DIRECT METHODS IN X-RAY CRYSTALLOGRAPHY

Elmurotova Dilnoza Baxtiyorovna1,
Esanov Shaxzod Shermat o'gli 2,
Sodiqov Farxod Husan o'g'li 3,
Ibrohimov Suhrob Vahob o'g'li 4
Tashkent State Medical University1,2,
Tashkent State Technical University Named After I.A. Karimov 3,4

Abstract
The paper considers the history of the creation of a direct method of X-ray structural analysis. There are 230 combinations of symmetry elements that a crystal structure, which are called space groups. The Bragg X-ray diffraction scheme, the structure of a sandwich complex of a mercury-containing macrocycle with borane, and the atomic scattering curves for a point atom, a stationary atom, and an atom undergoing thermal vibrations are studied.

Keywords: X-ray structural analysis, combination, element, space, structure, scheme, diffraction, atom, scattering, vibrations.

Introduction

In 1953, two American mathematicians, Jerome Karl and Herbert Hauptman, published a paper on the theory of direct methods in X-ray structural analysis. Thanks to these methods, X-ray structural analysis is the most powerful method for determining the structure of molecules in crystals. To date, this method has studied the structure of more than 200,000 molecules. In 1985, both mathematicians received the Nobel Prize in Chemistry for the development of direct methods.

In 1669, the Danish naturalist Niels Stensen published his work "On the Solid Naturally Contained in the Solid." This year can be considered the birth date of crystallography - the science of crystals. Stensen's work contains, in particular, the law of constancy of angles: crystals of different shapes of the same substance (mineral) have constant angles between the corresponding faces.

Hauy's law, discovered in 1783, are a consequence of the peculiarity of the internal structure of crystals - three-dimensional periodicity in the arrangement of material particles. This is how a crystalline body differs from an amorphous one. The first to express such a hypothesis was the French abbot, professor of mineralogy and crystallography René Juste Hauy . He suggested that a crystal is like a masonry of many tiny identical bricks, which he called integral molecules. In 1848, the French engineer Auguste Bravais , replacing the "integral molecules" with points, arrived at the concept of a spatial lattice as a geometric image reflecting the three-dimensional periodicity of a crystal. In 1855, he derived 14 types of spatial lattices.

The lattice is characterized by three vectors (translations), when shifted by which the structure coincides with itself. A parallelepiped constructed on three translation vectors is called a lattice cell. If we know the arrangement of atoms inside the cell, then, by "multiplying" the cell by translations to the entire volume of the crystal, we obtain the entire crystalline structure.

Therefore, it is said that the crystal structure has translational symmetry. In addition to translational symmetry, other types of symmetry are possible in crystals. The structure can be combined with itself by rotations, reflection in a plane, reflection at a point - inversion (i.e. an atom with coordinates x, y, z will transform into an atom with coordinates -x, -y, -z) or by successive execution of such transformations (for example, rotation with inversion, reflection with translation).

There are a total of 230 combinations of symmetry elements that a crystal structure can have. They are called space groups, because from the point of view of algebra, combinations of symmetry elements form a mathematical group. Space groups were discovered in 1890 independently and almost simultaneously by the Russian crystallographer Evgraf Stepanovich Fedorov (that is why in Russia they are often called Fedorov groups) and the German mathematician Arthur Schönflies. Due to symmetry, we need to determine the coordinates not of all the atoms in the cell, but only of some of them, which are called the independent part of the cell. The coordinates of the remaining atoms in the cell will be uniquely determined if we "multiply" the atoms of the independent part by the symmetry elements of the crystal.

The birth date of X-ray structural analysis can be considered to be 1912, when the German physicist Max Laue and his colleagues discovered the effect of X-ray diffraction as they pass through a crystal. In 1914, the English scientist William Lawrence Bragg proposed a visual interpretation of X-ray diffraction in a crystal as reflection from a series of nodal planes of the crystal (Fig. 1).

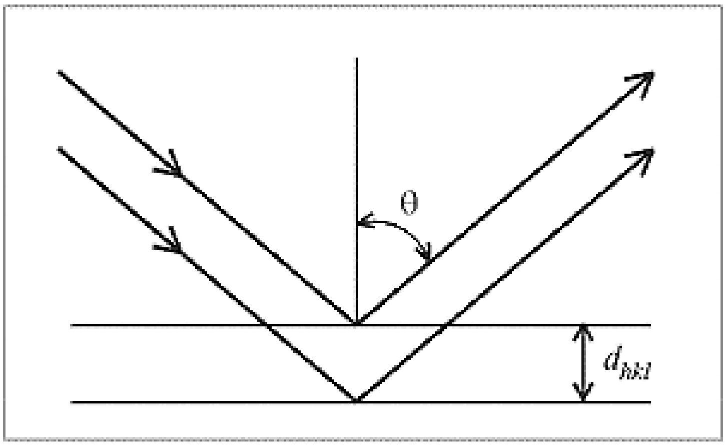

Fig.-1. Bragg X-ray diffraction diagram (d_{hkl} – interplanar distance; θ – angle of reflection from planes h, k, l).

A nodal plane is a plane that passes through three lattice nodes. Any nodal plane that is parallel to a plane passing through the origin of coordinates

Web of Technology: Multidimensional Research Journal
webofjournals.com/index.php/4

$$hx + ky + lz = 0$$

will have an equation

$$hx + ky + lz = p$$

where p is a constant.

Three indices, i.e. three mutually prime (irreducible) numbers h, k, l, characterize a whole series of nodal planes parallel to each other. Therefore, this series of planes is designated as (hkl).

Rays reflected by successive planes will not cancel each other out only if the difference in their paths is an integer number of wavelengths. From this, Bragg derived the relationship

$$2d_{hkl} \cdot \sin\theta = n \cdot \lambda.$$

This same equation was independently derived by the Russian crystallographer Georgy Viktorovich Wulf and is therefore called the Wulf– Bragg equation . It determines the angles at θ which reflection from a given series of planes (*hkl*) can occur.

The integer n is called the order of reflection. The reflections of the series of planes (*hkl*) are assigned indices *nh* , *nk* , *nl* . Therefore, the indices of reflection are not required to be mutually prime numbers.

The directions and intensities of the reflected rays are completely determined by the structure of the crystal. The X-ray structural method for determining the structure of matter is based on their analysis.

Only in this case we need to solve the inverse problem – using the known directions and intensities of the reflected X-rays, reconstruct the arrangement of atoms in the crystal.

In this way, complete information about the geometry of the molecules that make up the crystal is obtained. In many cases, X-ray structural analysis is the only method by which the structure of a molecule can be established, for example, as in Fig. 2.

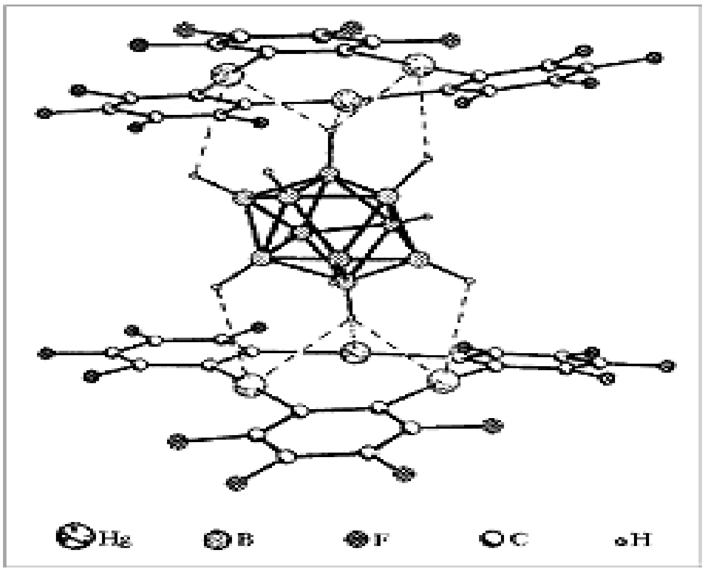

Fig.-2. Structure of a sandwich complex of a mercury-containing macrocycle with borane .

X-ray structural analysis is divided into two stages. In the first stage, firstly, the parameters of the crystal lattice and its symmetry are determined; secondly, the coordinates of the atoms in

Web of Technology: Multidimensional Research Journal
webofjournals.com/index.php/4

Web of Technology: Multidimensional Research Journal
webofjournals.com/index.php/4

the cell are found. Determining the cell parameters is usually a trivial task. There are various formulas (depending on the method of photographing the crystal) by which they are calculated if we know the angles of the rays reflected from the crystal. When the cell parameters are known, we can make initial assumptions about the possible symmetry elements of the crystal structure.

Each symmetry element, except for the inversion center, imposes certain restrictions on the unit cell parameters. For example, if the structure has an axis of symmetry, then the two angles of the unit cell are equal to 90 degrees. As symmetry increases, the number of restrictions increases.

In accordance with these restrictions on the values of the cell parameters, 230 space groups are divided into 6 classes, which in crystallography are called syngonies . The triclinic syngony contains the minimum number of groups (2), which allows only the presence of an inversion center and does not impose any restrictions on the parameters of the unit cell, the rhombic syngony contains the maximum.

Further determination of the space group is already associated with the analysis of reflection intensities. However, even after such an analysis, some space groups remain indistinguishable from each other. In this case, the researcher tries to decipher the structure in different groups. If the symmetry of the structure is not what is supposed, the structure will not be deciphered.

The second stage of structure decoding is the main problem. Knowing the coordinates of the atoms in the cell, we can calculate the theoretical intensities of reflections using the formula

$$I = K \cdot P(\theta) \cdot |F(hkl)|^2,$$

where K is a coefficient constant for a given sample, $P(\theta)$ is the polarization factor, and $F(hkl)$ is the structural reflection amplitude hkl .

The structural amplitude is calculated using the formula

$$F(hkl) = \sum_{j=1}^{N} f_j \exp[2\pi i(hx_j + ky_j + lz_j)],$$

Where x_j , y_j *and* z_j – coordinates of atoms, f_j – atomic scattering factor, shows how many times atom j scatters X-rays more strongly than an electron. The value f_j decreases with increasing $\sin\theta/\lambda$ (Fig. 3).

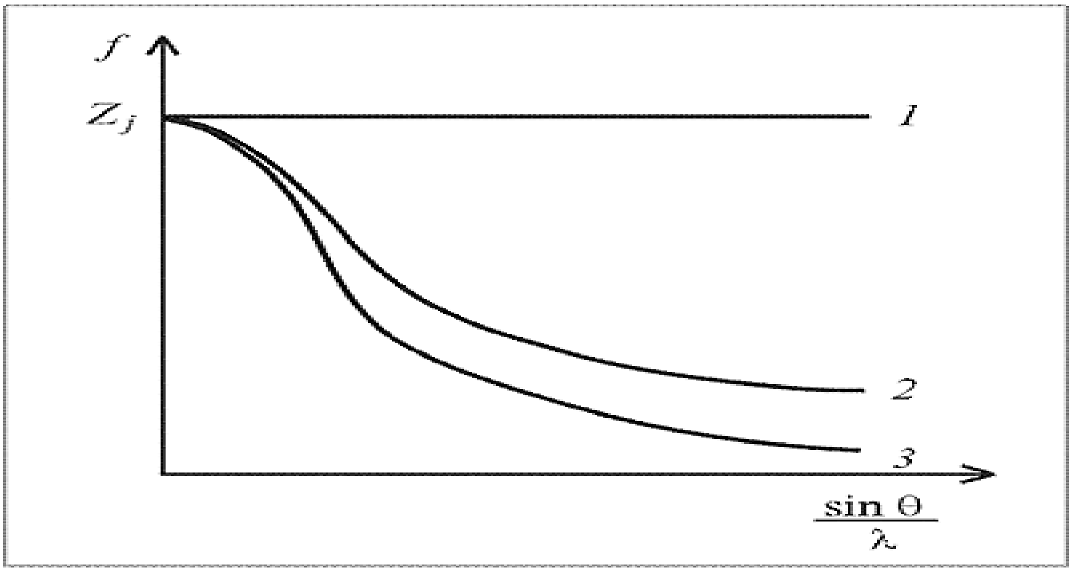

Fig.-3. Atomic scattering curves ***f*** for a point atom (1), a stationary atom (2) and an atom undergoing thermal vibrations (3)

This is due to the fact that the electrons of an atom are not concentrated at one point (the point atom model), but are distributed in space, so the rays reflected by different parts of the electron cloud partially cancel each other out. This effect is enhanced by increasing $\sin\theta/\lambda$. At $\theta = 0$ f_j equal to the number of electrons of the atom Z_j. Thermal vibrations of atoms further smear the electron cloud, which leads to an increase in the effect.

This is taken into account by introducing a temperature correction.

In general, *F(hkl)* is a complex value. It can be represented as $F(hkl)|\exp(i\varphi)$ where φ is the phase of the structural amplitude.

Knowing the structural amplitudes, we can reconstruct the distribution of electron density in the crystal. But, measuring the intensities of reflections, we can only calculate the modules of the structural amplitudes using the formula. At the same time, we know nothing about their phases. This is the famous phase problem of X-ray structural analysis.

References

1. Elmurotova D.B., Nishonova N.R., Kulueva F.G., Uzoqova G.S., Xo‘jamberdiyeva J.N., Jo’rayeva Sh.A. Mashaits: islamic interpretation of the greek philosophical heritage // South Eastern European Journal of Public Health (SEEJPH), (ISSN: 2197-5248) V.XXV, S2, 2024, Posted:05-12-2024, P.516-522, https://www.seejph.com/index.php/seejph
2. Shodiev A.A., Mussaeva M.A., Nishonova N.R., Elmurotova D.B., Islamova D.X. Improving Structure and Superconductivity of Coated Cuprate Tapes by Irradiation with Electrons and Gamma-Rays // Nanotechnology Perceptions, ISSN 1660-6795, V.20, N.7 (2024), P. 209-126, https://nano-ntp.com/index.php/nano/article/view/3822
3. I. Mullojonov, Q.I. Narziqulova , V.G. Makhsudov , E.Ya. Ermetov, D.B. Elmurotova, M.I. Bazarbayev. Study of the appearing molar volume of electrolyte solutions and its application in health-biological processes // MedForum: Int. Conf. on Patient-Centered

Approaches to Medical Intervention 2024, Dr. Tanima Bhattacharya et al. (eds) © 2024 Taylor & Francis Group, London, P.38-40.

4. M.I. Bazarbayev, B.T. Rakhimov, Sh.A. Isroilova, D.B. Elmurotova, D.I. Sayfullayeva. Enhancing biophysics problem-solving skills in medical students through a targeted three-step strategy // MedForum: Int. Conf. on Patient-Centered Approaches to Medical Intervention 2024, Dr. Tanima Bhattacharya et al. (eds) © 2024 Taylor & Francis Group, London, P.112-114.
5. М.И. Базарбаев., Д.Б. Элмуротова., Ш.К. Нематов., Ш.Ш. Азимов., Т.З. Даминов., А.Р. Махкамов. Современные подходы к гигиене рук медицинского персонала //The journal of humanities & natural sciences, Issue 8, V.1, 2024. P.208-217.
6. Elmurotova D.B., Odilova N.J., Jumanov Sh.E. Semmelweis against puberner fever in hungary // Western European Journal of Linguistics and Education, V.2, Iss1, January-2024 ISSN (E): 2942-190X, P.56-59, Germany. https://westerneuropeanstudies.com/index.php/2/article/view/255
7. Элмуротова Д.Б., Элмуратов Э.Б. Исследование и совершенствование техники и технологии по освоению скважин в сложных горно-геологических условиях на месторождениях Республики Узбекистан // Лучшие интеллектуальные исследования, Ч-13, Т.5, Январь-2024, С.11-23, Россия. http://web-journal.ru/index.php/journal/issue/view/89
8. Elmurotova D.B., Sayfullayeva D.I., Isroilova Sh.A. Terms of medical information system, World Bulletin of Public Health (WBPH), V.34, May, P.91-92, 2024 ISSN: 2749-3644, Berlin. https://www.scholarexpress.net
9. Elmurotova D.B, Majlimov F.B., Zuparov I.B., Kayumova K.S., Xudoyberdiyev B.A. A modern approach to hand hygiene in medicine // European Journal of Humanities and Educational Advancements (EJHEA), V.5 N.05, May 2024 ISSN: 2660-5589, P.51-53, Spain. https://www.scholarzest.com
10. Elmurotova D., Arzikulov F., Egamov S., Isroilov U. Organization of direct memory access // Intent Research Scientific Journal-(IRSJ), ISSN (E): 2980-4612, V.3, Is.10, October – 2024, P. 31-38., Philippines, https://intentresearch.org/index.php/irsj/article/view/345
11. Elmurotova D., Arzikulov F., Izzatullayev I., Olimov A., Abdurahmonov J. The role of remote diagnostics in medicine // World Bulletin of Public Health (WBPH), V.39, October 2024, ISSN:2749-3644, P.102-105. Germany, https://scholarexpress.net/index.php/wbph/article/view/4664
12. Elmurotova D., Fayziyeva N.A., Urmanbekova D.S., Bozorov E.H. Implementation of the method of teaching x-ray therapy in higher educational institutions // Web of Teachers: Inderscience Research, V.2, Issue 10, October-2024, ISSN (E):2938-379X, P.18-23. Spain. https://webofjournals.com/index.php/1/article/view/1868
13. Elmurotova D.B., Esanov Sh.Sh., Abduraxmonov S.A., Ulug'berdiyev A.Sh., Umarov J.S. Medical device reliability and measuring instrument specifications // Eurasian Journal of Engineering and Technology, EJET, V.34, October-7, 2024, ISSN: (E) 2795-7640, P.10-13, Belgium. https://geniusjournals.org/index.php/ejet

14. Shodiev A.A., Mussaeva M.A., Elmurotova D.B. Magnetic resistance and mobility of carriers of HTSC – YBCO tapes irradiated with 5 MeV electrons // Eurasian Journal of Physics, Chemistry and Mathematics, EJPCM, V.35, October-26, 2024, ISSN: 2795-7667, P.25-33, Belgium. https://geniusjournals.org/index.php/ejpcm/article/view/6393
15. Elmurotova D.B., Fayziyeva N.A., Odilova N.J. Properties of electron and neutron therapy // Web of Medicine: Journal of medicine, practice and nursing, V.2, Issue 10, October-2024, ISSN (E): 2938-3765, P.137-141, Spain.
16. Elmurotova D.B., Yoqubboyeva E.Z., Orifqulova M.F., Imanova L.N. Application of computer technologies in medicine // Western European Journal of Medicine and Medical Science, V.2, Issue 11, ISSN (E): 2942-1918, November-2024, P.1-12. Germany. https://westerneuropeanstudies.com/index.php/3.