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I. Introduction

All matter upon this earth is made of the elements (listed in the standard periodic table), singly or in combination. Combinations of the elements are called compounds, and millions of compounds are known.

Elements and compounds often exist in more than one solid form. The different solid forms of the same compound or element are called polymorphs. A classic pair of polymorphs are the substances graphite and diamond. These materials have radically different properties. Diamond is the hardest substance known, is transparent, does not conduct electricity, and has a density 36 percent greater than graphite. It is also rare and in its least costly form, that of industrial diamond grit, is valued at $6,000 per pound. Graphite, on the other hand, is soft and unctuous, is black and opaque, conducts electricity, is relatively common (the primary ingredient in the so-called lead-pencil is graphite), and costs but a few cents per pound. In spite of these gross differences, diamond and graphite are both composed of the element carbon. This singular fact was discovered by the French chemist, Antoine Lavoisier, in the year 1792. From that time forth scientists set about to find a way to transform the inexpensive graphite into the expensive diamond. As many of you know, it was my fortune to first effect this polymorphic change. Since the December day in 1954 when the first tiny, sparkling, man-made crystals were observed, more than 10,000 pounds (over 22,000,000 carats) of diamond grit have been manufactured for industrial consumption.

II. Crystals

At this point the important question could be asked, "Since graphite and diamond are both made of carbon, what is it that makes them so different?" The answer is, "The arrangements of carbon atoms in the two substances are different." Polymorphs differ from each other only in the spatial arrangement of their constituent atoms. This fact, long theorized to be true by mineralogists from their studies of crystals, remained unproved until the advent of the science of x-ray crystallography about 1912. In x-ray crystallography matter is probed with a tiny beam of x-rays. This beam is diffracted in a complex manner by the atoms. Proper interpretation of the diffraction pattern can reveal the arrangement of the atoms in a solid

substance. The use of x-ray diffraction to study substances has shown that the majority of solids are crystalline. The distinguishing feature of a crystal is its orderly periodic arrangement of atoms. Some substances may consist of a single large crystal. On the other hand, many substances consist of myriads of microscopic interlocking crystals. Steel and most metals are so constituted and are said to be polycrystalline. A few substances do not possess an ordered arrangement of atoms and are, consequently, noncrystalline or amorphous. Glass is noncrystalline. Some substances are partially amorphous and partially crystalline. Plastics are generally of this nature and consist of tiny, intermixed amorphous and crystalline regions.

III. Patterns

Before giving further attention to the matter of atomic arrangements in crystals, it will be instructive to pursue the interesting subject of patterns. Periodic patterns are to be seen everywhere. They appear in wallpaper, tiling, architecture, lacework, rugs, tapestries, etc. Two observations can be made concerning any periodic pattern: (1) The pattern consists of a motif; (2) the motif is repeated in a systematic way to produce the entire pattern. An infinity of motifs is possible. Any limitation here is imposed only by the artist's or designer's imagination. It may be surprising, however, to learn that there are a limited number of ways in which a motif may be repeated to produce a pattern. In two dimensions there are only seventeen possible ways that a motif can be systematically repeated.

IV. Symmetry

The limitation in the number of ways that a motif can be repeated is imposed by considerations of symmetry. Everyone is familiar with the ordinary symmetry of right and left handedness. This type of symmetry is called *mirror symmetry.* A left hand reflected in a mirror becomes a right hand; consequently, the right hand is said to be a mirror image of the left. Other types of symmetry are possible but are not generally as well known as mirror symmetry.

Rotational symmetry is that kind of symmetry in which the motif is symmetrically disposed around an axis like the spokes around a wheel. For producing patterns, rotational symmetry is limited to four kinds: two-, three-, four-, and sixfold rotational symmetry. A two-bladed aeroplane propeller possesses twofold rotational symmetry about its hub. A three-leaf clover possesses threefold symmetry about its stem, while a four-leaf clover possesses fourfold symmetry and so on.

Translational symmetry is present in all patterns. It is present when a motif is periodically repeated at regular intervals to form an ordered array.

Glide symmetry occurs when a motif is repeated by a two-step process in which a mirror image of the motif is first formed and then is translated a distance equal to one-half the motif repeat distance. Glide symmetry is present in the third pattern from the left top row of Figure 1.

There are other types of symmetry, but those enumerated above (mirror, rotation, translation, and glide) when used in combination are capable of producing all other types that are possible on a flat surface. When a motif is repeated in such a way that all possible combinations of the above symmetries are utilized, seventeen plane patterns are produced. These patterns, with the simple motif of the lower case letter "d," are presented in Figure 1. Note that the letters "b," "d," "p," and "q," are related to each other through mirror and twofold rotational symmetry.

Turning from the two-dimensional world of flat surfaces to the three-dimensional world of space, additional types of symmetry become possible. These additional symmetries make it possible to repeat a three-dimensional object (motif) in space in exactly 230 different ways. There are, then, 230 *space patterns* as compared to only 17 plane patterns.

V. Application to Atomic Systems

What has all this to do with atoms? Simply this: Atoms combine in various ways to form motifs. Atomic motifs organize themselves into any of the possible 230 space patterns to form crystals. Crystals have been found in nature corresponding to all of the possible 230 space patterns.

In determining the internal arrangement of atoms in crystals by means of x-ray techniques, two tasks must be accomplished: (1) the space pattern must be determined; (2) the shape of the motif must be determined; i.e., the number and kinds of atoms and their arrangement in the motif must be found. Both of these tasks can be difficult. However, the problem of determining the nature of the motif is usually much more difficult than the problem of determining the space pattern.

Parenthetically, a few additional remarks concerning symmetry seem appropriate before proceeding further in the sub-microscopic world of atoms. Patterns are evident in all fields of human endeavor, as may be seen from the titles of a few books from the library card file: *The Pattern of Hardy's Poetry, The Pattern of God's Truth, The Pattern of Authority, The Pattern of the Past, Patterns of Success, Patterns of Industrial Growth,* and so on. All patterns, regardless of subject matter, result from the systematic repetition of a motif, and the mode of repetition is based on considerations of symmetry! Symmetry is a basic unifying concept common to the arts, sciences, humanities or any other discipline one would care to mention.

Knowing the spatial arrangement of atoms in crystals is a necessary first step in obtaining an understanding of any property such as hardness,

electrical conductivity, transparency, solubility, melting point, density, malleability and so forth. In most metallic elements (two-thirds of the elements in the periodic table are metals) the repeating motif in the crystal is a single, spherical atom. If such an atom were magnified one billion times it would become about the size of an orange. Using oranges for atoms, four atomic space patterns are demonstrated in Figures 2, 3, and 4. Figure 2 shows the motif arranged in a square array. If additional oranges are placed directly over the oranges in this square array and the process is repeated until several layers are stacked over the bottom layer, a simple three-dimensional space pattern results. This pattern has been given the name *simple cubic* because lines drawn between the centers of any eight, appropriately chosen oranges define a cube. Oranges or atoms arranged in such a fashion do not occupy all the available space. (Note the somewhat square "holes" centered in the midst of any four oranges in Figure 2. These holes occupy 53 percent of the total volume in this pattern.)

A somewhat more compact pattern can be obtained by placing oranges over the holes visible in Figure 2 to form a second layer as shown in Figure 3. This layer has the same square-array appearance as the first layer but is shifted with respect to it. A third layer is now added with each orange located over a hole in the second layer and so on. The resultant space pattern is called *body-centered cubic.* The name is derived from the fact that eight oranges, with centers at the apexes of a cube, enclose an orange centrally located within the body of this cube. This arrangement still contains voids, but only to the extent of 32 percent.

A pattern of even greater compactness can be obtained by arranging oranges as shown in Figure 4. As the bottom layer of oranges is viewed from above, two types of triangular voids are noted. Alternate rows contain triangular voids with apexes pointing up. The in-between rows have apexes pointing down. If a second layer of oranges is placed over the up-pointing voids as shown in the figure, the second layer will have the same appearance as the first but will be shifted with respect to it. In placing a third layer over the second, a choice is available for placing oranges over up-pointing or down-pointing triangles. Should up-pointing triangles be chosen for this and all succeeding layers, a pattern is developed that is called *hexagonal close-packed.*

If the third layer of oranges (above) had been placed over down-pointing voids, the fourth layer over up-pointing voids, and so on to give an up-down-up-down sequence throughout the structure, a pattern would develop that is called *face-centered cubic.* Its overall symmetry is different from that of hexagonal close-packed. Consequently its x-ray diffraction pattern is different and its properties are different. Interestingly enough,

however, the percentage of voids in hexagonal close-packed and face-centered cubic patterns is an identical 26 percent. These two patterns give the closest (densest) packing of spheres that is possible. Arranged in any other pattern the percentage of empty space exceeds 26 percent.

When I was a young man of about sixteen years, an officer of the meat-cutters union hired several neighborhood boys to picket some grocery stores in Ogden, Utah. Wages were low considering that the job turned out to be hazardous to life and limb, but some of us needed money and continued to picket until the butchers and grocers settled their differences. One early morning, while I was picketing a store near 28th and Washington, a farmer arrived with a load of tomatoes and sold six bushels to the store manager. After the farmer departed, the manager brought over some empty bushel baskets and proceeded to repack all the tomatoes. When he finished there were seven bushels, and each looked as full as any in the original six. I was unable to figure out how the store manager accomplished this remarkable feat, and the event passed from conscious memory. Years later, though, as a graduate student, I encountered the subject of the packing of atoms. Suddenly, my mind was illuminated, and in a flash-back to the tomato-repacking incident, I felt as one who had just glimpsed a deep, dark secret—a secret that, in its practical aspects, surely was known to the merchant long before it came to the attention of the scientist. Returning to the data on the density of packing, note that in simple cubic patterns 53 percent of the total space is empty compared with only 26 percent in hexagonal close-packed or face-centered cubic patterns. If the farmer had packed his six bushels of tomatoes in a perfect closest-packed pattern and the merchant had repacked them in a perfect simple cubic pattern, nine bushels would have been obtained.

VI. High-Temperature Polymorphs

Polymorphs were first produced in the laboratory by applying heat to substances. Usually the new forms exist only at the elevated temperature and revert to the normal forms when the temperature is reduced. However, in some instances, particularly if the substance is cooled rapidly (a process known as *quenching),* the high temperature polymorph is retained at room temperature. High strength steel is made by heating an iron alloy until a high temperature polymorph is produced. The alloy is then quenched to room temperature, high temperature polymorph is retained, and a hard, strong steel results. If the iron alloy is cooled slowly, however, the high temperature polymorph reverts to the normal, room temperature form which is relatively soft and weak.

VII. High-Pressure Polymorphs

In recent years high pressure has been found to be a more effective means for producing polymorphs than high temperature. For example, fifty-three metallic elements when subjected to high temperatures have produced a total of only twenty-one new polymorphs. But the same metals, subjected to high-pressure, have yielded forty new polymorphs. It has also been found that the combined action of high pressure and high temperature is more effective than either agent used alone. For instance, ice subjected to high or low temperature produces no new polymorphs. High pressure produces one. The combined action of high pressure and temperature, however, produces five new forms of ice.

Pressure is a concept that is not quite as familiar as temperature. It is possible, though, by use of the imagination, to obtain some feeling for the tremendous pressures used in today's research. To do this, imagine the pressure that must exist at the bottom of the Washington Monument where it rests on its base. (The monument is a granite shaft one-tenth of a mile high.) Now, stack 2,000 Washington Monuments one atop another until they reach into the sky for 200 miles. The pressure at the bottom of this Tower of Babel will now approximate the pressures dealt with daily at Brigham Young University. Concurrent with pressures of this magnitude, temperatures greater than those required to melt steel can also be generated.

Upwards of fifty polymorphs that retain their identity following reduction of pressure and temperature have now been produced. After ten years of high-pressure, high-temperature research, however, diamond is still the only commercial polymorph, though some of the new polymorphs show promise of becoming commercially important, and all of them are of scientific interest.

Under the pressure discussed above, all known liquids turn into solids. Gasoline, water, alcohol, oil or any other material that is normally a liquid becomes a solid under the action of high pressure. Nevertheless, most liquids that have been caused to solidify by pressure return to their normal liquid form on release of pressure. Most solidified liquids can also be reliquefied while under pressure by increasing the temperature. But occasionally other things happen. For example, carbon disulfide, which normally is a clear, volatile liquid, becomes a white, crystalline solid on application of pressure. On release of pressure, this white solid reverts to the normal liquid. If, however, this solid is heated while under pressure, it does not melt but converts to a new polymorphic form. This new polymorph can be quenched to room temperature and retains its identity when pressure is released. It is black and is a semiconductor of electricity. Consequently, it could be made into transistors for use in electronic devices.

The common form of the compound SiO_2 (silicon dioxide) is known as quartz. Most grains of sand are small quartz crystals, and many large rock masses contain quartz as a major constituent. In recent years two most interesting polymorphs of quartz have been prepared by high-pressure, high-temperature techniques. Both polymorphs retain their identity after quenching and release of pressure. One polymorph is named coesite, the other stishovite. Coesite has a greater density than quartz, has a higher refractive index and is harder. Its most unusual property, however, is its exceptional resistance to attack by hydrofluoric acid, which will dissolve quartz. Coesite was the first mineral to be synthesized in the laboratory *before* it was discovered in nature. Several years after the laboratory synthesis coesite was found to be present in large meteor craters and has now been shown to form as a result of the high pressure and temperature generated by a meteor upon impact with the earth. Stishovite was also made in the laboratory before it was discovered in nature. It, too, is present in meteor craters. Stishovite requires a much higher pressure for its formation and is 45 percent denser than coesite, which is already 13 percent denser than quartz. It also has a higher refractive index and is harder than coesite. It is the first silicate mineral known in which six oxygen atoms surround each silicon atom in the space pattern. In all other minerals, no more than four oxygen atoms are coordinated about a silicon atom. The presence of stishovite or coesite in a depression in the earth now gives the geologist conclusive evidence that the depression was formed by a meteor.

Often it is possible by high-pressure, high-temperature means to form compounds in which atoms are combined in ratios never before observed. For example, it has been possible to cause equal numbers of boron and sulfur atoms to unite to form the compound BS (boron monosulfide). Previously, the only known boron-sulfur compounds had the composition B_2S_3 (two atoms of boron for every three atoms of sulfur) or B_2S_5. (two atoms of boron for every five atoms of sulfur). The boron monosulfide can be produced in two polymorphic forms. In one form the space pattern has six-fold rotational symmetry; in the other, the space pattern is related to the pattern of carbon atoms in diamond. The first form is of interest for its thermoelectric properties; i.e., its ability to generate electricity when heated. Heated to a given temperature, it generates a higher voltage than any other known substance.

Boron and oxygen have also been joined in a hitherto unknown combination to form a compound of composition B_2O. This material has a space pattern and properties similar to graphite. Attempts are underway to synthesize a diamond-like polymorph of B_2O which should be nearly as hard as diamond. In this connection a boron-nitrogen compound of composition BN has been made, again by high-pressure, high-temperature

techniques, with a diamond-like space pattern. It stands, at the present time, next to diamond in hardness. A current goal of high pressure researchers is to synthesize a material that will exceed the diamond in hardness. The discovery of a substance substantially harder than diamond could cause a minor industrial revolution.

Other polymorphs produced by high-pressure and temperature include a form of ice that sinks in water (normal ice floats), black phosphorus (normal phosphorus exists as either a white or a red polymorph), and new forms of germanium and silicon. Many new oxides and silicates have also been produced.

The new polymorphs discussed above are retrievable by quenching procedures and do not decompose or revert to their original forms on release of pressure. Consequently, these materials can be studied and their properties determined under normal circumstances. Most polymorphs formed under high pressure-temperature conditions, however, exist in the new form only as long as pressure and temperature are maintained. Consequently, they can be studied only while being subjected to the high pressure and temperature required for their formation. This is a difficult assignment because the structural members required to withstand the tremendous pressures are large and heavy and do not readily admit access to the confined materials within. Any kind of "window" or "conduit" providing for the passage of light, x-rays, electrical signals or the like to the interior must withstand the full pressure and temperature being developed. These problems seemed insurmountable in the early days of high-pressure research but are now gradually being overcome. For example, it is now possible to provide windows for the entrance of a primary beam of x-rays and exit for the diffracted rays. It thus becomes possible to determine the arrangement of atoms in polymorphs under the actual high pressures and temperatures required for their formation. A photograph of an apparatus for this purpose is shown in Figure 5. This apparatus, located at Brigham Young University, is the only one in existence at the moment, but a duplicate, now under construction, will soon be placed in the Paris laboratory of the French Atomic Energy Commission. These machines are expensive; the Frenchmen are paying $166,000 for theirs.

This apparatus has opened new doors to the further understanding of the behavior of atoms and molecules and has proven some prognostications to be in error. For example, it had been predicted that substances with simple cubic and body-centered cubic space patterns would eventually convert to closest-packed polymorphs under the action of a sufficiently high pressure. Once the closest-packed pattern was achieved, the substance was then supposed to stay in this pattern as pressure was raised indefinitely. These predictions were refuted, however, by high-pressure, x-ray diffraction studies

on the element ytterbium (Yb). This metallic element already exists, under normal conditions, in a closest-packed pattern; namely, face-centered cubic and according to the prediction should remain in a closest-packed pattern regardless of any volume changes that may occur due to pressure. X-ray diffraction studies at 600,000 pounds per square inch, however, revealed the startling fact that the atomic arrangement, at this pressure, changes to the more loosely packed arrangement of body-centered cubic. The gross volume, during this transformation, decreases only 2 percent but the x-ray data indicate that the individual atoms suffer an 11 percent reduction in volume. Thus there is ample room for the smaller atoms to rearrange into the more loosely packed pattern. Since the discovery of this polymorphic change in Yb, similar transformations from closest-packed to nonclosest-packed atomic arrangements have been observed in other substances.

Many other interesting effects have been observed in high-pressure research, but space does not permit their consideration. Suffice it to mention that high pressure has turned nonmetals into metals and metals into nonmetals, has increased the melting points of some materials and decreased the melting points of others, and has both accelerated and slowed the rates of chemical reactions.

In 1957 there were only two places where extreme pressure-temperature research was being conducted: Schenectady, New York, where the General Electric Company was using my "Belt" apparatus and Provo, Utah, where my "tetrahedral press" was in use at B.Y.U. The tetrahedral press was invented to circumvent the fact that G.E.'s proprietary interests and a U.S. Department of Commerce secrecy order prevented me from using my own invention for research purposes here. Since 1957 hundreds of scientists from around the world have visited the high-pressure facilities at B.Y.U. Interest in this work has mushroomed so that there are today more than 150 high-pressure research laboratories in the United States alone.

At first it proved difficult to interest others at B.Y.U. in this new field. With time, however, enthusiasm developed, and there are now twelve faculty members and eighteen graduate students engaged in high-pressure research at this institution.

VIII. Summary

Polymorphs are different crystalline forms of the same substance and are characterized by different interior arrangements of their constituent atoms. Polymorphs usually have widely different properties. Atoms in crystals are organized into motifs, which, in turn, are arranged in periodic, three-dimensional space patterns according to the laws of symmetry. Only 230 space patterns are possible. The ways in which an atomic motif in a crystal may be arranged has a counterpart in the number of ways an artistic motif

may be repeated in a wallpaper pattern. Polymorphs may be formed by the agencies of heat or pressure, the latter being the newest and most effective means for causing their formation. However, the combined action of heat and pressure is more effective in producing polymorphs than either agent used alone. High-pressure, high-temperature research is yielding new information concerning the behavior of atoms and molecules. High-pressure research has spawned one new and highly important industry, the manufacture of industrial diamonds, and it is expected that many more important products and processes will yet come from continued research in this field.

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