CHAPTER 14

X-ray Diffraction and its Impact on Physics

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14.1. Introduction

The intention in this chapter is to present, in the light of a backward look by one physicist who was privileged to work with Sir William Bragg from 1922 until his death in 1942, the overall significance of a half-century of development in the field of X-ray diffraction, *as it affected the study of physics*.

It will be apparent to those knowledgable in this field that some branches or crystal physics have received little or no mention here and that the treatment given to others is very unequal. This is deliberate. To write an adequate account of crystal physics would require not one chapter, but several volumes. Moreover, the subject considered is really not crystal physics at all. The early workers in the field of X-ray diffraction were not at first interested in the physics of crystals as such but in the fundamental problems of physics itself: properties of matter, heat, light, sound, electricity and magnetism. Crystals and the diffraction of X-rays by crystals were simply tools with which to investigate such phenomena as cohesion, rigidity, elasticity, changes of state, expansion, the nature and properties of radiation and its interaction with matter. Examples are given to illustrate the way in which this enormous project was tackled and the way in which it opened up what to most physicists was a new field: the study of the solid state as such. Some crystal properties had, of course, been known for many years, but they were not understood until the structure of the crystals became known. Other crystal properties were revealed during the course of the studies made. Examples of both kinds of investigation are given here. Later on, the subject became divided. Structure analysis tended to become tied to chemistry and mineralogy; solid state physics established itself as fundamental to many very important industrial developments.

It would have been tidy to have been able to divide the chapter under precise sub-headings. Some attempt at sub-headings has been made, but the subject, in analogy to most real crystals, is an untidy mosaic. The studies were interlocked from the onset and any attempt to sort them out chronologically here would mean losing the very flavour of research, part of the attraction of which is that one never knows what may turn up next! The task of presenting a really balanced account of the whole subject must be left to the historian, who would doubtless place a very different emphasis on the personalities involved. The fact that the writer was trained in a British school of research at the time when many of the most fascinating discoveries were being made has certainly biased this account. To remedy this in part, a selection of books and major articles has been listed and references given in the text to these more readily available books rather than to original papers.

14.2. Early Ideas

The early research workers in the field of X-ray diffraction from von Laue onwards were all physicists. Some of them were theoretical physicists. Their purely physical training was, indeed, a source of some embarrassment to some of the experimentalists among them, for while all chemists know some physics, few physicists include much chemistry in their training, or mineralogy either, for the matter of that. Yet mineralogical and chemical knowledge were necessary when it came to the proper selection of substances for X-ray structure analysis. The idea that the chemist and mineralogist might learn something from these studies came later.

The initial preoccupation of physicists in the early experiments was certainly not without cause. X-ray diffraction was an exercise in advanced optics, it gave information about the nature of X-rays and about the structure, sizes and behaviour of the atoms in solids and it gave promise of providing the solution to the problem so forcefully stated by Isaac Newton when he wrote (*Opticks* 3rd ed. pg. 364 and 369):

'The Parts of all homogeneal hard Bodies which fully touch one another, stick together very strongly. And for explaining how this may be, some have invented hooked Atoms, which is begging the Question; and others tell us that Bodies are glued together by rest, that is, by an occult Quality, or rather by nothing; and others, that they stick together by conspiring Motions, that is, by relative rest amongst themselves. I had rather infer from their Cohesion, that their Particles attract one another by some force, which in immediate Contact is exceeding strong, at small distances performs the chymical Operations above mention'd, and reaches not far from the Particles with any sensible Effect.—There are therefore Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions. And it is the Business of experimental Philosophy to find them out.'

The same problem was expressed in other words by Sir Oliver Lodge who said in the course of a lecture that the most extraordinary thing about a poker is the fact that if it is lifted up by one end, the other end comes up too. Until the structure of solids began to be understood there was very little hope of understanding the phenomena of rigidity and cohesion, or indeed many other properties of solid matter which have been known empirically both to workmen and to natural philosophers for centuries and have been used without being explained. A blacksmith does not have to know physics in order to fashion a horseshoe by heating and hammering. But once the facts of structure and of physical properties are related, it becomes possible to 'tailor' new types of solid to have certain properties that may be desired, as well as to frame and test physical theories.

Solid state physics, or crystal physics, has therefore assumed great importance during the last half-century, but the impact of X-ray diffraction on physics is much wider than would be covered by those terms alone.

14.3. Importance of the Ionization Spectrometer

The impact began with the building, by W. H. Bragg, of an extremely powerful new tool, the *X-ray ionization spectrometer*, a forerunner of the counter diffractometers of today. Of this instrument his son wrote:

'The X-ray spectrometer opened up a new world. It proved to be a far more powerful method of analysing crystal structure than the Laue photographs which I had used. One could examine the various faces of the crystal in succession and by noting the angles at which and the intensity with which they reflected the X-rays one could deduce the way in which the atoms were arranged in sheets parallel to these faces. The intersections of these sheets pinned down the positions of the atoms in space. On the other hand, a suitable crystal face could be used to determine the wave-lengths of the characteristic X-rays coming from different elements as sources. A 'purc' beam of monochromatic X-rays could be selected by reflection from a crystal and its absorption in various substances measured. It was like discovering an alluvial gold field with nuggets lying all round waiting to be picked up.'

The power of this instrument was brought forcibly home to the present writer on receiving delivery of a new X-ray Coolidge tube in or about 1925. A few diffraction-angle measurements with a crystal of rocksalt showed, within a matter of minutes, that the target was not of molybdenum, which had been ordered, but of rhodium (MoK α_1 0.708 Å, RhK α_1 0.612 Å). To have found this with certainty by absorption measurements alone would have been quite difficult and would have taken very much longer. In fact, although the discovery of the characteristic K and L radiations (with its subsequent influence on structural atomic theory) was made by Barkla and Sadler in 1908 on the basis of their differential absorptions, yet it was the ionization spectrometer, providing as it did an easy means of isolating X-ray lines from their continuous background, that enabled all the physical phenomena associated with radiation in this short-wave region to be intensively studied by many investigators, especially wave-length, absorption, dispersion, anomalous dispersion, fluorescence, interference, polarization and scattering, both coherent and incoherent. Thus this instrument, which provided a simple but accurate method of measuring intensity, could be used to measure the falling-off of atomic scattering power with increasing angle of deflection (or decreasing wave-length of incident radiation) not only for solids but also for gases.

14.4. Structure of the Atom

This in turn helped to throw light on *the structure of the atom* itself. Bohr proposed, in 1913, a model of the He atom in which the two electrons revolve in the same orbit at opposite ends of a diameter. But this led to a scattering curve at variance with that observed. Debye in 1915 and J. J. Thomson in 1916 independently solved the problem of the scattering of X-rays by atoms in which there were groups of electrons at fixed distances from each other. But again the calculations did not agree with the facts.

Ultimately it was found that the Schrödinger-type atoms did give reasonable agreement with experimental determinations of scattering fall-off, although no very exact calculations of electron distributions in real atoms are possible, especially when the atoms are in a state of anisotropic combination in molecules and crystals (valence state). The long list of methods and of references given in Volume III of the *International Tables for X-ray Crystallography*, Section 3.3, supplies evidence of the large amount of work carried out in connection with the calculation of atomic scattering factors. In recent years it has even been possible, from the scattering of neutrons by unpaired electrons in the magnetic elements, to calculate the distribution of these particular 3d electrons alone.

The scattering of X-rays by atoms in the forward direction was directly proportional to the number of extra-nuclear electrons; to the atomic number, that is, of the scattering element if not ionized, or to the total number of extra-nuclear electrons in the ion. But this quantity could not be measured directly, since the measured scattering curve began at a value of $(\sin \theta)/\lambda$ corresponding to the largest observable value of the crystal spacing, whereas $(\sin \theta)/\lambda = 0$ would correspond with $d = \infty$. Hence, even for the lightest atoms, it was not possible to deduce the state of ionization directly from the X-ray scattering curves. It was possible to do so indirectly by a study of interatomic distances, and hence to classify the various types of chemical binding. This gave the theoretical physicists data from which to begin to answer Newton's question: that is, to find out something, on a quantitative basis, of the forces that hold the atoms in various kinds of solids in their relative positions: both preventing them from coalescing into one dense agglomeration and from flying apart altogether.

14.5. Structure of the Nucleus

The intensity of scattering of neutrons by the atomic nuclei does not bear any simple relationship to their positions in the periodic table or to their chemical properties. It has had to be measured empirically for each element; and this has been done using apparatus which is a development of the early Bragg spectrometer, together with structure analysis techniques which are very similar in principle (though not in detail) to those used in the early days of X-ray structure analysis. The data thus obtained, when properly understood, will give information about *the structure of the nucleus* itself, its energy levels and the forces which hold together its component parts, forces of an altogether different nature from those that are important outside the nucleus.

14.6. The Nature of Radiation

In the chapter on X-ray Spectroscopy it is being shown how, using the X-ray spectrometer, the wave-lengths and frequencies of X-rays could be measured with extreme accuracy. When X-rays are scattered by any substance the diffraction spectra have a practically unchanged wavelength and frequency. But there is also a photo-electric effect: swiftly moving electrons are ejected at the expense of the energy of part of the incident radiation. In the course of a lecture on 'Photo-electricity' (which was intended as an introduction to a course of lectures on Wave Mechanics' to be given by Dr. E. Schrödinger at the Royal Institution in March 1928, with a final summing-up by Professor Whittaker), W. H. Bragg spoke of the difficulty he had experienced in accepting the idea of the undulatory theory of X-rays, until that theory was confirmed by X-ray diffraction experiments. He referred to the famous paper (Ann. d. Phys., 17, 145 (1905)) in which Einstein applied the idea of the Planck 'quantum' to the explanation of photoelectricity, thus resuscitating a corpuscular theory of light which would have somehow to be reconciled with the known phenomena of reflection, refraction and diffraction. Bragg then demonstrated some of the experiments that he had carried out in Australia in 1908, with R. Kleeman and J. P. V. Madsen, which showed that γ -rays falling on a carbon plate excited β -rays, a phenomenon parallel with the photoelectric effect for visible light. He went on to say 'The parallelism was not then so obvious as it is now, and for my own part I could not then believe in its existence. Our experiments fitted in perfectly with a corpuscular hypothesis of the nature of the γ -rays; and I supposed that the undulatory theory of light was unshakeable. I should, of course, have thought otherwise if I had been aware of Einstein's paper, to which I have already referred; but it is easy to miss a single reference when one is in a very isolated laboratory, and, as I said before, there are few if any allusions to the paper in the current literature of the years immediately following its appearance.' (My emphasis). All workers in isolated laboratories will know this situation, and will sympathize.

It was in fact not until 1912 that Einstein's photoelectric equation $E_{kin} = hv - \omega_0$, where ω_0 is the work done in pulling an electron out of an atom, was satisfactorily experimentally tested (see Compton and Allison (1935) pg. 45) and not until 1916 that Millikan showed that h was indeed Planck's constant. Meanwhile, the corpuscular and undulatory theories of X-rays had both been amply demonstrated and the quantum-mechanics theory of electromagnetic radiation became in

a sense inevitable once the phenomenon of X-ray diffraction had been proved.

This theory led L. de Broglie (*Phil. Mag.*, 47, 446 (1924)) directly to the inference that moving electrons and other 'particles' should also behave like waves and be diffracted by crystal gratings. In the lecture that has just been referred to W. H. Bragg spoke of the successful *electron diffraction* experiments carried out by Davisson and Germer in America and G. P. Thomson in Scotland and announced, not without real satisfaction, that the lectures by Schrödinger and Whittaker would be followed soon after Easter (1928) by one given by Professor Thomson on this newly-discovered phenomenon. This must certainly have been a historic series.

The Bragg spectrometer was used by A. H. Compton in 1926 to examine the weak scattered radiation that accompanied the X-ray diffraction spectra. He was able to show that this scattered radiation differed in wavelength from that of the incident beam and that this $\Delta\lambda$ depended on the angle of scattering only and not on the original wave-length or on the nature of the scattering material. This *Compton effect* was capable of a very simple explanation in terms of a quantum theory of X-rays.

The excitation of characteristic fluorescence radiation from a secondary radiator had been known before 1912, but the Bragg spectrometer made X-ray spectroscopy a precise study, and Moseley used a crystal to carry out a systematic photographic study of the X-ray spectra of the different elements. (Moseley's two papers in the *Phil. Mag.*, 26, 1024 (1913) and 27, 703 (1914) are a model of conciseness that should be studied by every research worker.)

14.7. X-ray Absorption and Related Phenomena

That the *absorption of X-rays by matter* is an extremely complex phenomenon was known to the physicists who first studied X-ray diffraction. They did not, however, realize the complexities that would arise in the quantitative application of the laws of absorption to the case of crystals. These have been slowly discovered by subsequent workers, to many of whom the diminution in intensity of the primary and diffracted beams, as they pass through crystalline material which may be of unknown texture or purity and of irregular shape or composition, is a major practical problem. Not least among the difficulties encountered is that of variable use of such words as *absorption*, *attenuation* and extinction. True absorption must involve the conversion of energy from the absorbed radiation into some other form of energy, whether heat, ionization, the recoil of bound electrons or the re-emission of radiation of different wave-length. But the primary beam intensity will be diminished also by scattering of radiation of unchanged wave-length and if a single crystal is used this effect will be a directional one; it will be particularly marked when selective reflection occurs. Using his ionization spectrometer W. H. Bragg was able to measure for diamond the abrupt diminution of the transmitted beam that occurs when a rotating crystal turns through a reflecting position. With a divergent beam of X-radiation and a stationary single crystal the same phenomenon is shown photographically as a pattern of white lines on a dark background.

The measured loss of intensity of a beam after transmission through matter is sometimes called its attenuation. This naturally depends upon the state of the scattering material whereas true absorption is independent of state. A recent tendency to write of 'attenuation coefficients' is wholly to be deplored, as it adds confusion to an already confused subject. Even the use of powdered material and monochromatic radiation does not permit an exact measurement of true absorption to be made, since even from powdered material the incident beam, after transmission, will in practice have lost energy by diffraction as well as by absorption. It is better to use an amorphous substance or a single crystal in a non-reflecting position. Measurements of absorption coefficients for low atomic-number elements are available for a wide range of wave-lengths, but for elements above Z = 30 the experimental data are scanty and not very consistent. This is unfortunate, for data are badly needed on which to build a reliable theory.

The dependence of true absorption on wave-length of radiation and on atomic number of the scatterer is therefore not accurately known either from the experimental or from the theoretical point of view. The *positions of absorption edges* were easily measured using the ionization spectrometer or photographic techniques; and the relationship between absorption edge and fluorescent radiation wave-lengths was readily established. But the absorption on each side of an edge is difficult to measure accurately.

In crystal analysis the effect of absorption depends upon the crystal shape and the composition of the primary beam. Earlier workers as a rule used short wave-lengths and their intensity measurements were not so precise, nor their structures so complex that absorption made much difference to their results. But they were interested in it as a physical phenomenon. (For example, see W. H. Bragg and S. E. Pierce, *Phil. Mag.*, 14, 626 (1914)).

The early workers realized also that X-rays must travel at slightly different speeds in different media, and they determined the *refractive index* by several methods, including that of measuring the apparent wave-length of the X-radiation when diffracted in various orders from sugar and other crystals (Stenström 1919, see Compton and Allison (1935) pg. 280; R. W. James (1948) pg. 168 for a number of references). It was realized, however, that in the neighbourhood of an absorption edge the refractive index would have anomalous values, and that the atomic scattering factor would also show anomalous dispersion effects, including an imaginary term. This will be referred to again later. The point now being stressed is that the discovery that a crystal could act as a diffraction grating meant that an immense variety of natural gratings was available for experimentation on various aspects of X-ray optics.

Moreover, the reason why the metals and the alkali halides have been used as diffraction gratings for such a wide range of investigations is not due to interest just in those substances as such. Their structures are simple enough to be amenable to mathematical calculation, and it is this that makes them important from the point of view of physics.

14.8. Crystal Dynamics

Nowadays X-ray crystallographers, particularly if their basic training is in chemistry, study *the dynamics of crystals*; but only because they *must*. In order to refine the structure of an organic compound to the point where accurate bond lengths and angles are obtainable it is necessary to find and to make allowances for the anisotropic atomic thermal vibrations. To the early research workers, as also to the crystallographer-physicist of today, the interest is in the dynamics itself, and in its relation to a host of independent physical properties. Humphrey Davy had suggested that melting involves an increase in the heat motion of atoms, a suggestion which seems obvious to us now, but only because we understand, so much better than he could, the final breakdown of crystal architecture involved in the process of fusion. As X-ray diffraction has shown, the reason why glasses soften, become plastic and finally liquify *without* any definite melting-point, is that their structures do not have the regularly repeating periodic pattern of a crystalline solid; and there is therefore in glasses no such directed system of long-range order to be broken down by the disturbing influence of increasing and varying local disorder.

The historical paper by Born and Karman on the theory of lattice vibrations preceded, by a few months, the discovery of X-ray diffraction by crystals. Indeed, we are told by Ewald that the question that first exercised the minds of some of the theoretical physicists of those early days, when the possibility of crystal diffraction was discussed, was whether the disorder produced by thermal vibration might not be so large as to prevent the observation of diffraction effects altogether. It has occasionally happened in scientific history that a discovery has been postponed for years because theoretical prediction has discouraged experimental workers from undertaking a difficult investigation likely to give a negative result. The Hall effect provides one such example. Fortunately, neither the doubts in this case nor an initial failure, were allowed to inhibit the crucial X-ray diffraction experiments, which showed that for diamond there was diffraction right round to back-reflection regions, but that for copper sulphate, zinc blende, rocksalt, etc. the intensity was so much affected, presumably by thermal vibration of the individual atoms, that no spots were observable at large angles of deviation.

In subsequent studies by Debye and others, notably I. Waller, (summarized by P. P. Ewald, Handbuch der Physik, 24, 270 (1933)) the effect that thermal vibration would have on the intensities of the diffraction maxima was calculated, and expressed as an exponential factor, $I_T = I_R e^{-M}$ where I_T is the intensity at a temperature T, I_R the corresponding intensity for a structure undisturbed by vibration or disorder. M a function dependent upon temperature, structure and the forces between the atoms. M could be expressed in many ways. It could be related to the elastic constants, to the specific heat, to the possible existence of crystal vibration even at the absolute zero of the temperature scale, when thermal vibration had disappeared (zero-point energy), and so on. Subsequent experiments, by R. W. James and others, were directed not just to the confirmation of the temperature factor as a correction to intensity measurements (which could have been and was also achieved empirically) but as a means of checking these important physical theories, which however have never been extended quantitatively to more complicated and less symmetrical structures or to temperatures near to the melting point, where anharmonic vibrations become increasingly important. Nor is there any really comprehensive theoretical study of the thermal expansion of the less simple structures, although certain empirical relationships with molecular form and

arrangement are obvious. It is, for example, an observed fact that whereas the expansion normal to the layer planes of graphite is 28 times that of diamond at room temperatures, it is only a fraction of that found for aromatic compounds such as anthracene or naphthalene, where again the expansion increases as the molecular size decreases. There is a contraction with increase of temperature within the layer planes of graphite and of hexagonal BN, up to fairly high temperatures. That the thermal expansion of face-centred cubic elements is

That the thermal expansion of face-centred cubic elements is related to the adiabatic compressibility at 0°K and to the molar specific heat was shown by Grüneisen before the discovery of X-ray diffraction and the fine structure of solid matter. Grüneisen and Goens subsequently extended this theory to hexagonal elements such as zinc and cadmium and explained the negative expansion at low temperatures normal to the c axis. The theory does not agree with experiment for body-centred cubic elements such as W, Li, Na, Pd, Ta, nor for most polyatomic compounds. A recent critical review of this entire field has been given by R. S. Krishnan (1958) together with much experimental data for thermal expansion and its variation with temperature.

It is clear that X-ray diffraction provides a method of measuring thermal expansion of the unit-cell parameters, as distinct from that of the macroscopic material. It is perhaps relevant here to point out that thermal expansion is one of many deceptively simple phenomena for which accurate measurements are obtainable, but for which not even the powerful new methods of X-ray diffraction and structure analysis have provided sufficient basic information for the formulation of a really comprehensive theory.

14.9. Crystal Texture

In other cases, it was the study of the X-ray diffraction intensities themselves that drew attention to *unexpected* physical phenomena. For example, physicists were interested in the shape of the curve showing intensity versus deflection-angle in the neighbourhood of a diffraction maximum, and in the resolving power of the scattering mechanism. Darwin tackled these as theoretical problems and so, later, but independently, did Ewald. Naturally they assumed a perfectly regular arrangement of scatterers at the points of a space lattice, and to simplify the calculations, crystal absorption was neglected. If anything, therefore, the observed intensities might have been expected to be less than those calculated. In fact, they were often many times greater; and they could be increased still more by roughening the surface of the crystal if the diffraction effects were being observed by 'reflection' and not by 'transmission'. The primary and secondary extinctions that were introduced by Darwin as the consequence of crystal perfection, and the need for a single crystal to approximate to a condition of 'ideal mosaicity' in order to give diffraction intensities that can form the basis of a structure analysis-these are a commonplace to the presentday crystallographer. They may involve him in tiresome corrections. But they were exciting discoveries to the early physicists; and many discussions followed as to what was the real nature of that hypothetical mosaic structure that must be postulated at least as a limiting condition, in order to get any sense out of the observed intensities. It goes without saying that there are again many properties of solids and particularly of metals, that depend upon texture as much as, or even more than, upon structure.

For example, if high-purity metal wires are twisted under slight tension beyond their elastic limit they begin to extend rapidly, but in a self-annealing metal such as lead the elongation for a given twist and tension depends on the rate of twisting (T. Lonsdale, *Phil. Mag.*, 8, 703 (1929); 11, 1169, 1187 (1931) gives reference to earlier work). The classic investigations by G. I. Taylor (*Phil. Trans. Roy. Soc.*, A 230, 323 (1931) (with H. Quinney); *Proc. Roy. Soc.*, A 145, 362 (1934)) extended this study to metal *tubes*, and thus he obtained data which could be compared with theoretical calculations and he could show that some kind of structural misfit or weakness must be present to account for the experimental results. (For work on NaCl see also A. Joffé, 1928.)

'The Theoretical Strength of Materials and their Practical Weakness' formed the subject of a lecture to the Society of Engineers given by Sir William Bragg in 1935, but even then he was not able to give a complete or quantitative answer to the question as to what kind of imperfection in fact exists which reduces the tensile strength of rocksalt two-hundred-fold from its theoretical value, although he rightly pointed out that no theoretical value could have been calculated until the fine details of its structure were found by X-ray diffraction. It happened, however, that only a few months before he spoke, a new idea, that of 'dislocations' in crystals, had been put forward by Orowan, by Polanyi and by G. I. Taylor, to explain the phenomenon of plastic deformation in metals and the misfit that must occur at mosaic boundaries; and this idea was developed by W. G. Burgers (one of W. H. Bragg's early research students at the Royal Institution) and others, in particular by F. C. Frank, to give a satisfactory theory of *crystal growth*. It is an interesting thought that a really perfect crystal could not be ruptured except by a force that could pull all its atoms (or atomic groups) apart simultaneously, nor could it grow except by the fortuitous (and, in practice, impossible) circumstance that a whole plane should be deposited in place at once. A perfect crystal has been described as being like Oliver Wendell Holmes' 'deacon's shay' the parts of which were so exactly adjusted that it could not collapse until the day when it disintegrated entirely and the deacon found himself seated on the road in a heap of dust. The postulate of dislocations, since proved by electron microscope pictures and demonstrated in other ways, provides just those necessary points of weakness which allow shear or yield to take place for an applied force far less than would be necessary to separate the material into its component atoms or molecules. In a similar way dislocations in the surface of a crystal provide the growing points where new atoms or molecules can be deposited. As Frank (*Crystal Growth*, pg. 54) has written 'The completely perfect crystal will not grow in any circumstance: the conditions which could cause it to grow would also soon make it imperfect.' In fact it could not even exist except as an abstraction, for a perfect crystal would have to be infinite in all dimensions. Any surface forces would mar its perfection.

The mosaic nature of a single crystal, whether due to dislocations or to some other discontinuity of structure, is not the only kind of 'imperfection' that can affect physical properties. One of the earliest substances studied was quartz. In a sense this was curious, because it was certainly not one of the simpler structures that would easily lend itself to mathematical treatment. Perhaps it was chosen because good crystals were at hand and because its *polymorphism*, its *optical activity* and its *pyro- and piezoelectricity* constituted a challenge that simply could not be resisted. Subsequent studies of α and β quartz led to a complete understanding of the four forms of *twinning* shown by α quartz, two of which are also shown by the high-temperature and more symmetrical polymorph (W. H. Bragg, *Trans. Soc. Glass Techn.*, 9, 272 (1925)). Again we may emphasize that the modern structural crystallographer is seldom concerned with the *study* of twinning for its own sake (although there are notable exceptions). He learns to detect twins in order to reject them; or if he must use them for structure analysis he does so warily, his object being to find the basic structure of the untwinned material. But twinning is of importance both in its own right and in relation to the *plasticity* of metals. Studies of cold working and of heat treatment bring the subject rather outside the range of the physicist and into that of the metallurgist, although the problem is essentially one of physics; but the understanding, for example, of the flow of metals and even of glaciers depends essentially upon the same principles: an applied force produces strain; the crystals in which the orientation, often achieved by twinning, is such that strain can be most easily relieved by slip, will tend to grow in size, given time, at the expense of those less favourably orientated and therefore retaining higher internal stresses. This explains why the ice crystals at the foot of a glacier may be several centimeters in linear dimensions, although those at the head are only a millimetre or two across.

14.10. Ferroelectricity

In 1945 Ubbelohde and Woodward (Nature, 155, 170) observed a new kind of 'imperfection' associated with a phenomenon that has assumed the greatest possible practical importance in physics. If Rochelle salt, sodium potassium tartrate dihydrate, is studied between $+24.5^{\circ}$ C and -20° C, it is found that reflections from certain (0kl) planes are split into two components of slightly different Bragg angle. The separation is greatest at about the middle of the transition range, 0°C, but is so small that at first it was doubtful whether it was a real effect. It corresponds to the break-up of the orthorhombic crystal into sub-crystalline monoclinic units, all having their a axis in common with that of the parent crystal, and their b and c axes respectively equal to those of the parent crystal but with an angle of 90° $\pm 2'$ replacing the former 90°. The new b and c axes are randomly +2' from their former positions, giving four new orientations all present simultaneously and all disappearing again, with a coalescence of the split reflections, when the crystal is heated or cooled to a temperature outside the above range. Now this is just the temperature range within which Rochelle salt had been known, since 1921, to exhibit its ferroelectric properties, that is a dielectric constant along a about 400 times as large as that along b, with a dielectric hysteresis which implied that some kind of polarization or electric displacement persisted when the applied field was removed or gradually reduced to zero. Similar very large and anomalous changes take place in the piezoelectric modulus along the a axis. That these phenomena are related to cooperative movements of hydrogen atoms was suspected on structural grounds, but was definitely proved much later, by Pepinsky and others, using neutron diffraction measurements. These showed that certain reflections which changed markedly in intensity within the relevant temperature range, were due to hydrogens only.

In the structurally simpler case of KH_2PO_4 and related compounds, the movements of the hydrogen atoms have been demonstrated by Fourier analyses based on neutron diffraction experiments at temperatures within and outside the ferroelectric temperature region. But there is a second class of compounds, of which barium titanate, BaTiO₃, is a typical example, which shows an even larger polarization effect, due to the ease with which a highly-polarizable ion can shift out of a symmetrical position, if the structure is already at the limit of stability and there is a change of temperature. The extraordinary behaviour of such compounds is admirably described in a number of recent textbooks and papers and it rapidly became a matter of much practical importance.*

In the case of ferroelectrics the observed changes of texture which accompany the structural second-order transitions are themselves a very subsidiary effect. The cause of the ferroelectricity is a response of the *structure* to an external stimulus in the shape of a change of temperature and an imposed electric field.

14.11. Fluorescence; Electrical and Thermal Conductivity

Other physical properties of great practical importance are due to *structural imperfections* of various kinds. In some cases the early workers were aware of the application without being aware of the cause, and even perhaps without being sufficiently curious about it to make it an object of intensive study. Every X-ray worker used a *fluorescent screen*. It was often regarded as being a distinct advantage if the material (ZnS or Zn₂SiO₄, usually) were phosphorescent, because then the screen could be inserted into a narrow gap and the luminescence

^{*} It even became a matter of political consequence. From 1952 to 1954 or longer, every physicist or crystallographer wishing to travel from Europe to the U.S.A. was liable, on applying for a visa, to be asked if he or she knew anything about (a) nuclear physics or (b) ferro-electric crystals. The writer of this article was so startled at this unexpected question (b) that she asked what was the reason for it, only to receive the reply 'I haven't the slightest idea. I only know that if you say "Yes" you go through one hoop and if you say "No" you go through another. Since you have said "Yes" your papers have to go to Washington for further investigation and I am afraid that you will have to wait some months for a visa.' It was granted in the end, however, and by this time a little thought had provided the reason for the question.

observed when it was withdrawn. It had long been noticed that many crystals become fluorescent when they are bathed in an X-ray beam (Röntgen 1896). None of the early crystallographers seem to deal with these interesting facts. Only in recent times have the details of the dependence of fluorescence and phosphorescence on the presence of impurities in the crystal structure been opened up to quantitative interpretation on lines very similar to the energy band theory of semiconductors which attracted so much interest and intense study because of its important applications in connection with rectifiers and transistors.

Some of these forms of 'structural imperfection' have already been mentioned. The more important of these, from the point of view of electrical and thermal conductivity or resistivity, are the presence of free or partially-free electrons, the existence of 'positive holes' caused by the removal of an electron from a previously neutral region, the effects of lattice vibrations, of impurities (interstitial or substitutional), and of a wide variety of lattice defects such as vacant sites, atoms or ions moved into interstitial positions, dislocations and the presence of foreign high-energy particles (nucleons). This is no place for a detailed description of the mechanism of the processes of conduction in a metal or of semiconduction in, say, germanium, cuprous oxide or indium antimonide, but perhaps it may be mentioned that the theory is based on an extension of the idea of energy levels of free atoms to that of atoms in close combination. The solid has filled, partially-filled, or empty energy bands. If under the action of an applied voltage the electrons remain in the filled energy levels of the solid the substance is an insulator. If the energy gap separating the highest filled level and the next unfilled (conduction) band is small (only of the order of the atomic thermal energy) the substance is an intrinsic semi-conductor. If the two levels overlap the substance is a conductor. If an imperfection such as the presence of impurity atoms causes electron jumps either from the impurity atom to the conduction band, or from the highest filled band to the impurity, then there is impurity semiconduction respectively of the excess (n) or defect (p) types. The 'impurity' may be an atom of higher or lower valency than that of the matrix; or there may be a deviation from stoichiometric composition in the shape of excess or defect anions or cations. X-ray diffraction methods may be used in some cases to distinguish these alternatives. From a knowledge of the crystal structure the energy levels or energy gaps may be calculated or estimated. Without it, the subject would be wholly empirical.

Sometimes the conductivity is of an ionic type. In a remarkable experiment by A. Joffé it was shown that the conductivity of a quartz crystal at 200°C could be reduced sixty-fold, and that of an alum crystal nearly fifty-fold, by passing an electric current through it for a long time, to expel foreign ions. Further purification of the alum by aqueous solution and recrystallization decreased the conductivity another 100-fold. Such ionic conductivity is strongly texture-sensitive, and is a kind of diffusion. But there is an ionic conductivity which is diffusion of another kind and is texture-insensitive but strongly temperature-sensitive, and which is also very sensitive to the size of and charge on the moving ions. A striking example of this ionic conductivity is that of AgI in its various forms. A few degrees below the transition from cubic to hexagonal at 146°C the electrical conductivity is very small; just above it the conductivity jumps 4000-fold and increases steadily up to the melting-point 552°C. Within the range 146°C to 552°C the iodine atoms occupy fixed positions at the corners and centres of the cubic unit cell, but the silver atoms behave almost like an interstitial liquid (L. W. Strock, *Z. phys. Chem.*, B 25, 441 (1934), B 31, 132 (1935); *Z. Kristallogr., 93,* 285 (1936)).

14.12. Atomic and Ionic Radii

This question of structure transitions and of mixed crystal and defect structures brings us back to one of the most fundamental of all the contributions that X-ray structure analysis has made to physics. It has provided a method of measuring atomic and ionic radii. This subject, because of its importance in connection with *bond lengths* and because of the influence of the radii upon the state of *co-ordination* (number of atoms or ions of one kind surrounding one of another kind) is often thought of as a branch of crystal chemistry. But from our point of view the structure and weight of the elements and the atomic number are all of physical no less than chemical interest; and the atomic radius is one of the factors controlling many very important physical properties of solids, including the possibility of *polymorphism*.

The original experiments with the Bragg ionization spectrometer gave very exactly the angles at which the diffraction spectra occurred when monochromatic radiation was used and hence, knowing the wave-length, the unit-cell dimensions could be calculated (from $n\lambda = 2d \sin \theta$); or knowing the unit-cell dimensions (from $a^3\rho = nM/N$) the wave-length could be found. Once the intensity distribution had been used to determine the structure, it was possible to decide the interatomic distances. The actual atomic (ionic) radii could only be found when some other technique, such as refractivity (Wasastjerna 1922), had been used to estimate the radius of at least one atom or ion. The discovery was then made that in the metallic state the apparent atomic diameter was quite different from what it was in an ionic compound and that even in ionic compounds the diameter varied slightly with the type of structure. This in turn gave valuable information about the types of binding in different types of structure, information that could be correlated with hardness, cleavage, polymorphism, melting-point, electrical, optical and magnetic properties. It also provided information about the effective diameters of the electron orbitals, when the atom was in different valence states.

Measurement of the unit cell dimensions combined with a knowledge of the molecular weight and number of molecules in the unit cell gives an 'X-ray density' which need not be quite the same as the macroscopic density, although it often is. Density is a property which enters into many physical theories; and an X-ray analysis can often give an 'X-ray density' in circumstances where it would be impossible to measure the macroscopic density; for example because the crystal is too small or too volatile, or because it is an inclusion or exists only as a transitory stage in a solid-state reaction.

In order to be sure that the values found are meaningful, it is of course necessary that the structure should be relatively free from defects. For instance, the density of a diamond single crystal can be reduced by about 8 per cent by means of neutron irradiation damage, the unit-cell parameter increasing by a corresponding amount. The damage, in fact, produces an overall increase of the unit-cell size and not an unequal spread of unit-cell dimensions. By heating the diamond to a temperature a little lower than that required to graphitize it, it can be annealed. The true carbon-carbon distance is that found in a diamond free from both impurity and defect. But the change in shape of the space taken up by a carbon atom in diamond and in graphite is a real indication of the change in electronic condition.

Caesium undergoes a transformation on compression, from a bodycentred to a face-centred cubic structure. Since the latter is closepacked, one would not expect any further change to be possible. In fact there is a further abrupt reduction of 11 per cent in the volume of caesium at a pressure of 45000 kg/cm² (P. W. Bridgman, Amer. Acad. Arts and Sci., 76, 55 (1948)) and this is supposed to be due to a transition of the valency electron from the 6s to the 5d level. At normal pressure and temperature the atoms of caesium undergo very large thermal vibrations indeed, having a Debye coefficient,

$$B = (\ln I_R - \ln I_T)\lambda^2/2\sin^2\theta,$$

of the order of 10, as compared with 2 for lead, 1 for antimony and 0.5 for gold. This will increase their apparent size; but a *discontinuous* change of volume is a sure sign of a transition, either structural or electronic.

Strictly speaking, *thermal vibration* (and perhaps zero-point energy) should be allowed for, or measurements should be made of unit-cell dimensions at low temperatures. Apart from the few measurements made by the physicists in the 1920's, however, there are hardly any accurate data for thermal vibrations even in binary compounds. This is partly because of the real difficulty of getting sufficiently accurate measurements of intensities, partly because of the problem of allowing for binding effects in the atomic scattering factor, and partly because there were and are so many other interesting things to be done.

The analysis of caesium antimonide by Jack and Wachtel (*Proc. Roy. Soc.*, A 239, 46 (1957)) has shown that the two kinds of atoms in such a structure may sometimes have vibration amplitudes which are as different from one another when combined as they are when measured for the separate elements. The Debye characteristic temperatures calculated from vibration amplitude measurements may be compared with those obtained from specific heat, elastic constants, electrical resistance, etc., thus extending our knowledge of the relationships between these properties for an increasing range of simple substances.

14.13. Magnetic Properties of Crystals

The atomic radii in the solid elements show a periodic variation according to their place in the Periodic Table. There is, however, only a small variation in the sizes of the transition elements V-Zn, for which the 3d sub-shell is filled up after 4s is already completed. Fe, Co, Ni have long been known to be *ferromagnetic*. Other transition elements, such as Cr, Mn, Cu are not normally ferromagnetic. For this to be the case, a condition, found empirically, relating the radius of the 3d shell and the interatomic distance in the crystal, must be satisfied; and this is rather critical. Certain combinations of atoms, such as the Heusler alloys AlMnCu₂ and SnMnCu₂, are ferromagnetic when annealed, but not when quenched from high temperatures, because it is only in the annealed state that the critical distance rule is satisfied and an internal magnetic field can exist. There are also non-ferromagnetic forms of iron (face-centred cubic, f.c.c.) and nickel (hexagonal close packed, h.c.p.) having structures which do not satisfy that rule; and at high temperatures the thermal vibrations are large enough to prevent, in all substances, the co-operative alignment of spins that is required to establish the 'molecular field'. The transition from ferromagnetism to paramagnetism at the 'Curie point' is accompanied by discontinuous changes in specific heat and other properties.

There are other compounds, however, in which the spins of 3d electrons in separate atoms interlock to keep each other polarized but in anti-parallel positions, through an intermediate ion such as oxygen or sulphur. Such substances are called 'antiferromagnetic'. The idea that such an arrangement might exist was put forward by Van Vleck in 1941, and applied by Néel in 1948 to explain a second-order transition shown by a specific heat discontinuity in the ferrites. The magnetic order-disorder transformation which occurs at high temperature produces very little change in unit-cell dimensions and is therefore not easily studied by X-ray diffraction, nor does antiferromagnetism result in any overall macroscopic magnetic moment which can respond to an external field. But since neutrons possess a magnetic spin there is a strong interaction between neutrons and magnetic atoms; and the existence of an ordered arrangement of spins in a structure, whether ferromagnetic, antiferromagnetic or a mixture of the two (*ferrimagnetic*), results in strong neutron diffraction peaks from which the direction of alignment of spins can be deduced and which disappear when the magnetism changes into paramagnetism (at the Curie or Néel point).

Moreover, there is now considerable work going on, mainly in Eindhoven, by Verwey, Gorter, Braun et al., on the tailoring of new magnetic materials which are strongly anisotropic, the magnetic axes being strongly linked with the crystal axes, and which have hysteresis curves of various desired shapes. This work is possible because of previous knowledge of the spinel structure of these materials and of the modification by substituting some ions by various percentages of others.

Magnetite and the spinel group of crystals captured W. H. Bragg's interest as early as 1915 (two letters to *Nature*). Even earlier than this, he had tried to use X-ray diffraction to explain the ferromagnetism of iron but had not succeeded. As is mentioned above, it was not the X-ray but the neutron diffraction method that did succeed in demonstrating the alignment of spins in magnetic substances.

In 1927 W. H. Bragg gave a lecture at the Royal Institution on 'Tyndall's Experiments on Magne-crystallic Action' and he followed this, at the time of the Faraday celebrations in 1931, with a note to *Nature* on 'Faraday's First Successful Experiment on Diamagnetism'. He did no experiments himself in this field but he was keenly interested in those of the Indian schools; especially as K. Banerjee had been able to correct Bragg's early anthracene structure by reference to its crystalline diamagnetic anisotropy; and then K. S. Krishnan who with his colleagues examined the diamagnetic susceptibilities of many aromatic crystals, was able to show that the orientation of the molecule could be fairly accurately deduced from such measurements in many cases.

If the crystal structure were already known, however, the magnetic susceptibilities of individual molecules could be calculated and related to their dimensions and electronic structure. Lonsdale was able to use diamagnetic data to measure the effective radii of the σ and π orbitals in benzene derivatives and in metal-free phthalocyanine and to prove conclusively that the π orbitals are of molecular dimensions.

14.14. Electrical Properties of Crystals

Sir William Bragg spoke of some of these results in a lecture at the Royal Institution in March, 1936. In a second lecture 'The Electric Properties of Crystals (II)' in May 1936, he went on to say:

'The recently acquired and more intimate knowledge of the manner in which the molecule is built into the solid allows a further insight into the problems of the dielectric constant and of the electric properties of the crystal. These problems have been widely studied of late because of their extreme importance in industry, especially in the transmission of electricity at high voltages. They are of remarkable interest also for their applications in radio telephony, where great use is being made of the piezo-electric property in the production of oscillators of known high frequency, and in the construction of various types of microphone.'

This lecture was illustrated by experiments showing how the polarity of resorcinol crystals was explained by the arrangement of molecular dipoles and how this could be varied by heat (*pyro-electric effect*). A model of Rochelle salt with flexible molecular linkages was used to exhibit a possible form of *piezo-electric action*; and various illustrations were arranged by the National Physical Laboratory and the Building Research Station to show the many uses of the piezoelectric properties of quartz. The phenomenon of pyro-electricity scems to have been known for many centuries B.C. That of piczoelectricity was discovered in 1880 by Pierre and Jacques Curie, who were also aware of its relationship to the crystal symmetry. But although an interesting physical property, little use was made of it until, during World War I, Langevin used quartz plates, excited electrically, to emit and receive high-frequency (h-f) sound waves under water. Langevin was thus the originator of the science of ultrasonics, now used extensively in the measurement of elastic properties and for many other scientific and industrial purposes. As Cady (*Piezoelectricity*, 1946, pg. 8) points out, however:

'Voigt came very near to being the originator of the piezo resonator. In the *Lehrbuch* he gave the differential equations for elastic vibrations in crystals, without, however, mentioning the bearing of the piezoelectric effect on such vibrations. He mentioned the use of h-f in the measurement of dielectric constants, recognizing the fact that anomalous results are to be expected at frequencies of molecular resonance. What he did not foresee was that similar anomalies would be found with all vibrating piezoelectric crystals whenever the applied frequency coincided with that of a normal vibrational mode of the entire crystal specimen. It was the electronic generator of h-f alternating current, supplanting the induction coil of Voigt's day, that paved the way for the advent of the piezo resonator.'

Communication, entertainment, adult education and propaganda have been almost entirely transformed during the past forty years because of this single development of an obscure and somewhat mysterious crystal property.

'Crystal sets' were used as receivers of wireless signals from 1913 on (one of the first in Gt. Britain was tested by the writer's elder brother in that year). These used zincite (ZnO) and bornite (Cu_5FeS_4) in conjunction. The writer possessed one of the original 'cat's whisker' sets. The crystal was silica (though others were possible), the resistance of which varied for some unknown reason with the direction of the applied voltage. The 'cat's whisker' probe was a fine copper wire, but not so fine as modern 'whiskers' of tin or cadmium! The signals received through head-phones were very weak and unreliable. Over 30 years later the original *transistors* were made at the Bell Telephone Laboratories by using two cat's whiskers, very close together, on a very pure crystal of germanium. Modern transistors are small, light and, unlike the original crystal sets, they are most reliable.

Nowadays, of course, quartz plates and other piezo-resonators and oscillators are cut with very precise orientations, to avoid disturbing effects of coupling between different modes of vibration and to avoid also the effect of temperature change upon frequency. Orientation can be accurately controlled by X-ray diffraction measurements. One of the more glamorous uses of piezoelectricity is in the *quartz clock*, where a vibrating quartz plate or ring replaces the pendulum and gives a time piece more constant than any other, being unaffected by slight daily variations in the acceleration of gravity or fluctations in the earth's rotation. The quartz clock has introduced a new order of precision into astronomical measurements.

In a simple compound such as ZnS the development of a piezo-electric moment normal to a (111) plate means either that compression has moved the Zn lattice relative to the S lattice, or that there is a has moved the Zh lattice relative to the S lattice, or that there is a change in the polarization of the bonds along the direction of the compression. The question that early physicists had to answer was: 'Does the positive charge develop on a Zn face or on a S face?' ZnS, which is of course hemihedral, has an equal number of larger shiny faces, and smaller rough ones. Ordinarily there would be no difference in the intensities of X-ray spectra diffracted from the (111) or from the opposite $(\overline{111})$ planes, even in the absence of a centre of symmetry (Friedel's rule). But the existence of anomalous dispersion in the neighbourhood of an absorption edge made it possible to distinguish the two. Coster, Knol and Prins used radiation from a gold target to study the (111), $(\overline{111})$ reflections from a plate cut from a well-formed crystal of ZnS. The wave-length of the ZnK absorption edge lies between AuL α_1 and α_2 . They found a difference in the (111), $(\overline{111})$ intensities which indicated that the atoms in the larger shiny faces are intensities which indicated that the atoms in the larger shiny faces are S, those in the smaller rough faces are Zn and that on pressure being applied the S faces become positively, the Zn negatively charged. Von Hippel has explained this by a change of the tetrahedral bonding angles, without change of bond length; and with a consequent movement of charge. Actual calculation of the piezoelectric field or of ferroelectric effects for a given strain is, however, a problem of an altogether different magnitude, involving a knowledge of the atomic dynamics as well as of structure and structural changes. Brave attempts have been made, particularly by the Indian schools, to relate piezo-electric and other physical properties to structure and to calculate electrical, elastic, thermal and optical properties at least for some of the simpler compounds the simpler compounds.

14.15. Optical Properties of Crystals; Absolute Configuration

The fact that quartz was found in right- or left-handed forms and that these rotated the plane of vibration of polarized light in clockwise and anticlockwise directions, respectively, was certainly one of the properties that led to its intensive study in the early days of X-ray structure analysis. A relationship with the spiral arrangement of atoms in the structure was at once expected.

It has been seen elsewhere that the discovery of X-ray diffraction by crystals grew out of Ewald's previous interest in the *double refraction* to be expected from hypothetical three-dimensional arrangements of atoms on a crystal lattice. It was not long before Born (1915) used the newly-determined structures of simple crystals to calculate various physical properties, including *refractive indices*. But it was necessary to know the dispersion curve of the ordinary ray in order to calculate that of the extraordinary ray and the optical rotatory power of quartz. These calculations, however, he made with considerable accuracy.

Recently it has proved possible to make quantitative calculations of the *optical activity* (S. Chandrasekhar, *Proc. Indian Acad. Sci.*, A37, 468 (1953); A39, 290 (1954)), and of its variation with temperature, by relating these effects to the characteristic frequencies of the substance and other physical properties. But a simple quantitative theory in terms of structure alone is not yet available.

The particular case of tartaric acid, which rotates the plane of polarization in one direction in the liquid state and in the other direction in the solid state was naturally something of a challenge to the early physicists and this problem was tackled by W. T. Astbury in 1922. But it was far too difficult a structure analysis to be solved at that time. This was accomplished by Beevers and Hughes in 1941. What became of even greater general interest later on was the question as to whether it was possible, by X-ray methods alone, not merely to differentiate between a right- and a left-handed screw but to determine the absolute configuration of an enantiomorph in any particular case. The solution was of importance to chemists because of its bearing on the Fischer convention. The determination of absolute configuration by Bijvoet et al. (Proc. K. Akad. Wet. Ned., 54 B, 16 (1951); Nature (Lond.), 168, 271 (1951)) which was a brilliant extension of the experiments of Coster, Knol and Prins referred to above, showed that light travels more slowly when the atomic spiral and that representing the electric field along the light beam wind in the same sense.

The quantitative determination of optical refraction indices by a

method much simpler than that of Born was made by W. L. Bragg, in 1924, for calcite and aragonite, two polymorphs of CaCO₃ (*Proc. Roy. Soc.*, A 105, 370). He assumed that each atom becomes an electric dipole under the influence of an electric field and he used the ionic refractivities as a measure of the polarizability of the ions (calculated theoretically in 1922 by Wasastjerna, and used by him in 1923 to give the first accurate estimates of ionic radii, see above). The mutual influence of nearest and next-nearest neighbours had to be taken into account in order to obtain a good approximation to the experimental data. The method was also successfully applied to other carbonates and nitrates, including the four polymorphs of NH_4NO_3 . A qualitative extension of this work to crystal structures containing ionic groups or molecules of various shapes and arrangements and in various states of rotation (for example, simulating spherical or cylindrical symmetry) has allowed birefringence and optical sign to be used, just as diamagnetic anisotropy can similarly be used, as a valuable adjunct to crystal structure analysis.

14.16. Thermo-optical Properties

A change of temperature can change the birefringence. Mitscherlich (best known for his studies of isomorphism early in the 19th century) showed that when a gypsum plate, positive biaxial at room temperatures, is heated, it becomes uniaxial at 90°C and then biaxial above that temperature but with its optic axial plane rotated through a right angle. Tutton (Vol. II, 1922) records the case of CsSeO₄ for which, over a 0°-250°C range of temperature each of the three axes of the optical ellipsoid in turn becomes the acute bisectrix. Naturally the temperature at which such changes take place depend upon the wave-length of the light employed.

wave-length of the light employed. In an excellent review of this subject, R. S. Krishnan (1958) points out that the thermo-optical behaviour of crystals depends upon their structures, thermal expansions and temperature variations of absorption frequency.

The absorption of light, whether in the ultraviolet and visible or in the infrared regions, was studied long before the discovery of X-ray diffraction. However, knowledge of crystal structure has shown that the colour of a crystal and particularly any pleochroism, or variation of colour with direction of vibration of light, is closely linked with structure. In organic crystals absorption in the visible region is greatest when the light is vibrating parallel or nearly parallel to such double bonds as $-\overset{i}{C}=\overset{i}{C}-$ and -N=N-. By the use of polarized infrared radiation also, the orientation of particular atomic bonds having known characteristic frequencies can be found. These are applications of chemical rather than of physical interest and indeed, the use of solid phase techniques is limited. The study of the Raman spectra of crystals does give information, however, about lattice and molecular (or group) vibrations.

It is only recently that enough experimental data for the elastic properties of crystals have been available to test relationships between these and the strength of atomic bindings; although for such simple structures as the alkali halides a reasonably good theory was available in 1922.

This brief and inadequate review of a tremendous field does less than justice to the crucial part in it played by that great physicist, Max von Laue. Attention is therefore especially drawn to the article by P. P. Ewald published in the *Biographical Memoirs of Fellows of the Royal* Society, 6, 135 (1960).

References

(additional to those in the text)

Bacon G. E. (1955) Neutron Diffraction, Clarendon Press, Oxford.

Bhagavantam S. and Venkatarayudu T. (1948) Theory of Groups and its Application to Physical Problems, Andhra University, Waltair, India.

Boas W. and Mackenzie J. K. (1950) Anisotropy in metals, Proc. Met. Phys., 2, 90.

Cady W. G. (1946) Piezoelectricity, McGraw-Hill, New York (Full bibliography).

- Compton A. H. and Allison S. K. (1960) X-rays in Theory and Experiment, Van Nostrand, New York.
- D'Eye R. W. M. and Wait E. (1960) X-ray Powder Photography in Inorganic Chemistry, Butterworth's, London (gives examples showing how to distinguish different kinds of defects).

Dunlop W. C. Jr. (1957) An Introduction to Semiconductors, Wiley, New York.

Evans R. C. (1946) An Introduction to Crystal Chemistry, University Press, Cambridge. (This gives information about physical properties in relation to structure.)

- Ewald P. P., Pöschl Th. and Prandtl L. (1932) The Physics of Solids and Fluids, Blackie, London.
- Flügge S. (Ed.) (1957) Encyclopaedia of Physics: 26 (1) Crystal Optics—Diffraction. 30 X-rays. 32 Structural Research.

Frank F. C. Crystal Growth, Butterworth's, London 1949, repr. 1959.

- Hartshorne N. H. and Stuart A. (1960) Crystals and the Polarizing Microscope. 3rd ed. Arnold, London.
- Herrmann K. and Krumacher A. H. (1932) Röntgenuntersuchungen an kristallinischen Flüssigkeiten IV. Z. Kristallogr., 81, 317 (19 intermediate states between solid and liquid, and diffraction effects.)

- International Tables for X-ray Crystallography (3 Vols.) Vol. III (1962) Physical and Chemical Tables. Kynoch Press, Birmingham, England.
- James R. W. (1958) The Optical Principles of the Diffraction of X-rays. 5th ed. Bell, London.

Joffé A. (1928) The Physics of Crystals. McGraw-Hill, New York.

Kittel C. (1956) Introduction to Solid State Physics 2nd ed. Wiley, New York.

Krishnan R. S. (1958) Progress in Crystal Physics, I. Viswanathan, Madras. (Many references.) Landolt-Börnstein (1955) I (4) Kristalle. Springer, Berlin.

Megaw H. D. (1957) Ferroelectricity in Crystals. Methuen, London.

Mott N. F. and Gurney R. W. (1953) *Electronic Processes in Ionic Crystals*. University Press, Oxford.

Nye J. F. (1957) Physical Properties of Crystals. Clarendon Press, Oxford.

Roberts J. K. (1947) Heat and Thermodynamics. Blackie, London.

Schmid E. and Boas W. (1950) Plasticity of Crystals (English ed.) Hughes, London.

Seitz F. (1940) Modern Theory of Solids. McGraw-Hill, New York.

Shockley W. (Ed.) (1952) Imperfections in Nearly Perfect Crystals. Wiley, New York.

Shubnikov A. V. (1958) Osnovy Optichiskoy Kristallografie. Acad. Sci. USSR, Moscow.

Wood R. W. (1948) Physical Optics. Macmillan, London.

Wooster W. A. (1938, repr. 1949) A Textbook on Crystal Physics. University Press, Cambridge, England.

Idem (1953) Physical Properties and Atomic Arrangements in Crystals. Rep. Prog. Phys., 16, 62. Phys. Soc. London.

Voigt W. (1910, repr. with addl. appendix 1928) Lehrbuch der Kristallphysik. Teubner, Leipzig.

Wasastjerna J. A. (1922) Soc. Sci. Fen. Comm. Phys. Math. 1, 38; ibid. 6, 18, 19, 21; (1923) Z. phys. Chem. 101, 193.

Zwikker C. (1954) Physical Properties of Solid Materials. Pergamon Press, London.