

The 75th anniversary of the discovery of x-ray diffraction

G. S. Zhdanov

M. V. Lomonosov State University, Moscow

Usp. Fiz. Nauk **153**, 619–631 (December 1987)

1. INTRODUCTION

Towards the end of the nineteenth century the physics of solid materials had achieved a high state of development. Methods had been worked out for studying various physical properties of solids, and a vast amount of factual material had been accumulated and was published in numerous physico-chemical handbooks. A phenomenological picture of the world had been created. It appeared that physics had entered a period in which its further development was related to striving for the "ninth decimal place." The technological working of materials (forging, stamping, casting, etc., had also achieved a high degree of perfection. Nonetheless, it was strongly felt that the situation that had developed in solid state physics was unsatisfactory. John Perry wrote about it¹: "I need not give you any more items of a long catalogue of curious properties of materials which we do not yet understand. Workmen know of and depend upon many of these actions, but nobody seems to have any clear idea as to how they take place. It is not merely that workmen temper steel and find that curious changes occur in the properties of their steel when it is altered a little in its chemical state; the philosopher and the workman are equally aware of these facts and equally ignorant of their real nature; but some workmen who deal with little mechanical contrivances make use in their trades of certain properties of brass and iron and steel which the philosopher is quite ignorant of, and it is possible that an observing workman who knows a little of chemistry and physics may discover the key to all the mass of hitherto unexplained facts which I have indicated."

Let us take another example. In the middle of the 19th century the ironclad ship appeared; it was invulnerable to bronze cannon, which were quickly replaced by steel cannon. It would appear that the steel compositions were selected, the metallurgical difficulties were overcome, and a batch of cannon was turned out that satisfied the requirements of the artillery. However, some cannon for some unknown reason blew up with the first shot, injuring the gun crew. When this happened they said "The steel did not accept the hardening." In 1864 the young metallurgist D. K. Chernov² started to work at the Obukhovskii factory in St. Petersburg; he had discovered the existence of two temperature points, which subsequently became known as the "Chernov points." If a gun barrel was heated below the first Chernov point the steel indeed did not accept the hardening. Heating above the second Chernov point gave the steel a coarse-grained structure, which was accompanied by a decrease in strength. The work of Chernov made it possible to organize in Russia the manufacture of steel cannon of high quality. As a tribute to his scientific achievements, D. K. Chernov was named the "father of metallography" at the 1900 world exhibition in Paris. Optical metallography certainly provides a great deal of information, making it possible to study the microstructure of metals and alloys at a magnification up to 2000 \times . It was observed that when steel was hardened a martensite phase

appeared, and this phase was responsible for the high strength of the hardened steel. After the death of D. K. Chernov (1921) it was found with the aid of x-ray diffraction that martensite is a highly supersaturated solid solution of carbon in a low temperature modification of iron—a ferrite. The unit cell of martensite becomes tetragonal with a ratio of axes that depends on the concentration of carbon in the steel. The atomic structure of martensite is highly distorted, and its specific volume is considerably greater than that of austenite, from which it is formed, or of ferrite. As a result, large internal stresses and phase hardening are produced in the hardened steel. These factors cause the high strength of the hardened steel.

The end of the 19th century saw a number of great discoveries in physics (cathode rays, radioactivity, x rays). W. Roentgen, who had discovered x rays in 1895, was always a very careful experimenter, who refused to make hypotheses. The only exception that he made was in the case of x rays, which, he hypothesized, were longitudinal vibrations of the ether.³ This turned out to be wrong.

2. THE PRE-HISTORY OF LAUE'S DISCOVERY

At the beginning of the 20th century conditions were created at the University of Munich that were favorable for Laue's discovery. At this time the institute (department) of experimental physics was headed by W. Roentgen and the department of theoretical physics was headed by A. Sommerfeld, who had created an internal experimental laboratory for the purpose of relating theory with experiment. The positions of assistant were shortly thereafter filled by the eminent theoretician P. Debye and W. Friedrich, the job of the latter being the experimental verification of the theory of x rays. In 1909 M. Laue, who was a student of Planck and a physicist with broad interests, began to work with Sommerfeld. In 1911, at the suggestion of Sommerfeld, who was the editor of a five-volume encyclopedia of mathematical sciences, Laue began to write the chapter on wave optics, in which he analyzed diffraction in one- and two-dimensional lattices. The institute of mineralogy was headed by the great scientist P. Groth. P. Ewald, who studied with Sommerfeld for two years, asked the latter in 1910 to take him on as a doctoral candidate. Sommerfeld agreed, and gave him a sheet of paper with 12 topics, which covered a broad range of problems. At the end of the paper was written the problem "Find the optical properties of anisotropically arranged isotropic oscillators," which Sommerfeld read with an apology, since he did not know how to approach the problem. Ewald immediately chose the last problem on the list. Ewald's problem required that he find the answer to two questions. The first had to do with the formation of the index of refraction and its frequency dependence. In other words, how does the scattering of elementary spherical waves by the resonators change the velocity c of the wave in vacuum to the velocity q in the medium? The second question concerned how

refraction and reflection arise at the surface of the medium.

The first question was analyzed with the use of the dispersion theories of Lorentz and Planck in the kinematical approximation, where the interaction of the elementary scattered waves with the primary wave is neglected. This approach described the wave field in the medium, but it did not deal with the phenomena of refraction and reflection, and the question of the "primary wave" remained open. Planck and Lorentz considered an unordered system of resonators which scattered the light isotropically, and the medium was characterized by a single value of the index of refraction. The idea of the work suggested by Sommerfeld was the following. Assume that the resonators are arranged in an orthogonal lattice. Will the dispersion and the refraction of this medium be analogous to that of a crystal, and in particular will there be birefringence, or must the answer be sought in an intrinsic anisotropy of the resonators? Ewald worked for two years on his dissertation; he used a complicated mathematical apparatus, obtained a general solution, and brought it to a form that would permit numerical calculations. On the advice of Groth, Ewald carried out model calculations for a crystal of anhydrite CaSO_4 and in spite of the crudity of replacing six atoms with a spherical resonator, he obtained qualitative agreement with experiment. The general result obtained by Ewald was at the time astonishing. It turned out that the refractive index of an infinite crystal, like the characteristic frequencies of an oscillatory system, is determined by the free vibrations of the system, which do not depend on the external perturbation. In the half-space of the crystal, the incident wave must be screened from the interior by the action of the boundary in order not to interfere with the establishment of the free vibrations of the system.⁴ Ewald wrote his dissertation in January 1912 and decided to discuss it with Laue.

3. GENESIS OF THE IDEA

Laue brought Ewald to his home after first meeting in a park, where Ewald stated the problem that he had been working to solve. To his surprise, he saw that Laue had no knowledge of the problem. Ewald explained that in contrast to the existing theories of dispersion he had arranged the resonators on the sites of a lattice, since it was generally believed that crystals have an internal regularity. This idea seemed to be new to Laue, and he asked what the distance between the resonators might be. The answer was—the order of $1/1000$ the wavelength of light, but for my problem the exact value is unimportant. On the rest of the way Ewald explained the method he used to solve the problem. That evening Laue listened to Ewald inattentively and again became interested in the spacing between the resonators. Finally he asked what would happen if waves of a considerably shorter wavelength passed through the crystal. Ewald found in his dissertation the appropriate formula that contained the result of a superposition of elementary waves emitted by the resonators independently of the wavelength, and which was valid also for short wavelengths, and he said "In a few days I present my dissertation, and I would like you to participate in a discussion of the formula, a copy of which I will leave with you." Ewald left Laue's apartment with the realization that his effort to discuss the problem that interested him was unsuccessful.

4. INTUITION AND DOUBT

Laue did not treat diffraction in a three-dimensional lattice in his chapter in the *Mathematical Encyclopedia*, but in his Nobel Lecture in June of 1920 he said that "My optical intuition told me that under certain conditions spectra must be produced." At the end of 1911 the Christmas (sic) holidays approached; the physicists usually spent these in the Alps. While skiing Laue was able to discuss his idea with Sommerfeld, Wien, and others. The results of the discussions were not favorable because of the interference caused by the thermal motion in the crystals. From estimates obtained from the reststrahlen in rock salt the amplitudes of the thermal vibrations of the chlorine atoms should be about 0.75 \AA , whereas the estimate of the wavelength of the x rays was $0.4\text{--}0.6 \text{ \AA}$, i.e., less than the amplitudes of the thermal vibrations of the atoms, a situation that should result in the loss of the phase relationships in the scattering by the resonators. The opposition was so strong that Sommerfeld did not permit his assistant, W. Friedrich, to carry out the experiment. The situation that prevailed with diffraction in crystals was then discussed by Laue at the Café Lutz in Munich, at the "Physics Table," where the colleagues at the university gathered. The general consensus was that experiment was more reliable than any theory, and therefore the experiment should be done.

5. THE DISCOVERY OCCURS

At this time P. Knipping, an assistant of Planck, had completed his dissertation and he volunteered to help W. Friedrich in his experiments and to assemble in his spare time the apparatus for carrying out the experiment. In the first attempt the cassette holding the photographic plate was placed in front of the crystal, by analogy with an optical reflecting grating—the result was negative. In the second attempt the plate was placed behind the crystal, as in an experiment with diffraction by transmission. The developed photographic plate showed clearly the first x-ray diffraction pattern (Fig. 1) from a crystal of copper sulfate, the first

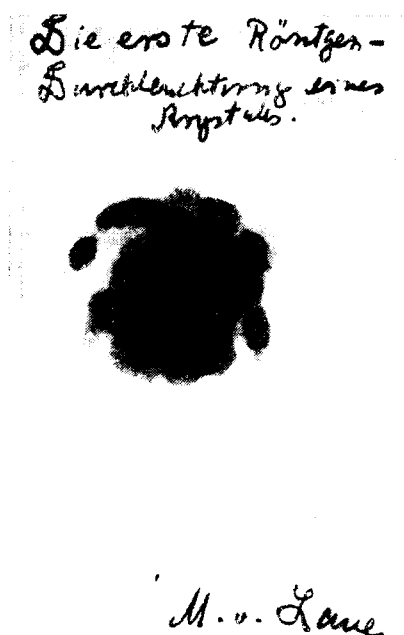


FIG. 1. The first x-ray diffraction photograph.

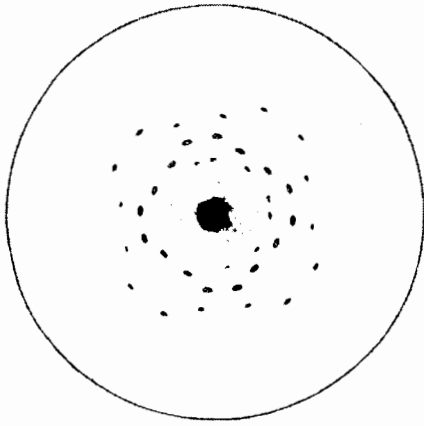


FIG. 2. X-ray diffraction pattern of a zincblende crystal.

crystal that came to hand. Laue learned of the positive result of the experiment in the Café Lutz, and he hurried to the institute. On his way along the street, as Laue writes in his autobiography, he was illuminated by the idea that to describe three-dimensional diffraction it was necessary to add a third equation. The Laue equations have the form

$$(a_i, \mathbf{k} - \mathbf{k}_0) = h_i, \quad i = 1, 2, 3, \quad (1)$$

where a_i are the lattice basis vectors, $|\mathbf{k}_0| = |\mathbf{k}| = 1/\lambda$ are the wave vectors of the primary and diffracted waves, λ is the wavelength, and h_i is the harmonic index of the spectrum of rays diffracted by the crystal.

Over a period of several weeks the experimental method was considerably improved, and for a zincblende crystal the symmetrical "lauegram" shown in Fig. 2 was obtained. Laue wrote Eq. (1) in a quantitative form and obtained agreement with the experiment. This day he called the decisive day of his life.

6. TWO "HARES." X-RAY SPECTROSCOPY

In the experiment of Laue the crystal could be regarded as the apparatus—a natural diffraction grating for studying spectra. X-ray spectroscopy—the first "hare" and a new field of science—was founded by W. H. Bragg (the father), who constructed the first x-ray ionization spectrometer for

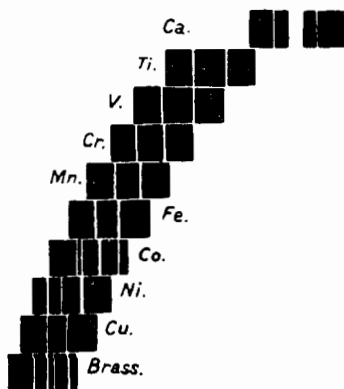


FIG. 3. X-ray spectra obtained by Moseley for the elements from Al to Au.

precise measurements of x-ray spectra and obtained the characteristic x-ray spectra for a number of heavy metals. The work was extended by Moseley in 1913 at the Rutherford laboratory in Manchester,^{5a} and in 1914 at the Townsend laboratory at Oxford.^{5b} With the use of a photographic method, Moseley obtained x-ray spectra of the elements from Al to Au and established their systematic shift (Fig. 3). The conclusions of the second of his papers have entered into the history of physics:

1. Each element from aluminum to gold is characterized by an integer Z which determines its x-ray spectrum.

2. The atomic number Z of an element is equal to the number of positive electric charges in the nucleus of the atom.

3. The atomic numbers of all the elements from Al to Au are determined if it is assumed that for Al, $Z = 13$.

4. The sequence of atomic numbers coincides with the sequence of atomic weights, except in cases where the latter do not agree with the variation in the chemical properties.

5. The elements are arranged in a sequence of all the integers from 13 to 79 except for three cases corresponding to as yet undiscovered elements.

6. The frequency of a line of the x-ray spectra is

$$\nu = A(Z - b)^2, \quad (2)$$

where A and b are constants. Formula (2) expresses Moseley's law.

The work of Moseley made it possible to create a basis for the theory of the atom and radiation; it made entirely clear the periodic system of the elements of D. I. Mendeleev, and provided an unambiguous method for the classification of the elements and for the discovery of new elements. At the present time a relative amount $\sim 10^{-9}$ to 10^{-10} of a chemical element is sufficient to identify it. X-ray spectral analysis permits the determination of the chemical composition of a substance without damage to the material. Moseley was killed in 1915 at the age of 28, fighting near the Dardanelles in the ranks of the British army.

At the same time, a crystal can be a subject for investigation. The discovery of Laue made it possible to create the method of x-ray structural analysis and opened wide the door to the previously inaccessible world of the atomic structure of matter, and marked the beginning of a new epoch in the development of natural science. This is the second "hare."

7. THE FIRST DETERMINATIONS OF ATOMIC STRUCTURES

Laue, in interpreting the x-ray diffraction pattern of a zincblende crystal, placed the atoms on the sites of a simple cubic lattice. In 1906–1910 Barlow and Pope (professor of chemistry at Cambridge, where the student Bragg (the son) studied) proposed a model for some simple cubic compounds, and distributed identical atoms according to a type of cubic close packing. From Laue patterns W. L. Bragg verified this arrangement for the simple NaCl structure, with the ions arranged like a checkerboard. Later he used the results of measurements with an x-ray ionization spectrometer constructed in 1913 by his father. A period commenced when the two Braggs—father and son—worked with inspiration day and night, each in his own field. On the recommendation of Wilson, the inventor of the cloud chamber, W.

L. Bragg studied the reflections of x rays from the cleavage plane of mica and showed that they are determined by a formula analogous to the diffraction formula for a stack of plane-parallel plates⁶:

$$n\lambda = 2d \sin \theta, \quad (3)$$

where n is an integer, d is the interplanar spacing, and θ is the angle of incidence of the primary beam on the cleavage plane. In 1913 W. L. Bragg determined the structure of zincblende, feldspar, cuprite, pyrite, sodium nitrate, and calcite. The honor of determining the structure of diamond he left to his father. In these investigations the basis of the x-ray structural analysis was completed. The war that began in 1914 caused a delay in the determination of crystal structures.

8. THE FIRST WORK IN RUSSIA

In 1885 professor E. S. Fedorov, the world-renowned crystallographer at the Mining Institute in St. Petersburg, completed his results and gave an outline of the 230 space groups that describe the complete symmetry of crystals. As the author himself wrote, "nature bows down before this creation of the armchair scientist." After the discovery of x-ray diffraction the tables of the space groups were published repeatedly outside of this country, frequently without acknowledging the name of the author, and they became the basis for the deciphering of crystal structure.

According to N. E. Uspenskii,⁷ Professor of the Physics Institute of Moscow University, P. N. Lebedev in 1910 proposed to one of his students that he obtain diffraction of x rays, and as a part of this work that he prepare, instead of the low-power ion tubes, a fundamentally new type of electronic x-ray tube using thermionic emission from a cathode heated by a current. It is difficult to say now how this work would have turned out, since in 1911 about 400 progressively oriented professors and instructors, including P. N. Lebedev and G. V. Vul'f,²⁾ left the university as a sign of protest against the reactionary politics of the Czar's minister, L. A. Kasso. By Kasso's decree the rector of the university, and two of his deputies were removed from office. Police were brought to the university to suppress the student rebellions. P. N. Lebedev and G. V. Vul'f lost their laboratories and the possibility of pursuing their scientific and teaching activities. It may be that Russia lost the honor of being the native land of the scientific discovery made by Laue in 1912 and the great technological achievement—the invention of the electronic x-ray tube (Coolidge, 1913). Lebedev died in 1912.

After leaving Moscow University, G. V. Vul'f found a temporary shelter at the A. L. Shanyavskii Peoples University in Moscow. He had been keeping up on the discovery of Laue, and he developed a great interest in investigations of crystal structure; he published in 1913 alone eight scientific and popular papers on the topic of interference of x rays in crystals. In December of 1912 at a meeting at the Moscow Polytechnic museum, G. V. Vul'f formulated the law of reflection of x rays, and in February 1913 he submitted to the editor of the journal *Physikalische Zeitschrift* a paper "Roentgenograms of Crystals" in which formula (3) was derived from the Laue equations (1). G. V. Vul'f showed that the diffraction spectrum of a crystal is formed by a combination of rays that are reflected not only by the outermost

plane, but also by the internal families of planes.^{8,9} Formula (3), which was established empirically by W. L. Bragg, was derived theoretically by G. V. Vul'f, and should be more properly called the Vul'f-Bragg formula.

9. THE SOURCES OF SOVIET X-RAY DIFFRACTION

After the Great October Revolution G. V. Vul'f in 1917 returned to Moscow University¹⁰ and began lecturing at the natural science division of the Physico-mathematical department, and included a course "X-Ray Methods of Investigation." Under his direction the Mineralogical Institute set up an x-ray laboratory and proceeded with work on x-ray diffraction (the structure factor, the structure of sodium chlorate, x-ray screens). At the university G. V. Vul'f enjoyed great authority and popularity. He was developing the idea of creating in the Physics department of the university a department of x-ray analysis. After the untimely death of Vul'f (1925) this department, the first in the world, was organized. A group of students was selected for the department, and in 1927 S. T. Konobeevskii began lectures on x-ray structural analysis. The first graduation of specialists occurred in 1930.

As early as 1918, on the initiative of V. I. Lenin, a grandiose plan was brought into existence for the development of science in Soviet Russia. In spite of civil war, intervention, blockade, and the post-war devastation, A. F. Ioffe organized in 1918 a physico-technical division at the institute of Roentgenology and radiology in Petrograd. In 1903–1906 Ioffe was a trainee and an assistant in the laboratory of Roentgen at Munich University, and in 1912 he was in Munich and happened to witness the discovery of Laue. In 1920 in Moscow at the first Russian conference of scientific metallurgists, a paper was presented by A. F. Ioffe, M. V. Kirpicheva, and M. A. Levitskaya on their discovery of asterism. On the diffraction patterns of plastically deformed crystals they observed instead of the diffraction spots radially smeared bands, which were explained by the curving of the atomic planes of the crystal when it was bent. At the same time in Moscow another investigation was carried out that entered into the history of x-ray diffraction. N. E. Uspenskii and S. T. Konobeevskii discovered the existence of crystal orientations in rolled metals and they determined these orientations.

The latter part of the 1920s and the 1930s was a period in which the theory was established, methods were worked out, and new areas of application of x-ray diffraction were discovered. The number of x-ray structural laboratories in institutes, industry, and universities grew rapidly. In addition to Moscow and Leningrad, new scientific centers for x-ray diffraction arose in the Urals, the Ukraine, in Belorussia, and other Soviet republics. The first All-Union conference on x-ray diffraction was held in 1936 in the Dnepropetrovsk Physicotechnical Institute. Since 1948 such conferences have been held every three years at the Leningrad Commission on x-ray diffraction, Academy of Sciences of the USSR. In 1954 the Soviet Union joined the International Union of Crystallography as the most prominent country in the world in the field of crystallography. At the International Congress on Crystallography that was held in 1966 in Moscow at the Moscow University, the Soviet delegation (~2000 people) was larger than the total number of participants

from other countries (~1500). A sign of recognition of the role of Soviet roentgenography was the election of Academician N. V. Belov as the president of the International Union of Crystallography.

10. THREE DIMENSIONAL DIFFRACTION AND X-RAY FOURIER OPTICS

The geometry of three-dimensional diffraction is described by the vector equation

$$\mathbf{k} - \mathbf{k}_0 = \mathbf{H}, \quad (4)$$

where \mathbf{k}_0 and \mathbf{k} are the wave vectors of the primary and diffracted beams, $|\mathbf{k}_0| = |\mathbf{k}| = 1/\lambda$, \mathbf{H} is a vector of the reciprocal lattice, whose basis vectors are \mathbf{a}_i and are related to the basis vectors \mathbf{a}_i of the crystal lattice by the Kronecker relation

$$(\mathbf{a}_i, \mathbf{a}_j^*) = \delta_{ij} \quad (i, j = 1, 2, 3). \quad (5)$$

Figure 4 shows a vector triangle OCE . The end of the vector \mathbf{k}_0 rests on the origin O of the coordinate system of reciprocal space, and its other end C is the center of the reflection sphere (the Ewald sphere), which has a radius $1/\lambda$. From formula (4) one obtains the selectivity of three-dimensional diffraction, since the vector \mathbf{H} , which emanates from O , must, for diffraction to occur, touch another reciprocal lattice point E and also rest on the Ewald sphere. For an arbitrary point C this requirement is not satisfied. To observe diffraction one must rotate the crystal around the point O (the rotating crystal method) so that the reciprocal lattice points will intersect the stationary Ewald sphere, or else one must vary the wavelength or use a continuous x-ray spectrum (the Laue method).

The Laue equations (1) are derived by scalar multiplication of both sides of (4) by the basis vectors \mathbf{a}_i of the crystal, while the Vul'f-Bragg formula (3) is obtained by projecting the legs of the triangle OCE onto its base ($|\mathbf{H}| = 1/a$).

Let us characterize the structure of an object by the electron density distribution function $\rho(\mathbf{r})$, for which we write two mutually related Fourier integrals

$$F(\mathbf{H}) = \int_{-\infty}^{+\infty} \rho(\mathbf{r}) e^{-2\pi i(\mathbf{H}\mathbf{r})} dV_{\mathbf{r}}, \quad (5a)$$

$$\rho(\mathbf{r}) = \int_{-\infty}^{+\infty} F(\mathbf{H}) e^{2\pi i(\mathbf{H}\mathbf{r})} dV_{\mathbf{H}}, \quad (5b)$$

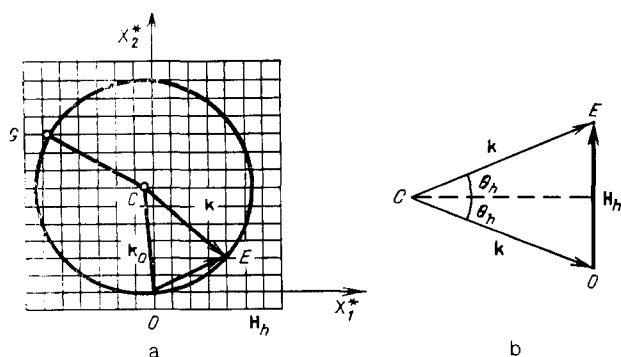


FIG. 4. a) Superposition of the reciprocal lattice of a crystal with the sphere of reflection. b) Vector triangle (formula (4)) determining the conditions for selective reflection.

where $dV_{\mathbf{r}}$ and $dV_{\mathbf{H}}$ are elements of volume in \mathbf{r} - and \mathbf{H} -space, $F(\mathbf{H})$ are the coefficients of the Fourier expansion of the density function and are determined from the intensities of the x-ray reflections

$$I(\mathbf{H}) \sim |F(\mathbf{H})|^2. \quad (6)$$

Formula (5a) describes the Fourier analysis of the density function, which is carried out automatically in an x-ray diffraction experiment, and formula (5b) is the Fourier synthesis—a mathematical summation, carried out by computer. For an object with a periodic structure (a crystal) the Fourier integral becomes a Fourier series. The equations of x-ray Fourier optics (5a) and (5b) provide an elegant solution to the problem of determining the atomic structure of crystals. It follows from formula (6) that to make this determination it is necessary to find the signs or the phases of the coefficients $F(\mathbf{H})$. The theory of structural analysis shows that the *phase problem* is solved if the diffraction maxima do not overlap; experimentally this condition is not satisfied. Under these conditions one uses *direct methods* for determining the phases—theoretical and experimental methods (the heavy-atom method, isomorphous substitution).

11. SOME ILLUSTRATIONS

Figure 5 shows a projection of the electron density in the square molecule of Pt-phthalocyanine. The crystal structure was deciphered by the heavy-atom method. Figure 6 shows the projection of the difference $F_{\text{exp}} - F_{\text{calc}}$ between the experimental and calculated Fourier syntheses of the electron density of a crystal of urea, where F_{exp} are experimentally determined Fourier coefficients at 292 °C, and F_{calc} are coefficients calculated for a model structure with stationary

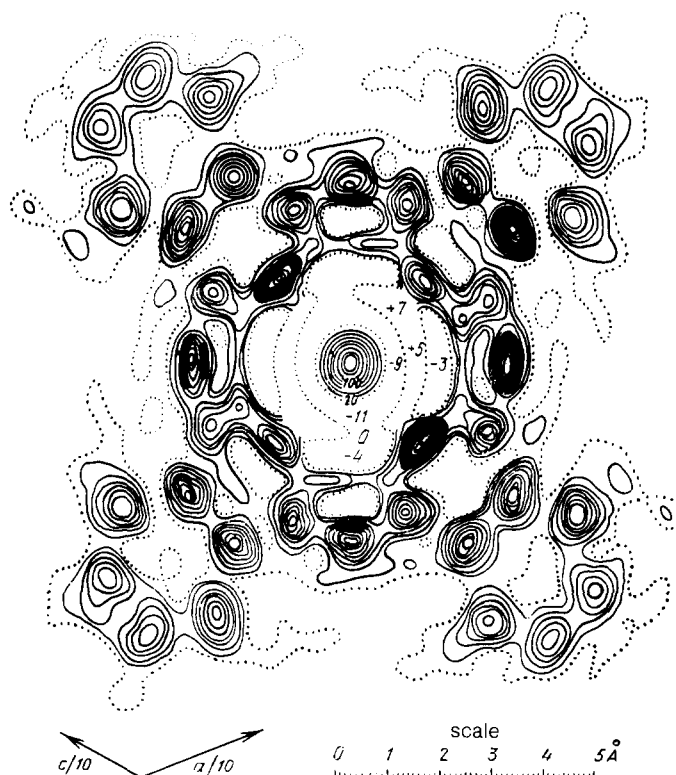


FIG. 5. Projection of the electron density in the Pt phthalocyanine molecule (at an angle of 26.5° to the plane of the molecule).

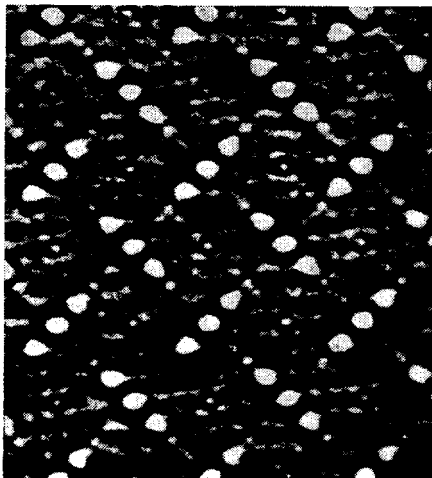


FIG. 6. Projection of the difference Fourier synthesis of the electron density of a urea crystal, showing the thermal vibrations of the atoms in the urea molecules.

atoms. The dark rings and the spots around the white circles, where the atoms were located before the subtraction, show the thermal motion of the atoms in the urea molecule. This method, which has been worked out in recent investigations, allows a determination of the thermal vibration tensors of the various atoms in molecules and makes it possible to study their dynamic properties. A study of diffuse scattering of x rays in reciprocal space and of the regions surrounding

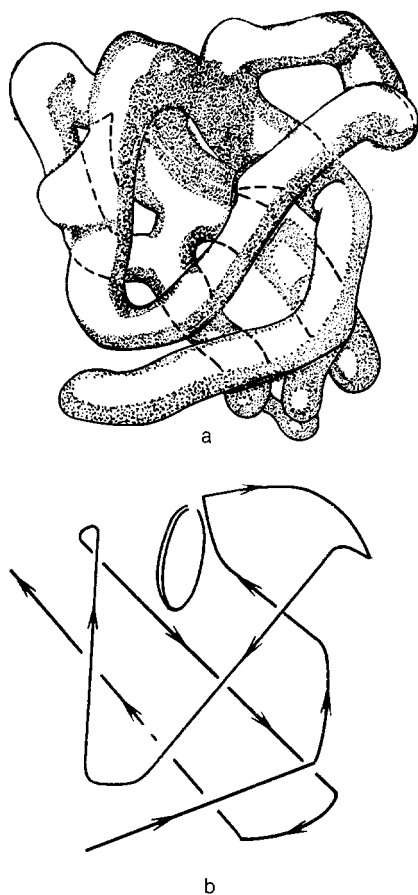


FIG. 7. Topology of a hemoglobin molecule. a) Three-dimensional representation. b) Schematic diagram (the disk is the gene, containing the iron atom).

the reciprocal lattice points provides the means to investigate the dynamics of crystals (the phonon spectra), and to measure by purely x-ray diffraction means the elastic constants of crystals and their Debye temperatures.

At the present time we know the atomic structures of many simple and complex compounds, metals, alloys, organic compounds, and the most complex of materials—objects of living nature: proteins (hemoglobin, pepsin, etc), the material of heredity—the double helix of DNA—and viruses. The structure of the hemoglobin molecule is shown in Fig. 7. Hemoglobin is a transport protein which gives the red color to blood, and whose purpose is to supply oxygen to all the tissues of the organism. All proteins are made up of 23 small groups of atoms, amino acid fragments, that are bound together and form a linear structure (a biopolymer). In each protein the set of amino acids and their sequence is rigidly fixed. If even one link in the chain is destroyed the function of the protein is disrupted and the organism acquires a specific illness—a molecular illness. The molecular weight of hemoglobin is about 16 000, one of the largest of the proteins. The hemoglobin molecule contains some two thousand atoms, not counting the hydrogen atoms, and to depict the structure at the atomic level is an extremely complicated matter. Figure 7a shows the topology of the molecule, in which a polypeptide chain forms a complicated, but at the same time a rather rigid, structure, whose shape is supported by intramolecular hydrogen bonds. Figure 7b shows a diagram of the hemoglobin molecule; the round disk located within the molecule is the gene, which contains the iron atom. Under the action of the appropriate enzyme in the lungs the molecule readily opens up and allows the adsorption of an oxygen atom on the iron atom. In the tissues, where the hemoglobin goes, the oxygen is desorbed, and a molecule of carbon dioxide is taken up and removed by reverse transport of the hemoglobin to the lungs.

In Fig. 8 a is shown the structure of the DNA double helix, which is also held in this configuration by hydrogen bonds. Each DNA helix is built up of four types of nucleotides (Fig. 8b) and the two helices are not completely identical, but are mutually complementary: From one of them one can automatically construct the other. This process occurs when cells divide, and in each of the two daughter cells that are formed identical double helices are reproduced. The individual part of the DNA chain that is responsible for the synthesis of a particular protein (the individual cells can synthesize up to 700 different proteins), is called the gene. In each cell of a specific organism the set of genes is identical, even though the functions of the cells are different. In the DNA helices is recorded all the information for the development of the organism from the original egg cell to the mature organism, and this information is then passed on to the descendants. The structure of the “inheritance” material of the DNA was determined by x-ray diffraction.

12. CONCLUSIONS

As Laue's discovery becomes more distant in time, the revolution that he brought about in the understanding of the structure and microscopic properties of the world of atoms and their aggregates around us becomes all the more significant. Laue's discovery placed the entire field of natural science on a strong foundation of atomic concepts. New con-

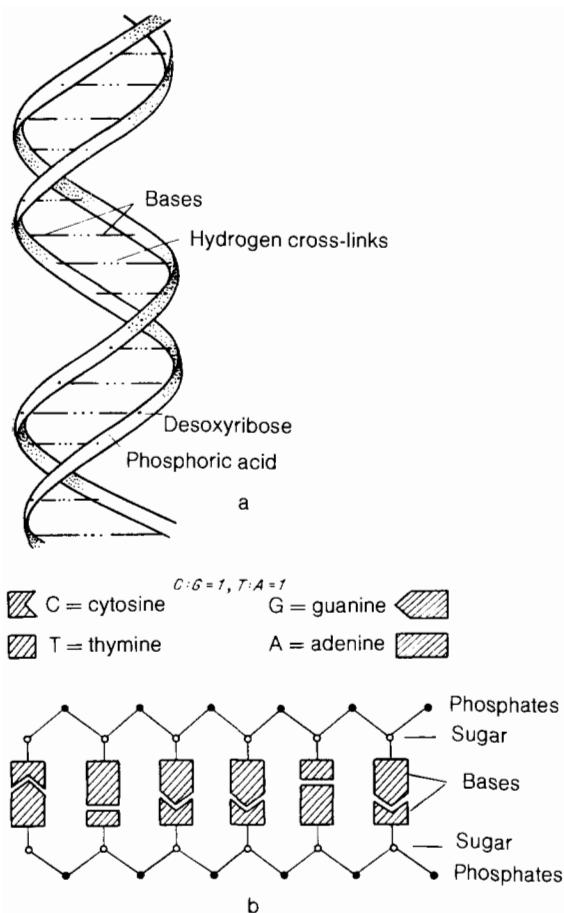


FIG. 8. a) Diagram of the DNA double helix. b) Diagram of the structure of part of the double helix of the DNA molecule.

cepts appeared in the scientific lexicon and took on concrete meaning: the ideal and mosaic crystal, the real crystal, structural defects, short-range and long-range order, the superstructure, the x-ray-amorphous state, incommensurate structures, interstitial phases, and many others. X-ray diffraction has characterized metastable states that frequently appear in solids because of the low rate of diffusion at rather low temperatures. The very first stages of advanced precipitation of submicroscopic plates of atomic thickness (Guinier-Preston zones) and chains of sequential transitions through the metastable phases $\alpha \rightarrow \beta' \rightarrow \gamma' \rightarrow \delta$ have been elucidated, revealing the meaning of the Gay-Lussac-Ostwald stage rule in solids. The form of this chain even for similar alloys is diverse, and, as x-ray analysis shows, it is impossible to predict it beforehand. Metastable states are extremely widespread and they have interesting physical properties; examples are quenched steel, metastable superconducting alloys; and diamond, which is the hardest material under ordinary conditions, is metastable relative to graphite. Therefore the synthesis of diamond requires high temperatures and pressures, where the thermodynamic balance shifts in favor of diamond. It is difficult to overestimate the contribution of x-ray diffraction to the theory of phase transformations, and the end of structural investigations in this field of solid state physics is not yet in sight.

Of great practical importance is x-ray phase analysis, carried out by comparing a Debye (sic) pattern of a sample with a set of standard x-ray diffraction patterns. At the pres-

ent time, when the bank of standards exceeds 50 000 and is increased by 1–2 thousand a year, this comparison, which is in principle a simple problem, requires automation with the use of a computer. It became necessary to develop a mathematical theory of the strategy for (the first stage) a preliminary search with the use of a vector in a space of a large number of measurements, and then (the second stage) a theory for estimating the reliability of the results, especially for the case where the sample contains not just one, but several phases. For this purpose, in the “FAZAN” system a packet of 10 programs were assembled, containing more than 5000 operators for processing the digital information with a capacity of $3 \cdot 10^6$ numbers. The “FAZAN” system is of interest to a variety of institutions (in geology, the search for new deposits of mineralogical materials, in chemistry, glass fibers, the car factory AvtoZil, the institute of forensic expertise, and others). An unusual application has been the study of the phase composition of the remains of a helmet found on the Kulikov battlefield.

In previous years there has been a radical change in the apparatus and the calculational resources on which x-ray analysis is based. The modest ionization x-ray spectrometer of W. H. Bragg has been transformed into an extensive family of computer-controlled, automated, and electronics-intensive x-ray diffractometers for single crystal and polycrystalline materials for various practical applications. The larger computers are used for the primary analysis of the experimental data (the diffraction patterns of proteins frequently contain more than 100 000 reflections) and subsequent calculations involving Fourier syntheses and the automated analysis and imaging of the structure of complex objects. To reduce the experimental time, sources with a high primary x-ray intensity are used (tubes with rotating anodes, synchrotron radiation in the x-ray wavelength range); also used are position-sensitive detectors, which permit the simultaneous detection of the position and the intensity of the x-ray diffraction pattern at more than 60 000 points, with recording of the information obtained in a computer and transfer of the information to a display.

Work in the field of x-ray diffraction has been marked by high scientific rewards. The first Nobel prize in physics was awarded to Roentgen (1901) for discovering the ray that bears his name. Laue became a Nobel laureate (1914) for the discovery of x-ray diffraction; also included are W. H. Bragg and W. L. Bragg (1915) for studying the structure of crystals, M. Perutz and J. Kendrew (1962) for determining the structure of hemoglobin, J. Watson, F. Crick, and M. Wilkins for determining the structure of the double helix of DNA and D. Hodgkin for determining the structure of vitamin B₁₂. The State prize and the Lenin prize were awarded to N. V. Belov for the structure of silicates, and the State prize was awarded to a group of investigators for studying the crystal chemistry of ferroelectrics, and others.

The human mind will continue tirelessly to penetrate into the secrets of the structure and properties of matter and into the practical requirements of mankind for the improvement and development of new materials, whose potential for synthesis on the basis of the Mendeleev periodic system of the elements is unlimited. In technology 8- to 10-component alloys are already in use, in organic chemistry about eight million compounds have been synthesized, and the number of syntheses of biopolymers is difficult to estimate. Carrying

out this program will involve the application and development of methods of x-ray diffraction, for the discovery of which Laue will always be gratefully remembered by mankind.

¹The "hare" refers to the Russian saying "to kill two hares with one blow."

²This is the crystallographer Wulff mentioned in the western literature. In Russian his initials are Yu. V., viz. Ref. 9.

¹J. Perry, *Practical Mechanics*, Cassel and Co., London, 1981.

²People of Russian Science, [in Russian], Gostekhizdat, M., 1948, Vol. 1, p. 950.

³W. K. Roentgen, Eine Neue Art von Strahlen, Physikalische-Medizinische Gesellschaft, Wurtzberg (1896) [Russ. transl. Gosudarstvennoe Izdatel'tsvo Tekhniko-Teoreticheskoi Literatury, 1933, p. 42].

⁴*Fifty Years of X-ray Diffraction*, (ed.) P. P. Ewald, N. V. A. Oosterhoek's Uitgeversmaatschappij, Utrecht, 1962.

⁵(a) H. G. J. Moseley, *Philos. Mag.* **26**, 1024 (1913). (b) H. G. J. Moseley, *Philos. Mag.* **27**, 703 (1914).

⁶W. L. Bragg, *Nature* **90**, 410 (1912).

⁷N. E. Uspenskii, *Pulsed (Superfast) Methods in X-ray Diffraction*. Pravda, M., 1949, p. 3.

⁸G. W. Wulff, *Phys. Z.* **14**, 217 (1913).

⁹Yu. V. Vul'f, *Selected Papers on Crystal Physics and Crystallography*, [in Russian], Gostekhizdat, M., L., 1952, p. 137.

¹⁰The Annals of Moscow University, 1755-1979, [in Russian], published by Moscow University, 1979, p. 178.

Translated by J. R. Anderson