# RECENT DEVELOPMENTS IN THE APPLICATION OF X-RAYS TO CHEMISTRY AND INDUSTRY

BY

CHARLES W. STILLWELL
*University of Illinois, Urbana.*

The possibility of determining the ultimate structure of crystals and other solid materials by recording their effect on X-rays was first realized by von Laue in 1913. It had long been known that an optical grating, consisting of many parallel lines ruled on a plane surface, would diffract visible light if the distance between the lines was of the same order as the wave length of the light. Von Laue had calculated that, if a crystalline substance were assumed to be built up of atoms regularly arranged in space, the distance between the planes of atoms in such crystals should be about of the order of the wave length of X-rays—one ten-thousandth that of visible light. Under these conditions crystals ought to diffract X-rays. Von Laue showed that they do, and out of his experiment has grown a new and productive branch of chemistry.

For many years after von Laue's experiment the only chemical application of this new tool was in the determination of the crystal structure of chemical elements and compounds of all sorts. A vast amount of crystal structure data accumulated but attempts to find some general principles which are followed by nature in building crystals of various sorts were, in the main, disappointing. Within the last two years the key to the situation has apparently been found through the efforts of V. M. Goldschmidt, Linus Pauling, and others, and we are now able to state the first law of crystal chemistry. "The structure of a crystal is determined by the ratio of numbers, the ratio of sizes, and the properties of polarization of its building stones. As the building stones of crystals we visualize atoms (or ions) or groups of atoms."[1]

It is important to note that atomic weight does not influence the type of structure which a crystal will assume, neither do chemical properties. A crystal does not weigh its building stones nor does it know any chemistry. It merely arranges them with regard to their number and their demand of space. Our conceptions of polymorphism,

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[1] V. M. Goldschmidt, Trans. Faraday Soc., p. 253, 1929.

isomorphism, and similar phenomena have been greatly clarified by this law. Before the advent of X-ray crystal analysis we knew nothing about the fundamental nature of solids and if X-ray analysis had produced no other results than this it would have justified itself.

About six or seven years ago, however, it was realized that X-ray analysis could also be used to advantage in the examination and control of many industrial raw materials and products. To enumerate the materials which have been studied would be to name almost every type of product in existence. It is more satisfactory to mention the general classes of materials and the kinds of information which may be obtained in such investigations.

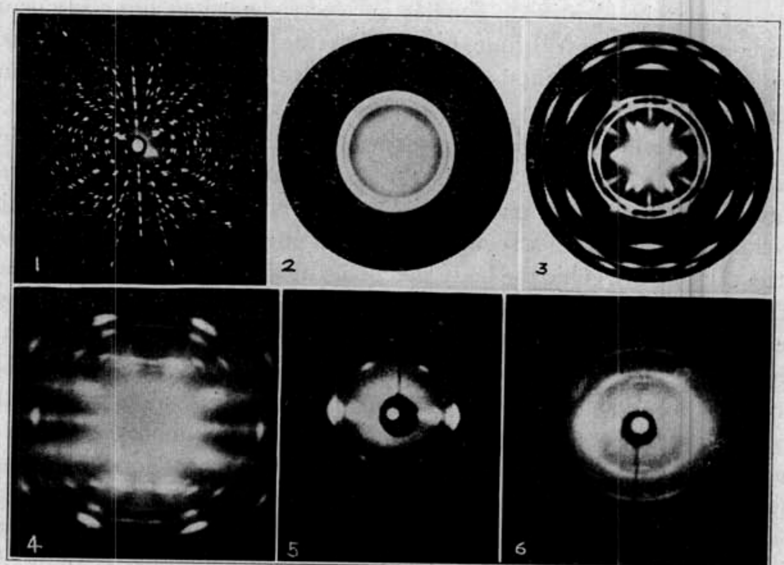


FIG. 1. Diffraction pattern of a single crystal of carborundum.
FIG. 2. Diffraction pattern produced by a large number of very small crystals in random arrangement.
FIG. 3. A typical fiber pattern showing preferred orientation of crystal grains along one axis. (Cold drawn aluminum wire.)
FIG. 4. Diffraction pattern for asbestos—an almost perfect mineral fiber.
FIG. 5. Diffraction pattern for ramie—the most perfect natural cellulose fiber.
FIG. 6. Diffraction pattern for rayon manufactured by an improved process. The high degree of fibering indicates high tensile strength.

If an X-ray beam is passed through a single crystal, a symmetrical pattern of spots is obtained (fig. 1). If the beam passes through a large number of very small crystals, the diffraction produces concentric rings on the photographic plate placed behind the specimen (fig. 2).

No two solids have exactly the same crystal structure, and no two give the same diffraction pattern. X-ray analysis, therefore, is very helpful in identifying crystalline substances, in detecting and identifying impurities, in detecting changes which may occur during industrial chemical processes to produce new compounds, changes which in many cases would be very difficult to detect by chemical means. Perhaps the most successful of all applications of X-ray analysis has been in the study of alloys. When two metals are fused together they may form intermetallic compounds; they may dissolve in each other forming solid solutions, or they may merely be mixed in a superficial manner. The properties of the resulting alloy are greatly affected by the sort of combination which occurs and the X-rays are able to distinguish between these three types. Alloys in galvanized iron and other metallic coatings may be identified. Studies on electrodeposited films are being carried on at the present time, particularly the study of electrodeposited alloys. The X-ray method of analysis is ideal for such problems, and there are many of them.

A field which has been developed with much enthusiasm during the past three or four years is the examination of so-called fibered matter, either natural or artificial. This is material in which the crystals are oriented in a regular manner in one direction. For example, if the crystals are cubic the body diagonals of the cube may all be in one direction which is designated as the fiber axis. This condition is intermediate between that existing in a single crystal and that existing in a large number of very minute crystals. If a beam of X-rays is passed through the crystals perpendicular to the fiber axis, along which the crystals are oriented, then the crystals will affect them exactly as a single crystal would and spots, rather than concentric circles, will appear on the pattern. The more perfect the orientation of the crystal grains, the sharper will be the spots. One is able to estimate the degree of orientation of the crystals, then, from the diffraction pattern (fig. 3).

It has been learned that very important physical properties are influenced by this fundamental arrangement of the individual crystals. Tensile strength is probably the most seriously affected, and it increases as the orientation of the crystals becomes more perfect. The value of this discovery has been far-reaching. It applies to such materials as wire (which is a typical fiber produced artificially), cellulose, wool, rayon and other artificial silks, rubber, muscle fibers, surgical cat-gut, asbestos (a perfect mineral fiber), and many others. Almost everything in the vegetable and animal world which can be classified as a fiber under the common meaning of that term, shows this fiber structure, characteristic of crystals regularly arranged in one direction. It seems to be a general law of nature for things to grow in this orderly manner. Of course the orientation does not exist to the same degree in all cases, as may be seen by an inspection of figures 4, 5, and 6. In many of these fibrous materials more perfect orientation may be induced by suitable chemical or physical treatment and the value of the material for certain uses improved thereby. To mention only one example, the process for spinning rayon has been almost completely changed as a result of information gained from X-ray diffraction patterns and the wearing quality of the product has been greatly improved.

Efforts are being made at the present time to design more powerful X-ray tubes so that the length of time required to obtain a diffraction pattern may be decreased. Remarkable progress has already been made, and there are tubes available that in from five to thirty minutes will take pictures which formerly required from four to forty-eight hours. Under very favorable conditions satisfactory pictures may be obtained in considerably less than five minutes. The possibility of instantaneous exposures opens up entirely new fields of investigation, especially the possibility of following chemical reactions in which structural changes occur. In many of the well established fields of X-ray research, however, time is not the important element.

Every conceivable type of substance has been examined by X-ray analysis. Much of this endeavor has produced definite and valuable results whereas some has been disappointing. In general, the more definitely crystalline a substance, the more complete will be the structural information obtainable. The development of crystal chemistry is just beginning and promises much. The structure of alloys may be deduced with great certainty and only a few of the several thousand possible alloys have been studied. The study of inorganic binary and ternary systems and the problems of mixed crystals, double salts, etc., offer a promising field for research. As one departs from purely crystalline substances one treads on less secure ground, and the less crystalline a substance is the less may be learned about its structure. The structure of cellulose has been rather definitely established; much is known of the structure of rubber and other fibers which are not as perfectly oriented as the best of cellulose fibers. The study of the X-ray diffraction of liquids, which of course are commonly classed as non-crystalline, is being persistently followed but so far has yielded very little conclusive information.

It is becoming evident that this new method of X-ray analysis has its limitations. It will be of little help in some types of problems, but this is in no way discouraging. It was necessary to attempt the analysis of all sorts of materials in order to reach the present stage of development, and it remains now to study more critically the fields in which X-ray analysis may be applied to advantage. A realization of the limitations of any tool enables one to use it more effectively.