CRYSTALS AND THE POLARISING MICROSCOPE

A HANDBOOK FOR CHEMISTS AND OTHERS

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EXTRACT FROM PREFACE TO THE FIRST EDITION

The relatively simple method of examining crystals which is afforded by the polarising microscope has long been indispensable to the petrologist and the pure crystallographer, but the many and varied chemical applications of this method have not received the attention they deserve. In recent years, however, there have been indications that chemists, particularly in America, are beginning to realise the value of the method in their work.

We have written this book with the main objects of making the chemical applications more widely appreciated, and of providing the chemist with a manual in which the method is treated with special reference to his particular problems. We have been guided and encouraged in our task by the many relevant instances of the use of the polarising microscope which we have encountered in the chemical literature, in private communications from various chemists, and in our own work; and by several years' experience of teaching the method to Honours Students of chemistry.

We hope that, on the theoretical side, the book will commend itself to other users of the polarising microscope. The treatment of the theory of the method is of a standard suitable for Honours Students of geology, who have at present little choice between the elementary works written for junior students, and the advanced treatises.

EXTRACT FROM PREFACE TO THE SECOND EDITION

The first edition of this book had the primary purpose of arousing the interests of chemists in the use of a crystallographic method which might prove useful to them in a variety of ways. With the object of demonstrating what might be done with the minimum expenditure of time and money, emphasis was laid on the simpler aspects of the subject, and the more difficult problems and techniques were avoided. There is nowadays, however, no lack of interest in the use of the polarising microscope, and we have therefore felt it desirable in writing the present edition to attempt to meet the needs of those whose researches call for a more advanced treatment, while not discouraging the beginner. A number of new chapters have been added, and large sections of the book have been rewritten.

PREFACE TO THE THIRD EDITION

The main differences between this edition and its predecessor may be summarised as follows. In Chapter I we have added a short section on the mechanism of crystal growth, and we make no apology for entering such a highly theoretical field in a book which is, we hope, essentially practical in outlook. Spiral growth patterns resulting from the presence of screw dislocations are observable by means of the optical microscope on the surfaces of many crystals, and every microscopist working on crystals nowadays who encounters such patterns should understand their cause and significance. In Chapter III the section on twinning has been somewhat extended.

Since the Second World War there have been considerable improvements in the design of polarising microscopes and their accessories. To take one example, the widespread use of high-quality polaroid in place of calcite polarising prisms has made possible the introduction of a simpler and more rational type of substage, by means of which the different conditions of illumination necessary, on the one hand, for the formation of a well-resolved image, and on the other, for the determination of optical data in parallel light, may be readily established without changing the lens combination of the condenser, irrespective of the power of the objective in use. In this edition, we have as far as possible confined the methods and techniques described to those which are suited to up-to-date equipment, and we have omitted a number of older methods which would be difficult or impossible to apply on a modern instrument, and which do not offer any special advantages, such as some of those proposed for isolating the interference figures of small crystals.

With the improved substages now available, even on simple instruments, there is little excuse for not illuminating the specimen properly, or for not understanding clearly the principles involved in doing this. The polarising microscope is, it should be remembered, a *microscope*, and should be treated as such, and not merely as a micro-polariscope. We have therefore devoted much more space than before in Chapter V to the principles underlying the resolution of object detail and to methods of illumination.

Quantitative methods involving the rotation of crystals about axes additional to that of the microscope stage now form the subject-matter of a separate chapter. This deals with 3-, 4-, and 5-axis universal stages, and also at some length with the simple, but very valuable, single-axis type of rotation apparatus, in the design of which advances have been made in recent years. The chapter on special methods contains as before a description of index variation methods, and a new section on hot and cold stages and their applications. The ability to vary the temperature of the specimen in conjunction with the use of polarised light opens up additional fields of investigation some of which were explored many years ago, notably by Otto Lehmann in his investigations on liquid crystals and by A. E. H. Tutton in studies of the temperature dispersion of the optical properties of crystals. More recent years have seen many developments in the design of hot and cold stages, and in their applications such as those in the field of organic chemistry by L. and A. Kofler, and we feel that the subject must now receive adequate notice in any book on polarisation microscopy which claims to be reasonably comprehensive.

More space has been devoted to the use of the polarising microscope in the study of quasi-crystalline materials such as fibres, biological tissues and liquid crystals, and the interesting phenomena associated with the spherulitic modes of crystallisation in high polymers are also described. This in turn has involved a fuller treatment of elliptical polarisation, the optics of systems of superposed crystal plates, and methods of measuring small birefringences.

Grateful acknowledgements are made to the following: Professor R. D. Preston (University of Leeds) for reading and bringing up to date the section on the cell walls of plants; Dr. H. J. Woods (University of Leeds) for helpful discussions with us on the microscopy of fibres; Dr. Conmar Robinson and Dr. J. C. Ward (Messrs. Courtauld's Research Laboratory, Maidenhead) for valuable criticism and help in connection with the section on cholesteric mesophases; Mr. B. O. Payne (Cooke, Troughton and Simms, Ltd.) for useful discussion on points of microscope design; Dr. F. M. Lea and Mr. R. W. Nurse (Building Research Station) for communicating new examples of the use of optical methods in building research, We also wish to thank Mr. W. Blackledge (University Photographer, University of Leeds) and his colleague Mr. R. M. Clemson for photographic assistance, and the following for the loan of blocks or the preparation of photographs for blocks: Messrs. Cooke, Troughton and Simms, Ltd.; Messrs. James Swift and Son, Ltd.: The Royal Microscopical Society; the Faraday Society; and the Mineralogical Society for permission to use a published figure as the basis for Fig. 294.

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INTRODUCTION

Every transparent crystalline compound is characterised by a unique set of optical properties. The polarising microscope is an instrument by means of which these optical properties may be determined with a degree of precision which depends on a number of factors, such as the shape and size of the particles to be examined, the refinement of the methods, and the quality of the instrument used. Theoretically it should be possible to identify any crystalline substance selected at random solely by means of its optical properties, if these have been previously recorded. In practice this cannot be done because of limitations imposed by the factors mentioned above. It is usually found, however, that any two crystal species can be differentiated by means of the polarising microscope with the greatest readiness, and that any crystalline compound, the optical properties of which are known, can be identified, once the field of enquiry has been narrowed by the knowledge that it belongs to a limited group.

It might be thought by many that the use of the polarising microscope for purposes of identification would have been largely superseded by the X-ray powder method. This is by no means the case. The X-ray method of identification is indeed a very valuable one, and, where the necessary apparatus is in regular use, convenient. It is also particularly useful where the state of division of the material is below the limit of microscopic resolution, or in the case of opaque substances which cannot be studied by ordinary optical crystallographic methods. But for the normal run of transparent crystalline material, it will commonly be found that the polarising microscope will give the required answer more simply and more quickly. Moreover, and this is important, the microscope gives direct visual information about the outward form, texture, and state of division of the specimen, and, if it is a mixture, the manner of aggregation of its ingredients, none of which properties (which may be of prime importance in the problem) is to be ascertained, at least directly, by the essentially "blind" X-ray method of attack. It should be said at once, however, lest the above should have given the contrary impression, that it is no part of our thesis to suggest that the two methods are in competition. They are in fact complementary, each having its appropriate application, and in many problems the one supplements information gained by means of the other. In this connection it should be said that the determination of optical properties is not only useful for the identification of substances, but makes an important contribution to the study of crystal structures by means of X-rays.

The applications of the polarising microscope in chemical and related problems may be stated in somewhat more detail as follows:

(*i*) *It is a general aid to the examination of all kinds of solid material.* The examination of solid material under the polarising microscope forms, in many cases, a useful preliminary to its analysis, since it may indicate whether it is homogeneous or heterogeneous, whether impurities are present, etc., and may even suggest the best lines upon which to carry out the analysis.

(*ii*) *It can frequently be used to identify and characterise solid compounds in cases where ordinary analytical and physical methods fail or are tedious, or where confirmation of the results obtained by these methods seems desirable.* Thus, in many cases, it can be used to identify the constituents of salt mixtures, the chemical analysis of which gives only the ions present; to identify the solid phases in phase equilibrium studies, thereby saving much of the analytical work, and settling questions which the analytical work has left open; to differentiate between isomers having no (or indefinite) melting-points, or lacking other distinctive properties; and to control the progress of fractional crystallisations and trial syntheses more simply and effectively than could be done by chemical methods.

(*iii*) *It affords a ready means of obtaining definite characteristic data with which to describe the crystals of new compounds for record purposes.* Descriptions limited to "white needles", "yellow leaflets" and the like, which are all too common in chemical literature, are really of little value, partly because they are meagre and vague, and partly because the same substance may exhibit many different habits when crystallised under a variety of conditions.

(*iv*) *It is essential for the determination of optical data required in certain X-ray structural studies.* Since the optical properties of a crystal are determined by its structure, they may be used to throw light on the way in which the crystal is built up. This may result in much saving of time in X-ray structure analysis, since certain arrangements of the building units may be at once ruled out as being incompatible with the optical evidence.

(*v*) *In conjunction with other methods, e.g. X-ray analysis and electron microscopy, the use of the polarising microscope plays a necessary part in investigations into the structures of imperfectly or partially crystalline materials, such as textile fibres, high polymers, and liquid crystals.*

Concrete examples of these applications are collected and discussed in Chapter XIII rather than here, as they will be more fully appreciated at that stage.

The polarising microscope may be immediately applied to crystals almost irrespective of their size, outward form, or of whether they are mixed with other matter. Crystals as small as 0·01 mm. in average diameter may be examined satisfactorily, and those that are too big to be mounted on a microscope slide may be crushed and the fragments examined. This is not to say that better results cannot often be obtained by studying a substance after it has been recrystallised, but it may be truthfully asserted that by means of the polarising microscope, some optical crystallographic data can be obtained on any specimen of a crystalline substance, without special preparation, unless its state of division is considerably less than 0·01 mm. The method is thus eminently suitable for examining crystals just as they happen to occur. It should also be noted that the quantity of material needed for an examination is usually extremely small.

As a guide to the beginner it may be as well to give an outline of the arrangement of this book. The subject matter of Chapter I which deals with the general properties of the crystalline state will be mostly familiar to the trained chemist, but it was thought desirable to include it for the benefit of others and in order to bring the reader into a "crystallographic frame of mind" at the outset. Chapter II deals with the methods of representing morphological and optical vectors by means of the stereographic projection, and while this is important in advanced optical studies, it may be omitted at a first reading. So too might Chapter IX on the somewhat special topic of liquid crystals, and Chapters X and XI which deal with special methods.

It is important that the subject-matter of Chapters III and IV should be fully grasped because these contain the foundations upon which the optical method depends. To assist the beginner the basic facts are collected in summaries at the ends of these chapters.

It has been assumed that the reader is familiar with the elements of the wave theory of light, the phenomenon of interference, and the properties of simple lenses.

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FOLDING PLATE

CRYSTALS AND THE POLARISING MICROSCOPE

CHAPTER I

THE CRYSTALLINE STATE

A WELL-FORMED crystal attracts attention because it is bounded by plane surfaces (*faces*) and usually shows some degree of symmetry. The external form of such a crystal, as expressed by certain of its interfacial angles, is entirely characteristic of the substance of which it is composed, unless it belongs to the cubic system of crystal classification. All crystals belonging to this system, which comprises the highest orders of crystal symmetry, have the same angles between corresponding pairs of faces.

These external properties of crystals result from the orderly arrangement in space of their atoms, the pattern of the arrangement being in every case characteristic of the substance when the interatomic distances are taken into account. The atoms may exist in the structure as individual units, neutral or ionised, or they may be combined as discrete molecules or polyatomic ions.

The internal structures of a very large number of crystalline substances have now been determined by the method of X-ray analysis, originally developed by W. H. and W. L. Bragg, and based on the suggestion by Laue in 1912 (confirmed by Friedrich and Knipping) that the regular array of atoms in a crystal could act as a diffraction grating for X-rays. These investigations may be said to have opened up an entirely new field in chemistry—the chemistry of the solid state. Some of the more important results of the application of this method are as follows. Previously it had been generally assumed that the ultimate particle in all chemical compounds was the molecule, although this could not be proved for the majority of solid inorganic compounds since the methods of determining molecular weights could not be unambiguously applied to them. The X-ray method has shown that in many types of inorganic compounds the molecule cannot in fact be distinguished as a structural unit in the crystal, which consists instead of a *continuous* array of atoms or ions. Examples of such structures are given below. Obviously for the term "molecule" to have any meaning at all in such cases, it must be applied to the whole crystal, which forms as it were one giant molecule. In crystals in which discrete molecules do occur, or in which polyatomic ions are present, the X-ray method has given valuable information regarding the structures of these units. The method has also yielded important data on interatomic distances, which have thrown much light on the nature of the bonds between atoms.

It is beyond the scope of this book to deal with the internal structures of crystals in detail, and for fuller information the reader is referred to the list of works at the end of this chapter. Some typical examples of the simpler structures are, however, shown in Figs. 1 to 8, and their essential features given below.

It should first be realised that the structure of a crystal is the result of its building units having packed themselves together so that the potential energy of the system has a minimum value at the prevailing temperature and pressure. The factors which determine the details of the structure are: (*a*) the nature of the bonds between the atoms, and in particular whether these bonds are directional (covalent) or non-directional (van der Waals, metallic, ionic), and (*b*) geometrical considerations depending on the effective sizes, and in the case of molecules and polyatomic ions, the shapes, of the building units.

In a crystal, adjacent atoms are in close proximity to one another, and some at least are to be thought of as being in "contact", though an atom has no fixed radius irrespective of its state of combination. In Figs. 1 to 8, the atoms are shown widely separated from one another, but this is purely with the object of bringing out more clearly their relative positions.

Xenon (Fig. 1*). Xenon is one of the inert gases, and the atoms of this group of elements are characterised by possessing extremely stable electronic structures. In consequence they have no tendency to enter into chemical combination, for this involves either a transfer or a sharing of electrons between the atoms concerned. The only attractive forces between the atoms of an inert gas are of the undirected van der Waals type, and these forces are extremely weak. These elements therefore only exist in the solid state at very low temperatures (the melting-point of xenon, for example, is — 140° C.). The non-directional character of the forces results in a structure like that shown by a set of equal spheres packed so as to occupy the

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* The *thin* continuous and broken lines in Figs. 1–8 merely serve to emphasise the relative positions of the atoms; they have no chemical significance. Directed chemical bonds, where these occur, are indicated by *thick* continuous lines.

minimum space. Actually there are two ways of packing spheres to meet this requirement, and the one adopted in the xenon structure is that known as *cubic close packing.* This is based on an arrangement of eight atoms situated at the corners of a cube, with six others at the centres of the cube faces, as may be seen from the elementary cell* of the structure shown in the figure. An example of the other way, known as *hexagonal close packing,* is given below.

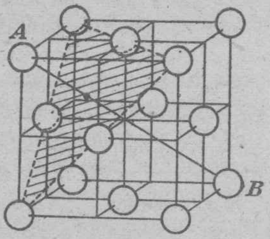

Fig. 1.—Xenon [Atomic—van der Waals].

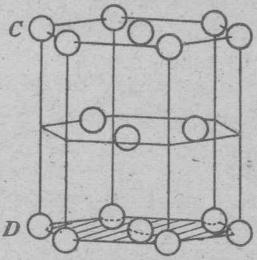

Fig. 2.—Magnesium [Metallic].

Magnesium (Fig. 2). Magnesium has a typical metallic structure. It is generally considered that the atoms in a solid metal have lost some or all of their valency electrons to form an electron "atmosphere" which permeates the whole structure. The structure therefore consists essentially of an assemblage of positive ions and electrons, the former determining the structure and the latter wandering more or less freely through it and cementing the structure together. Under the influence of an electrical potential difference, the electrons drift towards the positive pole, and this constitutes the familiar property of electrical conductivity which is typical of metals. The forces holding the structure together are either non-directional, or nearly so, and they are very much stronger than van der Waals forces. As a result most metals adopt structures based on the close-packing of equal spheres (or slightly distorted versions of these structures) and, owing to the stronger forces involved, they melt at much higher temperatures than do the inert gases. Some metals adopt a somewhat less compact arrangement, known as the *body-centred cubic* structure, the unit cell of which consists of eight atoms at the corners of a cube with another atom at its centre.

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* There are different ways of dividing up the space occupied by a crystal structure into cells which are representative of its architecture. The one shown in the figure, though not the true *unit* cell (see p. 51), is that which shows the essential symmetry of the structure most clearly.

In magnesium the atoms are arranged according to the hexagonal method of close-packing. The arrangement will be clear from the figure. The relationship between this and the cubic method of close-packing may be seen by considering the shaded layers of atoms in Figs. 1 and 2. The packing *in these layers* is the same in both structures, which also resemble one another in that they are built up by piling a series of such layers parallel to one another so that the atoms in any layer nestle in the depressions between the atoms of adjoining layers. The difference lies in the fact that in the direction normal to the layers, the hexagonal type repeats itself every *third* layer, whilst the cubic type repeats itself every *fourth* layer. Thus along this direction, in Fig. 2 atom C projects on to atom D, but in Fig. 1 atom A projects on to atom B and here there are two layers of atoms in between. The reason why these alternative methods of close-packing are geometrically possible is that the atoms in any layer occupy only one half of the depressions between the atoms in an adjoining layer. Therefore when two layers have been packed together, the third layer has two alternative positions relative to the first. It can either occupy a position such that its atoms, viewed along the direction normal to the layers, are superposed on those in the first layer, in which case the hexagonal structure results, or its atoms can occupy the other set of depressions in the second layer, in which case the cubic structure is obtained.

Sodium Chloride, NaCl (Fig. 3). This is a typical ionic compound of formula type AX, that is with equal numbers of positive (Na) and negative (Cl) ions. The attractive forces between these ions are electrostatic and non-directional. Consequently the crystal structure is based on the close-packing of spheres as in the cases described above, only here it is a question of packing together equal numbers of spheres of two different sizes. The sodium ions are the smaller with an effective radius of about 0·95 Å, and the effective radius of the chloride ions is about 1·8 Å.

In a system of this type, the maximum stability is achieved by an arrangement in which each positive ion is surrounded by a certain number n of negative ions situated at equal distances from it, and each negative ion is similarly surrounded by n positive ions. The value of n depends very largely on the ratio between the radii of the two kinds of ions, the principle being that the smaller ions do not have as nearest neighbours so many of the larger species that they have room to "rattle about" in the interstices, since such an arrangement would correspond to a separation of oppositely charged ions beyond their equilibrium distance of approach.

In the case of sodium chloride, n is 6. Each ion is surrounded by six of the opposite species arranged at the corners of a regular octahedron. This is clear from Fig. 3, in which the octahedral disposition of the chloride ions surrounding the central sodium ion of the unit cell is indicated by broken lines.

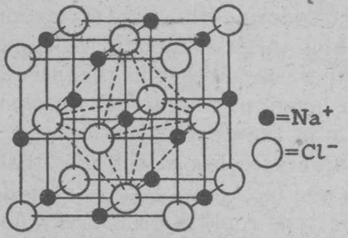

Fig. 3.—Sodium Chloride.
[Ionic—type AX].

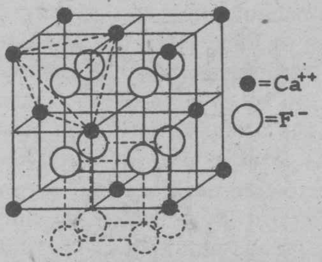

Fig. 4.—Calcium Fluoride.
[Ionic—type AX_2].

Calcium Fluoride, CaF_2 (Fig. 4). This is an ionic compound like that just considered, but of the formula type AX_2. The same principles determine the structure but it is now necessary to accommodate twice as many negative ions as positive ions, to preserve electrical neutrality. In calcium fluoride this is achieved by an arrangement in which each calcium ion is surrounded by eight fluoride ions situated at the corners of a cube, and each fluoride ion is surrounded by four calcium ions situated at the corners of a regular tetrahedron.

Mercuric Iodide, HgI_2, red modification (Fig. 5). In common with a number of other salts possessing a marked degree of covalent character (notably chlorides, bromides, and iodides of di- and trivalent metals), this substance crystallises in what is known as a *layer* type of structure, which may be thought of as being intermediate between the typically ionic structures (*e.g.* sodium chloride and calcium fluoride above) in which the ions pack together as independent units without any association to form molecules, and the molecular structures to be mentioned below, in which discrete molecules appear as units in the pattern.

The structure of mercuric iodide consists of parallel crumpled sheets composed of mercury and iodine atoms, running right through the crystal, the sheets being held to one another by van der Waals forces. Each mercury atom is attached to four iodine atoms arranged at the corners of a regular tetrahedron, and each iodine is attached to two mercury atoms. The bonds between the atoms are partly ionic and partly covalent, and so the crystal may be regarded as something between a pile of two-dimensional ionic crystals and a pile of molecules of formula $(HgI_2)_n$, where n is very large and is determined by the cross-sectional area of the crystals parallel to the layers.

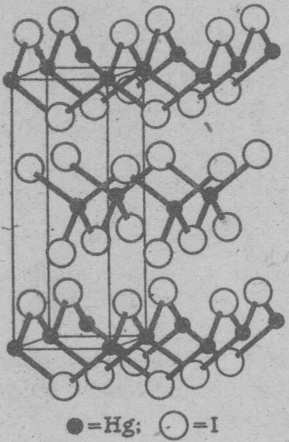

FIG. 5.—Mercuric Iodide (red modification), [Layer—type AX_2].

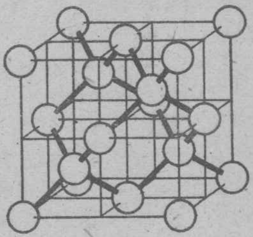

FIG. 6.—Diamond [Covalent—endless].

On account of the weak forces holding the layers together, crystals with this type of structure always cleave readily in the direction parallel to the layers.

Diamond (Fig. 6). This structure consists of a continuous array of carbon atoms, each one of which is surrounded by four others situated at the corners of a regular tetrahedron. The bonds joining the atoms are covalent, and so the whole crystal forms one "giant" molecule. This accounts for the resistance of diamond to high temperatures, and its extreme hardness. In the figure the bonds are indicated by heavy lines.

Iodine, I_2 (Fig. 7). In this structure the atoms occur in pairs, having an interatomic distance of 2·70 Å, whilst the smallest distance between atoms belonging to adjacent pairs is 3·54 Å. The pairs are iodine molecules, in which the two atoms are joined by a single covalent bond. The forces holding the molecules together in the crystal are of the weak van der Waals type; hence the much greater distance, 3·54 Å, between atoms belonging to adjacent molecules than between the two atoms in the same molecule. These weak