were found in meteoritic craters and was apparently produced by impact of a meteor with silicate containing substances.

Carbon analogs have been of great interest to high pressure researchers. Silicon and germanium of course normally exist in a diamond-like tetrahedral bonding structure. When these materials have been subjected to high pressures still further crystallographic modifications have been produced and some of these modifications have been retained at room temperature. These modifications include body-centered-cubic, distorted tetrahedra type, body-centered tetragonal white tin type, and hexagonal Wurtzite type. Interesting related structural transitions involving zinc-blend, wurtzite and sodium chloride arrangements of atoms have been found in such substances as CdTe, CdS, CdSe, and EuTe. In addition to these simple AB type compounds, compounds such as LiInS_2 have been prepared in structures similar to those discussed above.

The high pressure synthesis of new chemical compounds is indirectly related to pressure induced solid-solid transitions. A compound of composition B₂O has been synthesized at about 65,000 atmospheres and 1500°C that has a hexagonal structure related to that of graphite. Considering that oxygen contributes six electrons to bonding and each of the two boron elements contributes three electrons, the average number of bonding electrons per atom equals four--the same number as there are in carbon. Therefore, B₂O is an isoelectronic analog of carbon. Attempts to prepare a diamond-like form of B₂O have thus far been unsuccessful. B₂O is an "unsymmetrical," isoelectronic analog of a group IV element. Such "symmetrical" group IV analogs as BN, AlN, BP, GaAs, and so on have long been studied but the unsymmetrical types such as B₂O, BeN₂, MgP₂, Al₂S, and Al₃Cl have been completely ignored.

It is possible to completely generalize the isoelectronic analog concept by means of the following selection rule:

$$\bar{G} = \frac{\sum d_i e_i}{\sum d_i}$$

Where \bar{G} assumes the integral values 1, 2, 3, . . . corresponding to the periodic table groups I, II, III, . . . In this expression, the number of bonding electrons contributed by an atom of kind *i* is designated *e_i*, and *d_i* gives the number per formula weight of atoms of this kind. Both *e_i* and *d_i* assume integral values. The author has named compounds defined by this selection rule periodic compounds. When *e_i* is allowed to range from 1 through 7, this selection rule generates about 500 group IV analogs and if all the atoms of the periodic table which normally supply 1 to 6 valence electrons to bonding are considered. If the number of kinds of atoms used to form a group IV periodic compound is increased from 2 to 3, the number of possible compounds (when all atoms which normally supply 1 to 6 bonding electrons are utilized) is increased to about 13,000. The generalized isoelectronic analog (periodic compound) selection rule thus indicates that there remain thousands of unsynthesized, uncharacterized and unexplored group IV analogs that may be of possible scientific and technological value. This is also true for the group II, III, V, and VI periodic compounds. The possible configurations of group II through IV analogs involving two types of atoms and three types of atoms are given in tables 1 and 2, respectively. Each numerical configuration represents a number of possible compounds. For example, 2₃7₂ represents such compounds as Be₃F₂, Zn₃Cl₂ and Hg₃I₂, or any compound in which three atoms of one kind each contribute two electrons and two atoms of another kind each contribute seven electrons to chemical bonding.

Periodic compounds in which the average principle quantum number \bar{n} and the electronegativity difference ΔX between the elements making up a compound are small, tend to form, covalent bonds. In many instances such compounds would be amenable to synthesis by high pressures temperature techniques. In the past, there have been few guidelines to help a chemist formulate compounds that might be synthesized by high pressure, temperature techniques. Lists of periodic compounds together with values of \bar{n} and ΔX , should provide some useful guidelines for the future.

Table 1. Periodic compounds (binaries). Each numerical configuration represents a number of possible compounds: for example 2₃7₂ represents such compounds as Be₃F₂, Zn₃Cl₂, and Hg₃I₂, or any compound in which three atoms of one kind each contribute two electrons and two atoms of another kind each contribute seven electrons to chemical bonding. \bar{G} indicates the periodic group, II, III, VI . . ., being simulated. Absence of subscript indicates a subscript 1.

\bar{G}	Configurations
II	1 ₅ 7, 1 ₄ 6, 1 ₃ 5, 1 ₂ 4, 1 3
III	1 ₃ 6 ₂ , 1 ₂ 7, 1 4 ₂ , 1 5; 2 ₄ 7, 2 ₃ 6, 2 ₂ 5, 2 4
IV	1 ₂ 6 ₃ , 1 5 ₃ , 1 7; 2 ₃ 7 ₂ , 2 5 ₂ , 2 6; 3 ₃ 7, 3 ₂ 6, 3 5
V	1 6 ₄ , 1 7 ₂ ; 2 ₂ 7 ₃ , 2 6 ₃ ; 3 6 ₂ , 3 7; 4 ₂ 7, 4 6
VI	1 7 ₅ ; 2 7 ₄ ; 3 7 ₃ ; 4 7 ₂ ; 5 7

Table 2. Periodic compounds (ternaries). Nomenclature is the same as indicated in Table 3 with the addition at *n*, when it appears as a subscript, may assume any value.

\bar{G}	Configurations
II	1 ₉ 6 7, 1 ₈ 5 7, 1 ₇ 4 7, 1 ₇ 5 ₆ , 1 ₆ 3 7, 1 ₆ 4 6, 1 ₅ 2 _n 7, 1 ₅ 3 6, 1 ₅ 4 5, 1 ₄ 2 _n 6, 1 ₄ 3 5, 1 ₃ 2 _n 5, 1 ₃ 3 4, 1 ₂ 2 _n 4, 1 2 _n 3
III	1 ₅ 6 ₂ 7, 1 ₄ 5 6 ₂ , 1 ₃ 3 _n 6 ₂ , 1 ₃ 4 ₂ 7, 1 ₃ 5 7, 1 ₂ 3 _n 7, 1 ₂ 4 ₂ 5, 1 ₂ 4 6, 1 2 ₂ 5 ₂ , 1 2 ₂ 7, 1 2 4 ₃ , 1 2 6, 1 3 _n 4 ₂ , 1 3 _n 5; 2 ₇ 6 7, 2 ₆ 5 7, 2 ₅ 4 7, 2 ₅ 5 6, 2 ₄ 3 _n 7, 2 ₄ 4 6, 2 ₃ 3 _n 6, 2 ₃ 4 5, 2 ₂ 3 _n 5, 2 3 _n 4
IV	1 ₃ 5 6 ₄ , 1 ₃ 6 ₃ 7, 1 ₂ 2 6 ₄ , 1 ₂ 4 _n 6 ₃ , 1 ₂ 5 ₃ 7, 1 2 ₃ 7 ₃ , 1 2 5 ₅ , 1 3 ₃ 7 ₂ , 1 3 5 ₄ , 1 3 6 ₂ , 1 4 _n 5 ₃ , 1 4 _n 7, 1 5 6; 2 ₄ 6 7 ₂ , 2 ₃ 4 _n 7 ₂ , 2 ₃ 5 ₄ 6, 2 ₂ 5 ₂ 6, 2 ₂ 5 7, 2 3 ₄ 6 ₃ , 2 3 ₂ 6 ₂ , 2 3 5 ₃ , 2 3 7, 2 4 _n 5 ₂ , 2 4 _n 6; 3 ₅ 6 7, 3 ₄ 5 7, 3 ₃ 4 _n 7, 3 ₃ 5 6, 3 ₂ 4 _n 6, 3 4 _n 5
V	1 2 ₂ 7 ₅ , 1 2 6 ₇ , 1 3 6 ₆ , 1 3 7 ₃ , 1 4 ₂ 7 ₃ , 1 4 6 ₅ , 1 5 _n 6 ₄ , 1 5 _n 7 ₂ , 1 6 ₂ 7; 2 ₂ 3 7 ₄ , 2 ₂ 5 _n 7 ₃ , 2 3 6 ₅ , 2 4 6 ₄ , 2 4 7 ₂ , 2 5 _n 6 ₃ , 2 6 7; 3 ₂ 6 ₂ 7, 3 4 ₂ 7 ₂ , 3 4 6 ₃ , 3 5 _n 6 ₂ , 3 5 _n 7; 4 ₃ 6 7, 4 ₂ 5 _n 7, 4 5 _n 6
VI	1 2 7 ₉ , 1 3 7 ₈ , 1 4 7 ₇ , 1 5 7 ₆ , 1 6 _n 7 ₅ ; 2 3 7 ₇ , 2 4 7 ₆ , 2 5 7 ₅ , 2 6 _n 7 ₄ ; 3 4 7 ₅ , 3 5 7 ₄ , 3 6 _n 7 ₃ ; 4 5 7 ₃ , 4 6 _n 7 ₂ ; 5 6 _n 7

Solid-Liquid Transitions Solid to liquid transitions have normally been brought about by increasing the temperature until melting occurs. Solid to liquid transitions may also be brought about by applying pressure to some solid substances. Melting will occur in these as pressure is applied if the fusion curve (a plot of melting temperature vs. pressure) has a negative slope. In other words the melting temperature of the solid is lowered by an application of pressure. This occurs for substances in which the solid (at the melting point) is less dense than the liquid. The pressures available today can drastically alter melting points. For example, the normal melting point of Germanium (about 900°C) is lowered to about 300°C by application of a pressure of 120,000 atmospheres. The melting point of such substances as silicon, bismuth and water is also lowered by increasing pressure. Most substances have their melting temperatures increased by application of pressure. As an example, white tin which normally melts at 232°C has its melting point increased to about 570°C at a pressure of 100,000 atmospheres. Actually there is a cusp (triple point) in the melting curve of tin at 34,000 atmospheres and 310°C caused by the formation of a new, high pressure phase. A complex variety of melting phenomena have been observed in recent years including the phenomena of a maxima in the melting. Such maxima has been observed in cesium.

Isostructural Transformations One of the most interesting types of solid-solid transitions that has been observed to occur by application of pressure is a transition from a face-centered-cubic structure to another face-centered-cubic structure of higher density. This phenomenon was first observed in the element cerium. At a pressure of about 7000 atmospheres cerium, which normally has a face-centered-cubic structure, undergoes a volume transformation (with a 14% reduction in volume) to another face-centered-cubic structure of higher density. This transformation is reversible, but it is quite sluggish. A similar transformation had been postulated to occur in the element cesium. Proof that such a transition does occur was recently obtained by use of a tetrahedral, x-ray diffraction press. However, the excellent pressure resolution of this device indicates a more complicated situation to exist than had previously been suspected. Two, closely separated (in pressure) transitions in cesium occur near 42 kilobars. The first consists of a face-centered-cubic to face-centered-cubic change with a volume reduction of 9%. This is immediately followed at a pressure of 42.5 kilobars by a transition from face-centered-cubic to a hexagonal close-packed structure with a variable C-axis repeat distance, The volume change is about 2%. These two transformations; i.e., in cerium and cesium, have been attributed to changes in electronic structures and have been referred to as "electronic" transitions. There are other types of electronic phenomena that might be induced by high pressure that have not yet been observed experimentally. For example, many of the atoms in their normal state have unpaired electrons. It is conceivable that under some circumstances high pressure might force these unpaired electrons to become paired. Experiments to detect this phenomena would be worthwhile. The only other isostructural transformation currently known occurs in the compound europium telluride which has both low and high pressure polymorphs with sodium chloride type structures.

Close-Packed to Non-Close-Packed Transformations Transformations from close-packed structures to non-close-packed structures occur in many substances when the temperature is increased. It might be expected that such a transformation would never occur as pressure is increased on a substance. As a matter of fact, the discovery of the face-centered-cubic to face-centered-cubic transformation in cerium led most high pressure researchers to conclude that, once a close-packed structure was achieved, the application of pressure (if it led to the formation of a more dense phase) would always lead to another close-packed structure. It came as a surprise, then, when the element ytterbium (which normally exists in a face-centered-cubic structure) was found to transform to a body-centered-cubic structure at about 40,000 atmospheres. No violation of the laws of thermodynamics occurs in this transformation. There is a small discontinuous decrease in the volume. Therefore, in order for the atoms to rearrange into the more loosely packed body centered cubic symmetry, there must be a discontinuous decrease in the effective atomic radius of the ytterbium atom. The ytterbium transition has been classed as an electronic transition along with cesium and cerium. After the nature of the ytterbium transition was elucidated by high pressure x-ray diffraction techniques, similar transitions were discovered in strontium, titanium and zirconium.

It is supposed that electronic transitions involve the forcing of an electron (speaking from an isolated atom point of view) from an outer to an inner electron shell. Such an event of course would be possible in the transition or actinide elements. The energy levels between some of the inner and outer electronic orbits are rather small in such elements as cesium, ytterbium, and cerium. Consequently, the electronic phase changes are rather easily promoted by the application of pressure to these elements. For most elements, however, it is likely that pressures much greater than those currently available in static pressure apparatus will be required to produce such changes. If it were possible to increase pressure indefinitely, an element or compound might be forced to go through very many phase changes—many of them of an electronic nature.

Eventually a situation would occur similar to that in some e_i the dense stars in which only a "soup" of electrons and nuclei exists. Under such circumstances, chemistry as we normally know it would cease to exist. Before this point would be reached, however, chemistry, which depends on the behavior of the outermost electrons, would be different for elements that had passed through electronic phase changes than the chemistry would be for elements in their normal electronic states at one atmosphere. If pressures could be increased to hundreds of billions of atmospheres, the atomic nuclei could be pushed to within the critical distance of about 10^{-13} centimeters wherein nuclear reactions would take place. Reactions between electrons and nucleons would undoubtedly occur long before these kind of pressures were reached. The type of phenomena known as K-capture wherein an electron in the K shell falls into the nucleus could probably be made to occur with greater rapidity at one million atmospheres than it does at one atmosphere for some elements in which this normally occurs.

Non Metal to Metal Transitions One of the most interesting phenomena that occurs in solid-solid transformations under high pressures is the transformation of a non-metal into a metal. Such a possibility appears to have been first recognized by Wigner and Huntington in 1935 when they calculated the energy necessary to transform hydrogen into a metal. Their calculations indicated that this should occur near 450,000 atmospheres. Later calculations put the figure much higher and out of the range of static apparatus. It has been calculated that ammonia should become metallic at a pressure of approximately 250,000 atmospheres. It is unlikely that hydrogen and ammonia would remain in a metallic condition on release of pressure at room temperature, but the permanence of the metallic form might be enhanced at low temperature. Although no one has as yet converted hydrogen and ammonia to metals, sulphur, iodine, germanium, indium antimonide, and other substances have been converted. Some of the transformations are discontinuous while others continuously vary from a non-conductor through a semi-conductor to the metallic state. One of the substances, indium antimonide, has been captured in the metallic state by cooling to low temperature before the release of pressure. When this material is slowly warmed, it begins to transform to the normal form around -63°C . Sometimes a material passes from a conductor to a non-conductor.

Metal to Non-Metal Transitions The element ytterbium is normally a metallic electrical conductor, As temperature and pressure are both varied on this substance, non-conducting regions are observed. There are also regions in which ytterbium is a good semi-conductor and there are regions in which it is definitely metallic. The electrical conductivity of the element cesium can be made to decrease by a factor of 10 on increasing pressure. Similar decreases have been observed in other metals.

Growth of Large Crystals The application of pressure to a substance should favor the formation of single crystals. This is so because the regions between crystal grains (the grain boundaries) are of high energy. Since the density of grain boundaries is higher than the density of a single crystal, pressure should tend to remove grain boundaries and other imperfections to produce a single crystal. The activation energy for removal of grain boundaries must be relatively high, however, for many substances, because pressure induced single crystal growth from polycrystalline aggregates has only been observed in a few substances. Fine grained polycrystalline cesium subjected to high pressure at room temperature tends to grow into large single crystals. It may be that this occurs readily in cesium because of the softness or "fluidity" of this material. The growth of large crystals of sodium chloride from small crystals at high pressure and moderate temperature has also been observed.

Magnetic Transitions There are other types of transformations that are brought about in solids by the application of pressure. Magnetic transitions are currently coming under the scrutiny of the researcher. The technique of using neutron diffraction under high pressure conditions is currently producing useful experimental information on magnetic changes. The Neel point transformation in chromium has been studied by this means. This transformation occurs at the relatively low pressure of approximately 3000 atmospheres. Electron and nuclear magnetic resonance techniques are also now being used under high pressure conditions.

In conclusion, ten years ago there was almost a negligible amount of research being conducted at high pressure. Today there are more than 250 laboratories around the world engaged in high pressure studies. Most every type of measurement previously used under atmospheric conditions is being reconsidered with the added variable of pressure. From a thermodynamic standpoint pressure, of course, is just as important a variable as temperature and composition. However, apparatus capable for providing the very high pressures and temperatures needed to bring about significant changes in atoms and molecules has only become available in the past ten years. It is to be expected that the field of high pressure will continue to expand

rapidly and will reveal much additional, fundamental information concerning the properties of atomic and molecular systems.

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