Recent Advances in the Study of the Crystalline State

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IT IS NATURAL FOR ME TO CHOOSE as the subject of my address the field of X-ray analysis of crystals, in which I have always worked. The accidents which determine the nature of any man's scientific investigations have always interested me. A main factor in my own case was my father's interest in the nature of X-rays, because he so often discussed with me the significance of Laue's discovery of X-ray diffraction in the summer vacation of 1912. I doubt, however, whether this would have been more than a passing interest of mine had it not been for some contributory factors during my time as a student at Cambridge. Our lecture courses at that period only partly covered the field of physics, going intensely into some branches and leaving others quite untouched; they were very different from the conscientious reviews of the whole subject represented by Honors courses in universities today. They did, however, leave us a good deal of time for reading, which I know I pursued in a very desultory and haphazard way. But one course particularly fired my imagination, the course on Optics given by C. T. R. Wilson. It was not a very easy course to follow, because the blackboard often heard a good deal more of the lecture than we students did, but his way of thinking about optical problems had the qualities of style and grace. It was like being shown how to produce a stroke by a master of a game; he taught us the technique of scientific thinking. He was also in charge of the practical classes. Like all young students, I was keen to 'finish' an experiment and go on to the next. C. T. R. was too gentle and kindly ever to suggest we might be wrong or had skimped our work, but by a series of apologetic and hesitant comments we were somehow made to feel that there was a great deal more to it and that we had better try all over again. I would like to take this opportunity of paying tribute to one whose teaching must have profoundly influenced, directly or indirectly, the physics courses in most of the universities in this country, for many who are now in responsible positions have been his pupils. He gave me a love for physical optics which was a major influence in deciding me to research in X-ray optics. Another factor, which illustrates the part chance plays in deciding one's line, was a particular meeting of a very small and informal society in Trinity formed to discuss scientific papers. The subject of one of these papers was the Pope-Barlow theory of valency-volume, according to which atoms packed together as if they were spheres with a volume proportional to their valency. The theory was wrong, but our talk occurred at about the time Laue's discovery was made, and it made me think about the geometrical ways in which atoms could pack together in the solid state. Nowadays most scientists have some acquaintance with the three-dimensional geometry of crystalline arrangement, because so much light has been cast on physical and chemical problems by the success of crystal analysis. At that time, hardly anybody except a few isolated enthusiasts had given it a thought. Barlow was one of these enthusiasts. His pictures of close-packed atoms were a fertile source of inspiration and just supplied the missing link in understanding the optics of X-ray diffraction. It has always been a lesson to me in the value to young students of small scientific societies where they themselves give the papers, especially when they spread themselves over a wide field. Science is so rich and unexpected in its surprises that one never knows what odd bit of information may supply the necessary clue to the solution of a problem. I wonder sometimes if we are not too efficient nowadays in planning well-rounded and comprehensive courses which demand all of our students' time and energy, leaving them little opportunity to browse in less specialized regions. In my case, at any rate, it was this interest in Barlow's geometrical constructions which led me to seek a new interpretation of Laue's diffraction pictures, and so to the idea that they revealed the arrangement of the atoms in crystals.

Sir Edward Appleton recently asked me to quote some examples of new achievements in science and technology which have been the direct result of X-ray analysis. I confess that I found it a hard question to answer. In the case of such discoveries as that of the electron by J. J. Thomson, or the nature of the nucleus and its disintegration by Rutherford, one can at once point to a new physics and a new technology which has been or will be made possible by them. The analysis of the arrangement of matter by X-rays has had a far-reaching influence, but one of another and less direct kind. No new fundamental particle has been revealed by the X-ray microscope. The in-

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formation it has provided has been of a type which one might have predicted in a vague and uncertain way. What it has done has been to replace guesses by accurate and precise knowledge of atomic architecture in matter, and this has led to its having a profound influence on all the physical sciences. It may well in the near future have an equally great influence on the biological sciences. I count myself fortunate in that my subject has been one which has taken me into so many fields and involved collaboration with colleagues in so many branches of science. Mineralogy, inorganic chemistry, organic chemistry, metal chemistry, metal physics, colloid chemistry, biochemistry—X-ray analysis has had as close a connection with these sciences as it has with experimental and theoretical physics. In each case former ideas have been modified and clarified, and new lines have been opened up, by our now being able to see the precise way the atoms are related to each other in space.

In my own subject of physics there is a parting of the ways at the present time. The main principles of atomic structure, the great puzzle in the early years of this century, have been discovered. Though the complexity of the problem still often defeats a close quantitative analysis, we can understand the nature of the forces which bind atoms together into chemical compounds and these again into larger-scale structures. One great army of physicists is being lured on to explore the mysteries of the fundamental particles, working in the fields of nuclear physics and cosmic rays, and building machines for their experiments whose size is in inverse ratio to that of the bodies they are examining. But there is another great field of physics which has equal attractions. Starting with our ideas about the structure of the atom, we can go back to classical physics, to what used to be generalized as the 'properties of matter,' and interpret them anew in the light of our new knowledge. This is the field to which I have always been attracted. I consider it important that when they come to choose their researches our young students of physics should realize that there are problems here as difficult and as fascinating as those of nuclear physics. Their importance to industry is as great as their scientific interest. This is an age of new materials, and we must attempt to understand how the properties of matter in bulk are determined by its atomic construction.

Our country has played a leading part in the development of X-ray analysis from the first. But we now have so many centers of X-ray analysis in this country that it has been no easy task to choose a team to play for the side. Most of our experts came originally from three schools of research, my father's group at the Royal Institution, the Crystallographic Laboratory at Cambridge, where Bernal inspired so many fruitful new lines of work, and my school at Manchester. But I cannot forbear contemplating with considerable pride and complacency all the active centers where work of first-rate importance is now being done, and I have taken as the subject of my address a review of these centers. It would perhaps be logical to arrange my matter under subject headings—minerals, organic compounds, metal structures, etc.—but I do not propose to adopt this plan. I see the development of X-ray analysis as due to a number of centers, inspired by original and brilliant leaders, and I wish to consider some of these centers in turn and describe their work.

It is natural to speak of Bernal's work first, because no one has done more than he has as an explorer and pioneer. Time and again, when reviewing some branch of X-ray analysis which is now very active, we have to acknowledge that the first critical experiment was due to his inspiration. Settlers have moved in to farm the land, but he has been the pioneer who pushed the frontier forward. In the early days we painstakingly examined X-ray diffracted beams one by one with an ionization chamber. Highly accurate analyses are now made by the far more rapid method of recording all the beams on a photographic plate. The method itself was not new, but it was Bernal who showed us how to systematize and docket the observations and draw logical and far-reaching conclusions from them about the architecture of complex compounds. The paper by Bernal and Fowler on water will always be a classic, as showing how much information could be got from the diffuse X-ray haloes produced by a liquid. I well remember his first review of metal structures and the wide generalizations he made. It was he who first obtained a regular diffracted pattern from a protein crystal, and he advanced further to study the scattering by the very large-scale regularities in virus preparations. These fields have now been far more intensively studied; his work only gave an indication in each case of what might be discovered, but it made the first steps possible.

Another center in London will be represented at this meeting by Mrs. Lonsdale, who started her investigation of diffuse X-ray scattering at the Royal Institution. The analysis of crystal structure is based on diffraction of X-rays by the regular pattern of the crystal. Each periodic variation in density due to the repeat of the pattern reflects a corresponding X-ray beam. However, any periodic variation of density produces the same effect, and consequently the thermal waves in a hot crystal diffract X-rays, as was first shown by Guinier and Preston. It is indeed interesting that X-ray analysis should find such an unexpected application as a harmonic analyzer of the elastic ripples running in all directions in a hot body. Mrs. Lonsdale was one of the first two women ever to be elected to Fellowship of the Royal Society. She was shortly followed by another X-ray crystallographer, Mrs. Hodgkin, and we may claim with pride that X-ray crystallography has indeed contributed to history by providing a field in which they established their reputations.

Mrs. Hodgkin is to tell us this morning about her work on penicillin, and no better example could be found of the art of crystal analysis. I would like to remind you of some characteristics of this art. The experimental work consists in recording, indexing, and measuring a large number of spectra or diffracted beams of X-rays, each of which corresponds to a periodic element in the crystal pattern. The number of these measurements often rises into four figures. These periodicities must be accounted for by the arrangement of the atoms, and the more complex the crystal, the larger is the number of coordinates which are needed to define the positions of the atoms. The progress of crystal analysis can be measured by the increase in the number of coordinates or parameters which can be dealt with. In the first structures my father and I analyzed in the early days, the atoms were at points of symmetry, and there were no parameters to determine. An early triumph was the analysis of crystals with one parameter, such as calcite and pyrites. But nowadays crystals with anything up to 100 parameters are confidently tackled—a task which would have seemed almost beyond the bounds of possibility to the early workers. The inherent difficulty of such work consists in its being very rarely possible to deduce the structure directly from the observations. On a strictly analytical basis, the observed diffractions might be caused by an infinity of structures, since the relative phases of the periodicities do not affect the strengths of the diffracted beams, and the solution only becomes unique when we impose certain conditions, in general that the pattern-unit consist of a discrete number of atoms of known form. No way has as yet been found of arriving directly at a solution consistent with these conditions by a mathematical treatment, though attempts to do so have been made, and crystallographers have to fall back on a process of trial and error. In effect, one has to guess a likely structure, calculate how it would diffract, and compare with observation; if there is no correspondence, a fresh guess has to be made. So, in solving a crystal with 100 parameters, one is trying to guess successfully all their values simultaneously.

The observations themselves are generally not difficult to make. Sometimes a crystal is very small, or unstable; sometimes it is difficult to get a perfect specimen. But on the whole the making of the observations is a matter of routine. The real work lies in their analysis. So, in an X-ray laboratory one finds a deserted room full of apparatus in which the photographs are taking themselves, and a series of annexes in which absorbed workers are wrestling with masses of observations and calculations. I always find it an interesting contrast. Here, on the one hand, are a few photographs of some unknown structure. Hidden in the pattern of diffracted spots lies all the information required to establish the structure, if only one can find the 'open sesame' which would reveal the treasure. The material is so simple, the analysis so very difficult.

How is it done? The analyst has before him the separate bits of a jig-saw puzzle, each one of them being a periodic element in the structure, and he has to fit them together so that they build up a picture which makes sense, meaning by this a distribution of scattering matter corresponding to the atoms which he knows to be there. In making guesses at possible arrangements, he draws on a wealth of experience of the way atoms associate together in space, obtained from previous analyses. He pushes the atoms this way and that, remembering, as he does so, the many other alleys he has previously explored which have proved to be blind. It is, alas, a long time since I last analyzed a structure personally, but I can well remember the intense concentration. One lived with the structure. Finally, after 6 months or longer, and if one were fortunate, everything suddenly clicked into place. An arrangement was found which fitted so well to the most important observations that it was clear that one was on the right track at last. Once the general scheme is discovered, the final adjustments are relatively easy, and one more example is added to the growing list of known structures. Again there is a curious characteristic of this crystal work: we can be sure of our results. Further refinement may be made later, but the evidence that our guess is right in the main is quite overwhelming and certain.

These analyses take a long time and can be made only by the expert. What is the reward which lures him on to concentrate so intensely on establishing a picture of some 20 or 30 atoms arranged in a pattern? There are so many structures to do, and so few people who can work them out, that it seems an endless task to examine them all. But it is not really so hopeless, because the successful analysis of one structure often leads to a quite new understanding of a whole range of forms of matter. The structure of diopside, for example, marked the turning point in our understanding of the nature of all silicates; the structure of one polyacid shows how they are all built up; the structure of a few simple salts led Pauling to formulate the rules which determine the structure of inorganic compounds in general. It is all the more important that really key structures should be chosen for examination, as likely ventures in which it is justifiable to sink one's capital.

I have made this digression here because the nature of X-ray analysis is so well exemplified by Mrs. Hodgkin's work. Her success in analyzing penicillin is a natural sequel to earlier triumphs, such as the solution of cholesteryl iodide, which verified the nature of a typical sterol complex. She is a leading expert in the most difficult kind of pure crystal analysis, establishing the shape of very complex and unsymmetrical molecules. It is fair to claim, I think, that our country has almost a monopoly of this art in its highest form, and I would like to refer to a few other cases which to me are outstanding examples. One of these is Jeffrey's analysis of geranylamine hydrochloride. Some may wonder why a structure with so exotic a name was considered of high importance, but the point is that it has elements of isoprene linked together, and rubber is polymerized isoprene. This intense study of two joined links of a rubber chain may cast a flood of light on the general nature of rubber-like bodies. Another recent example is the solution of a sucrose compound by Beevers and Cochran. The sugars form very unsymmetrical molecules; in this case a 6-fold and a 5-fold ring are joined together and the bond lengths and bond angles have been determined. I always find an elegance in the method of attack on such complexes which is aesthetically satisfying. The solution seems so obviously right once it has been found, and explains so much.

Beevers is in charge of the Dewar Crystallographic Laboratory in Edinburgh, another center where highly complex molecules are being analyzed like the sucrose molecule mentioned above. His earlier work was largely on water of crystallization and the structure of complex hydrates generally. At present J. H. Robertson, in his laboratory, is making an attack on the alkaloids. The structure of strychnine is still not known with complete certainty, although it has been studied so intensively by the organic chemists. The workers in the Dewar Laboratory have made considerable progress with compounds of strychnine and brucine; it will be a very real triumph if their exact configurations are determined by X-ray analysis.

In another side to the work on organic compounds the emphasis is upon the accurate determination of atomic positions. Robertson at Glasgow has been making a systematic examination of relatively simple molecules in which the chemist already knows the relative positions of all the atoms, his object being to translate such 'chemically known' structures into terms of exact bond lengths and valency angles and correlate them with valency theory. He has determined the carbon-carbon distances in a number of molecules, showing that there are many intermediate stages between the standard single, double, and treble bonds. He is now engaged in a three-dimensional analysis of naphthalene and anthracene, the two structures which were analyzed by my father some 25 years ago and were the first organic compounds ever to be determined. He is examining long saturated CH_2 chains in a series of dicarboxylic acids and finding an alternation of long and short bonds. He is also examining long sulfur chains in polysulfides and polythionates.

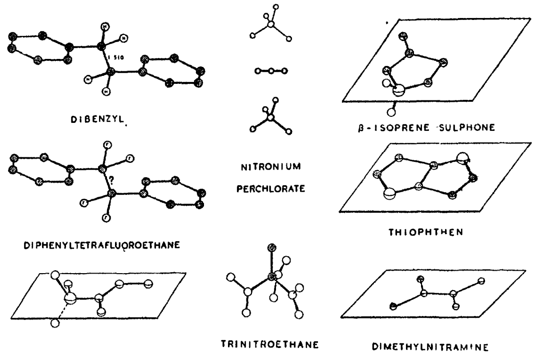

FIG. 1. Examples of structure determinations done in the Chemistry Department, University of Leeds (Prof. E. G. Cox). The shaded atoms are carbon.

Another center where both new structures and bond lengths of known structures are being examined is Cox's laboratory in the Chemistry Department at Leeds. Prof. Cox has kindly supplied me with a composite diagram (Fig. 1) which enables one to see the scope of his recent work at a glance. In diphenyl and the related compound, where hydrogens are replaced by fluorine, the interest lies in the nature of the central bond. It is shorter than the 1.54 A characteristic of a carbon-carbon single bond in diphenyl, and Cox is studying the effect of the fluorine atoms in an attempt to discover the nature of the bond. Nitronium perchlorate is a compound in which $(NO_2)^+$ plays the part of a positive ion, as had been deduced by Ingold on chemical evidence. The analysis of $K_2SO_3 \cdot 2NO$ establishes the nature of the negative ion; chemists have speculated about the structure of this compound for the last hundred years. According to the classical stereochemistry of nitrogen, the N—N bond in dimethyl tetramine should be of the normal single type; it proves to be 1.26 A in length instead of 1.40 A, which is characteristic of a single bond, and to be co-planar with other bonds to the nitrogen atom, so it has more of a double-bond character. The other figures show interesting heterocyclic compounds.

Powell at Oxford has an X-ray center which collaborates closely with the chemists. One interesting line of work has been on complex intermolecular compounds—for instance, that of iodoaniline with trinitrobenzene. A similar line of work has been developed in James' laboratory at Capetown University. In Powell's compounds the two large molecules are of such a shape that they conveniently pack together in equal proportions. James has studied more complex cases, in which each type of molecule is stacked in rods, and the rods are packed side by side. The repeat distance may not be the same for each kind of rod, so that there is no simple ratio between the number of molecules of each kind, and very complex and beautiful X-ray diffraction effects are produced. Perhaps the most striking of Powell's recent analyses has been that of substances which he calls 'clathrates.' Quinol molecules link together to form two systems of interpenetrating networks. Each is like a wire-netting structure in three dimensions, continuous in space but not bonded to the other though interwoven with it. There are large open spaces in the meshes, and gas molecules act as 'filters' to occupy these spaces and stiffen the two networks relatively to each other. It has long been a mystery how such molecules as SO_2 could be bound by quinol so firmly that the whole structure had to be destroyed before they could be released. They are now seen to be very loosely held chemically, but completely caged in physically.

We have at Cambridge a group working on organic chemical problems, of which Cochran is the leader. Pyrimidines and purines are being analyzed, as primary building stones in the nucleic acids. This group works closely with Prof. Todd and his chemists.

The investigations described in the last two paragraphs are essentially part of an enquiry into the physical basis of the chemical molecule, an attempt to understand its dynamics more completely by discovering the relative positions of its atoms. The examples given, to which many more could be added, come under the head of 'chemical crystallography.'

The forms of matter which come under the heading of 'minerals' are an interesting group. The essential property of a mineral is stability; in other words, its atoms are arranged in such proportions and positions that a minimum of potential energy is attained lower than that of any alternative grouping. Hence arise both the limited numbers of minerals and the very rigid geometrical laws which their structures obey. The deducing of the structural relationships in the mineral kingdom, particularly those in the silicates, has been one of the triumphs of X-ray analysis. The broad outlines of the scheme are now clear, but there are several fascinating lines of work to pursue.

The work which is being carried out at the British Museum of Natural History by F. A. Bannister is an excellent example of the use of X-ray methods. Mineralogists have collected and named varieties from all parts of the globe. There is so much isomorphous replacement in minerals that composition is often an uncertain guide to the identity of a specimen. It is very interesting to note, now that we know more about internal structure, how right the mineralogists have been in allowing themselves to be guided by external form rather than composition in classifying their mineral species and families. But many minerals are in a microcrystalline state where external form is of no assistance. Bannister is carrying out a planned program of mineral examination which is leading to improved identification and classification. New minerals are being discovered which were previously unsuspected constituents of specimens, and minerals to which different names had been assigned are being shown to be of similar structure. Since X-rays readily tell us the number of atoms in each unit of pattern, formulae can be rewritten with far more certainty.

The felspars are the most important constituents of the earth's crust, and are outstanding in their importance to petrologists who study the history of rock formations. They vary in composition and symmetry, but their external form shows that they are closely related. W. H. Taylor first established their structure, showing that they are all based on the same characteristic pattern. Typical formulae are KAl_3SiO_8, $NaAl_3SiO_8$, $CaAl_2Si_2O_8$. The aluminium and silicon atoms form with the oxygens a continuous framework of tetrahedra, in the meshes of which the other ions are incorporated. But, although the same structural type is common to them all, they are rich in variety, and there are many fascinating differences of second order in their structures and properties. Minerals of the same composition may have different optical properties and even different symmetry, and these differences are related to the history and mode of formation of the rock in which they appear. Taylor is now trying to study these finer details. Why does a pure potash felspar appear sometimes to be monoclinic in symmetry and sometimes triclinic? What is the cause of the irreversible change in optical properties which some specimens undergo on heating? How do the structures fit together in felspars which are alternate slices of potassium and sodium felspar? Finally, what is the structure of the intermediate forms between $NaAlSi_3O_8$ (albite) and $CaAl_2Si_2O_8$ (amorthite)? This last is a very intriguing problem. The series has always been regarded as a typical case of simple isomorphous substitution, but X-ray diffraction shows that it is really a very complex phenomenon. Extra diffraction spots show that larger-scale repeats are superimposed on the simple felspar pattern, in a way which depends on the proportions of sodium and calcium. The problem is interesting for its own sake as an example of X-ray optics, but also important because we wish to understand what conditions have produced these variations in the rocks.

Finally, I must refer to the work on clay minerals which G. W. Brindley is doing at Leeds. Clays are composed of minute spangles of mineral, tiny sheets of mica-like structure which are often polar in their nature. One face of the sheet is different from the other—they have 'bread' and 'butter' sides—and it is probably this polar nature which prevents their crystallizing on a large scale owing to their tendency to curl and warp. These sheets form, as it were, the experimental benches on which the chemical operations in the soil are carried out. Nothing could be more important to soil chemistry than knowledge of the structures of the clay minerals and their related species.

Passing now to the structure of metals, we may conveniently distinguish between two fields of investigation. On the one hand, there is what may be called 'metal chemistry,' the physical basis for the types of structure formed by metal atoms in various proportions; on the other hand, there is the study of what may be called the 'physical geography' of metallic aggregates. By this last is meant the size and orientation of the crystallites in a metal, their strains and structural distortions incipient segregations into different phases such as take place in age-hardening, and exchanges of atomic position such as take place in the order-disorder change. The physical properties of a metal or alloy are much influenced by these characters. On both sides, X-ray analysis has made contributions of really vital importance.

I think it may be fairly claimed that alloy chemistry had no rational basis until structures were determined by X-rays. There is an interesting difference in character between a metallic compound and other kinds of chemical compound. One can, of course, find examples of all intermediate stages, but we are concerned here with broad generalizations. A typical metal compound is composed of markedly electropositive atoms. It follows, as a consequence of the dynamics of such a structure, that wide variations in composition of any one alloy 'phase' are possible. In an extreme case, such as copper and gold, all proportions can unite to form a single structure. This is in complete antithesis to the relationship between sodium and chlorine, for example, when we find pure sodium, pure chlorine, or sodium chloride with the exact stoichiometrical relationship represented by the formula NaCl. To call the former a case of solid solution and the latter a true chemical compound takes us no further in explaining the physical basis of the difference. We may perhaps express the nature of an alloy by saying that different possible arrangements of the metal atoms, or different phases, are separated by fine second-order differences in their potential energy so that very little tips the structure in one direction or another. A compound such as NaCl is at the bottom of a deep, narrow pit of potential energy, and the slightest variation in composition increases the energy greatly. An alloy is at the lowest point of a very shallow bowl with many alternative bowls open to it whose bottoms are nearly at the same level. What is equally important is that metal atoms are very mobile and readily exchange positions, and as a consequence these finer differences have an opportunity to be effective. Hence arises the rich variety of changes that can take place in an alloy system, and the great influence upon it of its thermal or other history.

It would take too long to tell the whole story. I will just remind you of the early work of Westgren on alloy phases, the realization by Hume-Rothery and by Westgren that similar free-electron atom ratios often produced similar phases, the work of Bradley on the structures of complex intermetallic compounds which provided so many examples of the Hume-Rothery rule in binary, ternary, and quaternary phase systems, and the theoretical work of Jones on the explanation of the Hume-Rothery rule by the filling of Brillouin zones.

Raynor at Birmingham has as his general objective an understanding of equilibrium relationships and the occurrence and structure of intermediate phases in alloys, so that a comprehensive theory of alloys may be developed, permitting quantitative prediction of the results of mixing metals together. He is concentrating mainly on compounds of aluminium with the transition metals. Fig. 2 will serve as an indication of the type of prediction which may be made.

All this work is still on a semiempirical basis. It is clear that the Hume-Rothery rule corresponds to one highly important factor which determines which phase a given composition of metal atoms will adopt, but also that it is not the only factor. For instance, relative sizes of the atoms play their part as well as the electron-atom ratio. We need to know the structures of far more intermetallic compounds, and these are often very complex and the analysis is lengthy. Mrs. Douglas at Cambridge is collaborating with Raynor, doing the structure analyses of the phase systems he is surveying. If we are examining an inorganic or organic compound, we can safely assume that neighboring atoms have certain well-established relative configurations and conform to rules with which we are familiar. So far we have no such rules for intermetallic compounds, and each structure presents quite a novel problem. We are only at the beginning of an understanding of metal chemistry.

Investigations of alloy phases are concerned with the arrangement of the atoms in the unit cells of a regular crystalline pattern. But the perfect regularity is an ideal state which is attained only under special conditions, and I pass on to describe the application of X-ray analysis to study the many interesting and important types of departure from the ideal lattice.

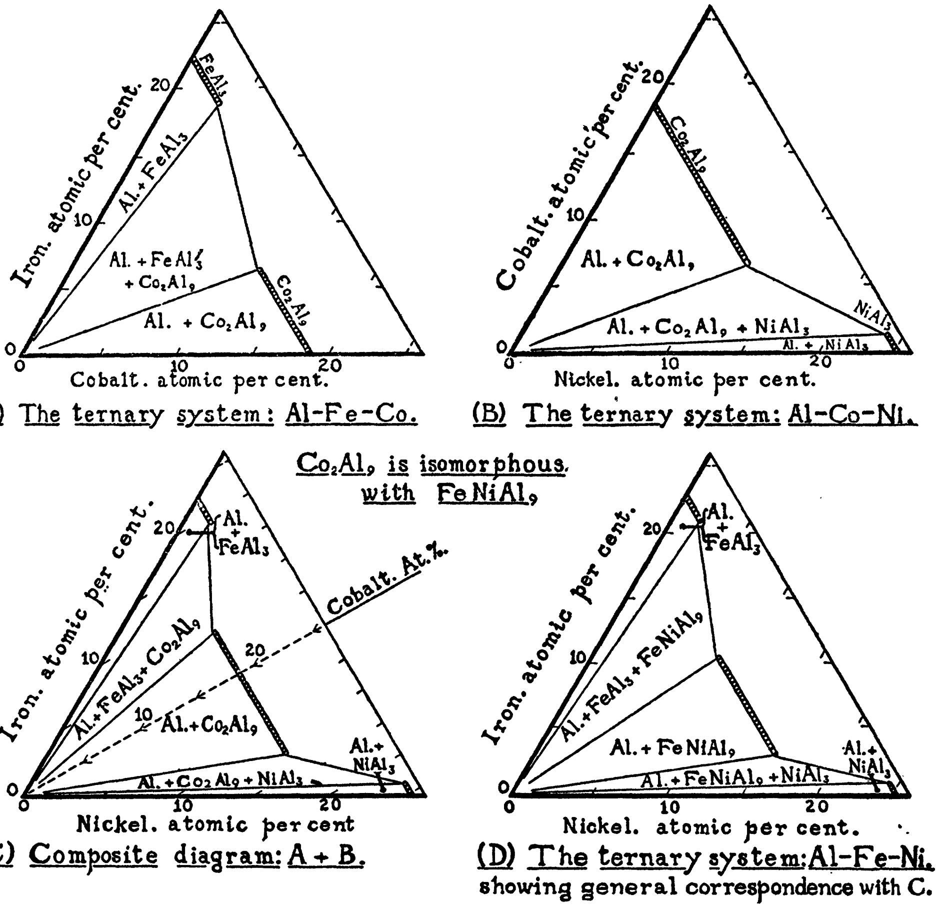

Fig. 2. Diagrams showing equilibrium at 600° C. A and B represent, respectively, the aluminium-rich isothermals at 600° C for the systems aluminium-iron-cobalt and aluminium-cobalt-nickel. In C, these two diagrams have been redrawn in triangles with angles of 90°, 60°, and 30° and placed together with the aluminium-cobalt axis common. The composite diagram is closely similar to that established experimentally for the aluminium-iron-nickel alloys (D); agreement is quantitative, except that Co_2Al_9 is less sensitive to a reduction in the electron-atom ratio than the less stabile isomorphous $FeNiAl_9$ phase. These relationships are due to the fact that, electronically, Fe + Ni = 2Co. (Dr. G. V. Raynor.)

We know of many cases where two metals are completely miscible over a wide range of composition at higher temperatures, with atoms of either kind occupying the sites of the same lattice in a random manner, but where interesting changes in structure take place when the temperature is lowered. Two broad classes may be distinguished; there may be a tendency for like atoms to get as far apart as possible, or to associate together. The former state of affairs leads to the well-known order-disorder change, first examined by Borelius and then by Bradley and Sykes, using X-ray analysis. A very imposing literature now exists devoted to this phenomenon alone. Order-disorder is observed only when the composition is near a simple one such as AB or A_3B; the alloy Cu_3Au is typical and has been intensively studied. At high temperatures copper and gold atoms replace each other at random on a face-centered cubic lattice; at lower temperatures the gold atoms segregate to the cube corners, leaving the face-centers to the copper atoms. In this way the gold atoms find positions as far apart as the composition permits, and a larger-scale regularity is superimposed on the simpler lattice. The thermodynamics of the change is of such interest as to have attracted theoretical physicists of the order of Bethe and Peierls, among many others. With different rates of cooling, a series of intermediate states is produced. The ordered states grow from nuclei which are out of step with each other, different points of the lattice being chosen as cube corners for the gold atoms. The more rapid the cooling, the smaller are the domains in which the same scheme of order is preserved. Lipson at Manchester has been investigating these stages more deeply by obtaining diffraction effects from single crystals of Cu_3Au (Sykes had previously used the powder method to establish their existence), and he has found some very interesting features of the way the different nuclei dovetail into each other. The order-disorder transformation in metals has proved to be very interesting indeed, because it is a simple example of a general phenomenon, lends itself readily to theoretical treatment, and gives information about the exchanges of position of atoms.

The converse phenomenon is to be observed when like atoms tend to come together. The final consequence of such a process, if it proceeds to equilibrium, is, of course, two separate phases, one of which is rich in atoms A and the other in atoms B. Again, however, a set of intermediate states is formed if the temperature is lowered too rapidly. The atoms remain in a single continuous crystal lattice, but they segregate so that parts of the lattice are rich in A and other parts rich in B. The lattice is consequently modulated because the lattice constants are slightly different in the A-rich and B-rich regions. The crystal planes are corrugated in a more or less regular manner. Such modulations produce sidebands to the X-ray diffraction lines in a powder photograph, and the nature of the modulation can be deduced from the sidebands.

These metastable states are of immense importance to technology, because they confer certain physical properties on the metal in which they are formed. The modulations of structure set up intense local strains. Their X-ray diffraction effects were first studied in permanent magnet alloys by Bradley. Age-hardening alloys, studied by Guinier and Preston, afford another example. The intensely hard martensitic structure in steel is caused by the dissolved carbon atoms taking up preferred sites, so modifying an initially cubic crystal by making it a mosaic of slightly tetragonal regions which have their C axes in different directions, but still all form part of a single modulated lattice.

The literature which describes the X-ray study of the effect of plastic distortion upon metals would form the material for a book. Preferred orientation, crystal break-down, and the locked-up stresses in the crystallites have been studied. Some very interesting work on this last subject has been done recently by Greenough at Cambridge and at Farnborough, by Lipson, and by Brindley.

These examples only indicate the kind of work which is going on, but they will serve to show the importance of X-ray analysis in metallurgy.

The last field I shall consider is represented by the paper which Perutz is giving to us in this session. X-ray analysis is being extended to more and more complex substances. Can we establish the structure of the molecules of which living matter is made? Protein molecules contain thousands of atoms. Each kind of protein appears to consist of identical molecules, for they crystallize and give X-ray diffraction patterns which indicate a highly perfect structure. The photographs which Perutz and others have taken are like a message in code which we cannot yet decipher. The information is there, if only we can discover the key. It would be a wonderful climax to the progressive advance of X-ray analysis if protein structure were solved by its aid. Perutz will describe how far we have gone thus far. The full analysis seems an almost impossible feat, but the analysis of sugar or of penicillin would have seemed equally impossible in the early days of X-ray analysis.

The proteins are being attacked from another side by Astbury and his school. Such substances as hair and wool, horn nail or spine, are a more or less irregular mass of the same chains which are so perfectly arranged in the protein molecule; they are a kind of oakum of protein strands. In some respects they are more simple than the large protein molecules, because one is dealing with the fragments of a feature common to all such structures; in another sense their study is far more complicated because their arrangement is so imperfect. They give correspondingly diffuse and limited X-ray diffraction effects, and Astbury has been engaged in extracting the maximum amount of reliable evidence from these very unsatisfactory witnesses. If the way in which polypeptide chains are folded in the protein could be established, a big advance would be made, and Astbury's work has done much to help with this problem.

I should have liked to have added an account of the applications of X-ray analysis in some of our great industrial laboratories. Bunn, of I.C.I., has made contributions to fundamental research as well as to the elucidation of technical chemical processes; for instance, he collaborated with Mrs. Hodgkin in the analysis of penicillin. The late A. H. Jay, working in the research laboratory of United Steels, made a name for himself as an expert on refractories. The General Electric Company, Jessops, Firth-Brown, and many other firms have flourishing X-ray centers. The industrial laboratories are as well represented as are the university centers at the annual meetings of the X-ray Analysis Group of the Institute of Physics. But it would lead me too far afield if I were to begin to do justice to the importance of the contributions from so many centers, and I have had perforce to content myself with a survey of the work going on in our university laboratories.

Laue discovered X-ray diffraction only a generation ago. X-ray analysis has now come to be of such importance that the formation of an International Union of Crystallography has been approved by the Council of International Unions this year. It has indeed attained its majority, and I feel deeply moved when, on such an occasion as this, I review the tree which has grown from the seed of Laue's original discovery and the early attempts by my father and myself in 1912 to discover the arrangement of atoms in crystals.

A New Zealand Expedition of the American Museum of Natural History

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BETWEEN NOVEMBER 1947 AND MARCH 1948, field work for the American Museum was carried out in New Zealand by the writer and Mrs. Murphy. Aims of the expedition comprised the acquisition of material for two habitat exhibits in the Whitney Memorial Hall of Pacific Bird Life, systematic study of oceanic bird collections, negotiation of intermuseum exchanges, and the excavation of moas and other extinct birds. The writer also represented the Pacific Science Board in discussion of plans for the Seventh Pacific Science Congress, to be held in Auckland and Christchurch next February. Financial support of the undertaking was provided by the Whitney Memorial Fund, a gift to the American Museum of Natural History from Mr. Cornelius Vanderbilt Whitney.

The scientific program was arranged in advance with Dr. Robert A. Falla, director of the Dominion Museum at Wellington and president of the Royal Society of New Zealand. The State Department at Washington simultaneously requested necessary privileges from the New Zealand Government, with the result that the Department of Internal Affairs, acting through Secretary J. W. Heenan, extended generous and effective cooperation during travel and investigation from end to end of the Dominion. Related aid was given by the Marine Department, by the authorities of the museums and university colleges at Auckland, Wellington, Christchurch, and Dunedin, and by other institutions and individuals too numerous to list.

Field operations began at the Snares Islands, 62 geographic miles south of Stewart Island. This small and relatively inaccessible group had not previously been visited for more than a few hours by any scientific investigator. It has the great advantage over nearly all other islands in the subantarctic belt of being pristine. It has never had human inhabitants, introduced organisms are lacking or unobtrusive, and the extraordinarily interesting vegetation and animal life, including daisy-trees (*Olearia*) and the endemic crested penguin pictured on the cover of this issue of *Science,* have remained essentially undisturbed since the era of sealing in the early part of the 19th Century. The only mammals are three species of seals, for the Snares have escaped the curse of man's satellites, such as rats, pigs, etc. There are 25 kinds of native birds, of which three are endemic land birds. The vascular plants total about the same number as the birds. In a zone where a visitor might expect to find antarctic beeches (*Nothofagus*), the dense "goblin forest" is, on the contrary, made up of tree-composites of subtropical affinities.

A band of New Zealand scientists, led by Dr. Falla and including other naturalists, a geologist, and a geodesist, conveyed the American Museum representatives to the Snares in the 73-foot Diesel craft *Alert,* commanded by Capt. Alexander J. Black, of Dunedin, who is himself a well-informed naturalist and a famous leader and instructor of Sea Scouts. A telephonic radio station was established, after which the party of 9 men and 1 woman camped on the main island from November 24 until December 6, 1947, when the vessel returned. Collecting the abundant bird life was limited to specimens intended for installation in the exhibit in New York. Other organisms, such as plant specimens, were more liberally sampled, and, despite characteristically unfavorable weather of the west wind zone, a Kodachrome motion-picture record was obtained of birds, seals, landscape, and some of the activities of the investigators. The