

2014 - International Year of Crystallography

Un'introduzione storica alla diffrazione, di M. von Laue

I. HISTORICAL INTRODUCTION

by M. VON LAUE

The science which the *International Tables* are intended to serve is concerned primarily with the atomic theory of crystals, and secondarily with optical theory as applied to the short wavelengths of X-radiation. Moreover, now that we know of electron and neutron diffraction by crystals, it must include quantum mechanical wave theory, which is also of importance in the branch of optics already mentioned. This introduction has to deal, therefore, with the history of these three branches of physics. Let us begin with the most important and the oldest branch, the theory of crystals.

We may take as a beginning the small pamphlet written in the year 1611 by the great astronomer Johannes Kepler, which bears the title *Strenuus de nive sexangulari*, in translation "A New Year's gift to the astrologers, dedicated to one of his patrons at the court of the Emperor Rudolph II, whose friendship Kepler enjoyed during his stay in Prague. Kepler's astronomical works show that throughout his life he believed that the material world was the creation of a Spirit delighting in harmony and mathematical order. Had he not tried in his youth to deduce the radii of the planetary orbits from the dimensions of certain regular polyhedra, and had he not printed in 1596 (*Harmonices Mundi*) the title *Harmo-nia Mundi?*" It need not surprise us, therefore, that it was the appearance of these regular and beautifully shaped snowflakes rather than the appearance of the crystals of the mineral world that inspired Kepler with the idea that this regularity might be due to the regular geometrical arrangement of minute and equal brick-like units. Thus he was led to the cleaved sphere, and, although he did not coin the expression "space lattice" and although his development of these ideas is not always correct, we can find among his illustrations the first pictures of space-lattices.

Nevertheless Kepler felt uneasy about these speculations. He realised, quite correctly, that his way would lead to an atomic theory; yet the idea of the atom, as handed down from the ancient Greeks, lacked an empirical foundation and therefore had not been the subject of excessively fanciful speculation even until well into the nineteenth century. Hence it was not without reason that the natural scientist in Kepler mistrusted this idea and

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would not take it seriously. He toyed with the double meaning of the word "mīx," which in Latin means snow but in German dialect "mixts" —nothing. And so from beginning to end he repeatedly explained the whole idea away as a mere "nothing."

In these circumstances the little pamphlet, even though it was printed, naturally made no deep impression. It was soon forgotten. Crystallography took another direction, that of the description of the external form of crystals, after Niels Stensen had in 1669 pointed out the existence of characteristic angles between crystal faces. By devious ways this led eventually to the Millerian indexing of faces (1839), to the laws of symmetry and to the classification of crystals in 32 classes, which was accomplished in 1830 by Johann Friedrich Christian Hessel and in 1867, independently and rather more simply, by Alex Gadolin.

This consistently phenomenological approach was not abandoned, even though the crystal-optical discoveries made early in the nineteenth century by such men as Baptiste Biot, David Brewster, Augustin Fresnel and Frederick William Herschel had led to the development of the important idea that the same laws of symmetry which were valid for the physical properties of crystals also controlled the physical events inside the crystal. This was first made clear by Franz Neumann in 1833.

Apart from these trends of thought, however, ideas about the internal structure of crystals continued to appear. Thus Christian Huygens' fundamental work on the wave theory of optics, *Traité de la lumière*, which was published in 1690, contains among other things a wave-theoretical explanation of the cleavage of crystals which ascribes to calcite structures made up of ellipsoids of revolution the threefold periodicity of this arrangement characterises it as a space-lattice, although Huygens, like Kepler, did not define it as such. It was the cleavage along three planes which led him to this idea. Like Kepler's pamphlet, however, this part of the otherwise famous work was soon forgotten. Independently of Huygens, crystal cleavage in general led Torbern Bergman in 1773 and René Just Haüy in 1782 to suppose that all crystals consist of a kind of masonry of equal, parallelepipedal building bricks. That these "molécules soustractives"

were often supposed to consist of "molécules intégrantes" of other shapes need not concern us here. A structure of this kind involves a space lattice, and Haüy could hardly have expected from his idea to deduce the laws governing the geometry of crystal faces, already empirically known. But it would be premature to describe this as an atomic theory of crystals. No wonder! For the scientific theory of atoms had yet to be created, in its own good time, by the great chemists of the eighteenth century. The theorem that a lattice may be divided into unit cells, we should say today, in an infinite number of different ways would have made no physical sense to Haüy, who, as we have seen, would have admitted, of course, its geometrical correctness. Moritz Ludwig Frankenheim and Auguste Bravais took up this problem, and in 1850 Bravais described the 14 pure translation lattices which have been named after him. Incidentally, his papers also contain the concept of the reciprocal lattice, which was later rediscovered and used in connection with the study of interference patterns of X-rays. The geometric theory of crystals, however, was not yet fully developed. We have mentioned that Haüy's was trying to find an explanation of the thermal expansion and the elasticity of solids, of which he quite rightly believed crystals to be the normal type. He found the bricklike structure unsuitable for his purpose, since he argued, the only view compatible with this picture would be that the single bricks themselves possess these physical properties, which does not solve the problem, which only pushes it one step further back. Haüy, who was still very much a man of the eighteenth century, introduced instead the idea of a structure consisting of chemical atoms or molecules (at the time these two concepts were not strictly differentiated), whose mutual distances are determined by the balance of attractive and repulsive forces, thus forming a system of stable equilibrium. External disturbances cause certain changes of position—this is his explanation of elasticity—and possibly also elastic waves, which he called "acoustic" waves. Seeger, of course, did not visualise thermal vibration; he explained thermal expansion in terms of the temperature dependence of the attractive and repulsive forces. In order to retain the sound parts of Haüy's postulate, Seeger placed each of his molecules, assumed by him to be spherical, at the midpoint of the cell which would have formed one of Haüy's "molécules soustractives"; he thus arrived at a "parallelepipedal arrangement of the indivisible parts of matter," as he describes it at the end of his paper. In our language such an arrangement implies a primitive translation lattice, and it is not far from this concept to the idea that each unit cell of the space lattice is occupied by several atoms.

It is not surprising that such doubts, and even whole scientific

theory at first attracted little attention. Moreover,

the very reality of atoms was doubted again and again right up to the end of the nineteenth century.

Even in the absence of such doubts, and even when collaboration with Pope had given the chemical application of Bravais's theory, there was still no way of testing the hypothesis, which had been confirmed by their results, simply consisted of the diffraction conditions for a cross-grating, with the addition of a third condition to take account of the three-dimensional periodicity of a space lattice.

The diffraction of visible light by gratings, which mostly consisted of lines scratched on glass or metal, had already been described by Grimaldi in the seventeenth century, and again by Joseph Fraunhofer at the beginning of the nineteenth. The relevant literature is very full, and a comprehensive treatise by Friedrich Magnus Siedentopf, *Braggungserscheinungen, aus den Fundamentalsatzes der Unendlichtheorie analytisch entwickelt* (1835). The grating was still the most important instrument in spectroscopy. Later physicists engaged in work on optics have often referred to Schrödinger's theory. In particular, Lord Rayleigh frequently emphasised that the essentially characteristic feature of the periodic repetition of the elements and not the size of the period. Round about 1910 M. von Laue, in writing an article on wave theory for the *Encyclopädie der mathematischen Wissenschaften*, set himself the task of elaborating, as clearly as possible, this idea of Rayleigh's, and arrived at an equation for the position of the diffraction maxima which could be extended without difficulty to the case of double periodicity as it exists in cross-gratings; in the latter case two such equations had to be formulated.

In the meantime the science of optics had been extended far beyond the limits of the visible spectrum. The farthest extension on the short-wave side had come about in 1895 through Röntgen's discovery of X-rays; soon afterwards (1896) Emil Wiechert and George Gabriel Stokes concluded from the way in which X-rays are produced that they must be produced by the motion of electromagnetic waves. This was confirmed by the observation of their polarisation, made by G. G. Barkla in 1906. Wilhelm Wien in 1907 estimated their wavelength to be 7×10^{-8} cm. on the basis of their observed photoelectric effect, while A. Sommerfeld in 1912 calculated a value of 4×10^{-9} cm. from their diffraction by a slit. On the other hand, they showed such strong quantum effects that this was only another way of expressing the corpuscular theory of X-rays.

Meanwhile the experiments of Friedrich and Knipping, and von Laue's interpretation of them, had become known in England, and had inspired much discussion and further investigation, particularly by W. H. and W. L. Bragg. The story of what happened is here continued by Sir Lawrence Bragg:

"In the summer of 1912 my father showed me von Laue's paper, which had aroused his intense interest because of his work on the exciting of cathode rays by X-rays, which pointed to the projectile-like properties of X-rays, and he discussed with me possible alternative explanations for the effects which von Laue had found. I understood some experiments at Leeds that summer to see whether we could explain von Laue's spots by the diffraction of electrons, or by the diffraction of the crystal lattice rather than by the diffraction of waves, experiments which were of course abortive.

"On returning to Cambridge in the autumn of 1912 I studied von Laue's photographs very intensively, and was very naturally forced to the conclusion that they must be due to diffraction. I also concluded at the same time that one must modify the explanation of them which von Laue had given.

Von Laue had remarked that one did not get all the spots one would expect from a simple cubic lattice, but only a selection of the whole range. He ascribed this to the existence of five characteristic wavelengths chosen so that they approximately satisfied the diffraction conditions for the spots which actually appeared in the photographs. I, on the other hand, concluded that von Laue's spots were due to the diffraction of "white" X-radiation, representing a continuous spectrum of wavelengths over a certain range. I was led to this first by the fact of the changing shape of the Laue spots when the angle of incidence of the X-ray beam to the crystal was altered. This in turn led me to consider the diffraction effect as a reflection of X-ray pulses by the lattice planes of the crystal. I pointed out that this was equivalent to the selection from the continuous spectrum of a wavelength determined by the lattice spacing of the crystal. I tested this by reflecting the X-rays from a mica plate set at a series of angles, getting in every case a spot of a definite size and so showing, as I believed, that all the wavelengths were represented over a certain range in the X-rays. The problem then remained to explain why only certain spots appeared in the Laue photographs, and I ascribed this to the fact that the essential underlying lattice of the crystal was face-centred and not simple cubic. I communicated these results to the Cambridge Philosophical Society in November 1912. The paper which I then appeared in this paper (p. 46) in the form $\lambda = 2d \cos \theta$, but in later papers d was defined as the glancing angle and not the angle of incidence.

"Professor Pope at Cambridge was very interested in these results, because the close-packed lattices which he and Barlow had devised for atoms which they believed to be of equal size were face-centred cubic. He procured crystals of potassium bromide and iodide, and I took their Laue photographs. I showed him that I could be explained by an arrangement of alternate scattering centres in two interleaved face-centred lattices, the NaCl structure in fact, and that these centres must be equal in scattering power in KCl but different in scattering power in NaCl.

"This work was done at Cambridge before I collaborated with my father. We worked along different lines at first, which came together later. My father was very interested in my explanation of the diffraction effect as a reflection, and he set up at Leeds the first X-ray spectrometer. He was primarily interested in the nature of X-rays. He checked that the reflected rays were really X-rays,

a point on which he wished to satisfy himself because of his speculations about the corpuscular nature of X-rays. He found as I did that there was to be a continuous spectrum, but his spectrum was not so good, and by improving the apparatus he soon narrowed these down so much that it was clear that they were monochromatic. Incidentally I think it is not often realised how much work did on characteristic X-rays before Moseley made his brilliant generalisations. My father considered this and about a dozen different anti-cathodes and identified Barkla's K and L radiation, showing that the K-radiation was produced by the L three peaks. He related the wavelengths to the atomic weights of the metals in each anti-cathode (the idea of atomic number had not yet come to the fore) by a simple law. In fact he gave the first hint of Moseley's relations, and it was his work which inspired Moseley to his broader generalisations.

"My father then examined with his spectrorometer crystals of KCl and NaCl such as I had used for my Laue photographs, and found the reflections of the characteristic peaks from the (100), (111) and (110) faces. It was clear at once that the spectrometer was a far more powerful way of investigating crystal structure than the Laue photographs, which I had used. It was only at this stage that we joined forces. In particular, I had been trying to analyse the diamond structure by Laue methods without success, but my father merely noted it on the spectrometer and the answer became immediately obvious. We wrote a paper on the diamond structure together, but the results which gave the clue to it were obtained by him. I was able, however, to work along with him with the spectrometer in the summer of 1913, and so to work out the structures of zincblende, fluor spar, pyrites and some of the carbonates, which showed fairly good anti-spectrometer could be. My father was at first inclined to believe that the X-ray spectra and X-ray absorption edges, but crystal structures also fascinated him, and from that point on we both mainly devoted ourselves to structure analysis."

These experiments, together with those of Friedrich and Knipping, not only confirmed von Laue's diffraction theory but gave a direct proof of the existence of the space-lattice, and provided a simple expression (the Bragg law) for the relationship between the wavelength of the X-rays used and the lattice spacings of the crystal. The ionisation

currents obtained by means of the Bragg spectrometer showed clearly that the "mirror-image reflection" postulated by Bragg is selective and is conditioned by multiple interference. The Bragg equation was first published in its usual form in a paper by W. H. and W. L. Bragg in the *Proceedings of the Royal Society*, 88, page 426 (1913). Soon afterwards von Laue, *[Physikalische Zeitschrift]* 14, 421 (1913) was able to show that this equation was only another way of expressing the results of the geometrical space-lattice theory. Ionisation spectrometer measurements also revealed another reason for the absence of many of the interference spots at first expected by von Laue. The pulse theory of X-rays predicted much wider interference maxima than the Bragg equation. In fact, as W. Duane and F. L. Hunt established in 1915, this spectrum ends abruptly at the short-wavelength limit given by the now well-known quantum rule.

Still further credit is due, however, to W. H. and W. L. Bragg. X-ray diffraction patterns had made it possible to compare the wavelengths of X-rays with the three lattice constants, whose axial ratios were already known. Absolute values of the lattice constants in the crystal without a knowledge of the absolute value of the lattice constant of at least one substance. It was necessary for this purpose to know the number of atoms in the unit cell, and this was impossible without a knowledge of the structure. The Braggs' measurements, however, had shown that sodium chloride really did possess one of the hypothetical structures postulated by Barlow. Thus it was possible to deduce the absolute value of the lattice constant to this value, this in turn provided an absolute measure of the wavelength of X-rays, and hence the absolute lattice constants of all other crystals investigated. Rarely has the value of hypothesis in research been so strikingly demonstrated.

This brings us to the end of the historical introduction as far as X-rays are concerned, since all

that has followed is merged into present-day practice. Yet the space lattice has had another most important part to play in physics.

In 1924 L. de Broglie put forward in his *Thèses* the basic idea of wave mechanics, which was rapidly accepted. In a letter to the editor of *Naturwissenschaften*, pointed out that the de Broglie waves of electrons must cause space-lattice interference effects, and that experiments by Davison and Germer on the reflection of electrons from a platinum sheet had actually shown the maxima of the expected kind. When in 1926 E. Schrödinger published his communications on *Quantisierung des Eigenwertproblems*, C. J. Davisson and L. Germer, in Germany, independently of de Broglie, also showed that the interference of electrons with a crystal lattice was to be expected. In March 1927 they were able to publish a note in *Nature* to say that their efforts, made on a single crystal of nickel, had been crowned with success. In May of the same year G. P. Thomson and A. Reid announced that an electron beam of several thousand volts had, on passing through a celluloid film, produced Debye-Scherer rings, and G. P. Thomson found the same effect even more clearly with a thin foil. Thus the theory was now confirmed and the plausibility of all proofs had been given of the connection of a wave with the movement of a corpuscle.

Admittedly the geometrical theory of space-lattice interference does not apply so well to electrons as it does to X-rays, especially not to low-energy electrons. But it has enjoyed further triumphs in the diffraction of neutrons, observed first by D. P. Mitchell and P. M. Powers, then by W. H. Zacharias, F. G. Ross, and other American physicists using the cyclotron or the uranium pile as a source. Here a new possibility has to be taken into account: the atomic structure factor, which is characteristic for the scattering of single atoms, may be negative as well as positive. This branch of research is, however, still in its infancy. It appears to be capable of great development.

Introduzione storica del secondo volume delle International Tables for X-ray Crystallography, pubblicate dalla International Union of Crystallography

L'introduzione storica è a cura di Max von Laue, premio Nobel per la Fisica 1914 per *his discovery of the diffraction of X-rays by crystals*

Notare che nel testo il ruolo fondamentale dell'autore appare minimizzato mentre è in chiara evidenza il ruolo, di grande importanza, di William Henry Bragg e di suo figlio William Lawrence Bragg, anch'essi premio Nobel per la Fisica 1915 per *their services in the analysis of crystal structure by means of X-rays*. È interessante osservare come nella sua introduzione Max von Laue riporti il suo contributo per mezzo di scritti originali di William Lawrence Bragg che citano espressamente i lavori di Laue sulla diffrazione di raggi-X. Max von Laue dimostra di essere un uomo di grande statura in tutta la sua vita.

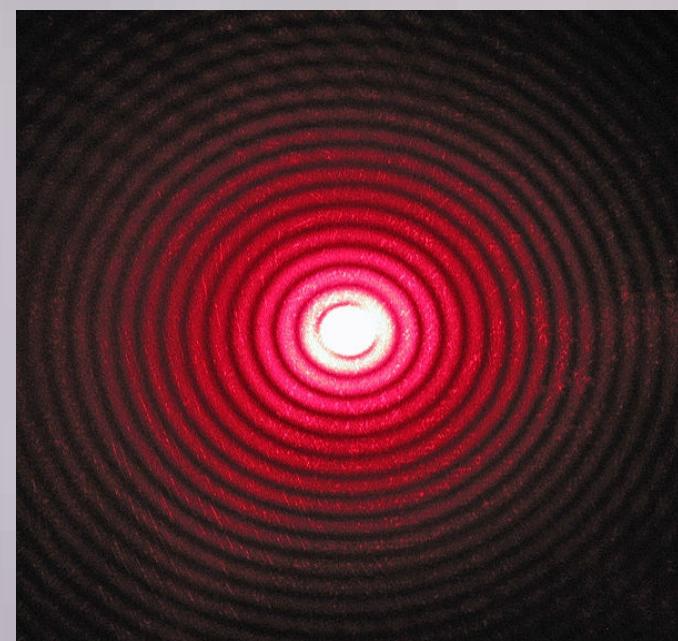
William Henry Bragg e suo figlio William Lawrence Bragg, sono l'unico esempio di padre e figlio che abbiano ricevuto insieme un premio Nobel per il medesimo argomento al quale hanno entrambi contribuito in modo diverso e in luoghi diversi.

Vari altri premi Nobel si sono susseguiti nella cristallografia, dalla definizione della struttura del DNA allo studio della struttura delle proteine, informazioni che hanno un'importanza basilare nella moderna tecnologia dei farmaci.



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La diffrazione è un fenomeno fisico causato dall'interazione di un'onda con un oggetto di dimensioni opportune



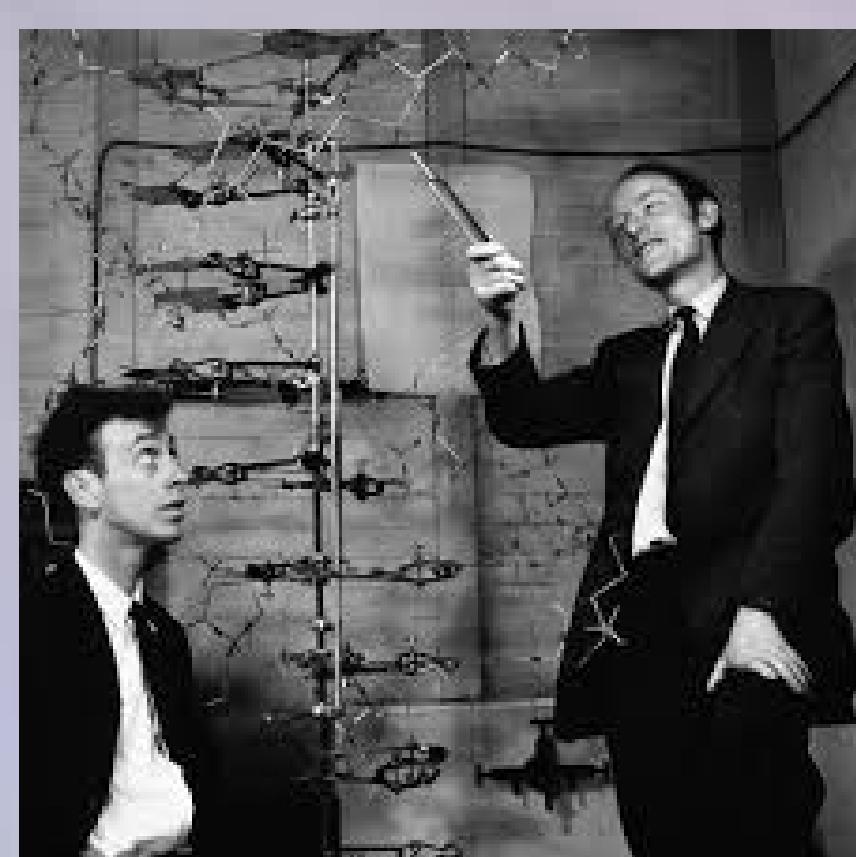
Laser rosso dopo un piccolo foro



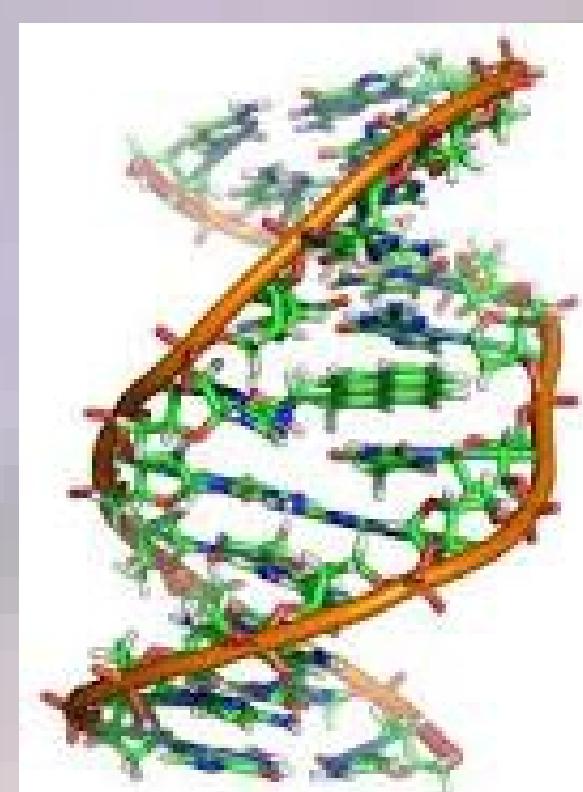
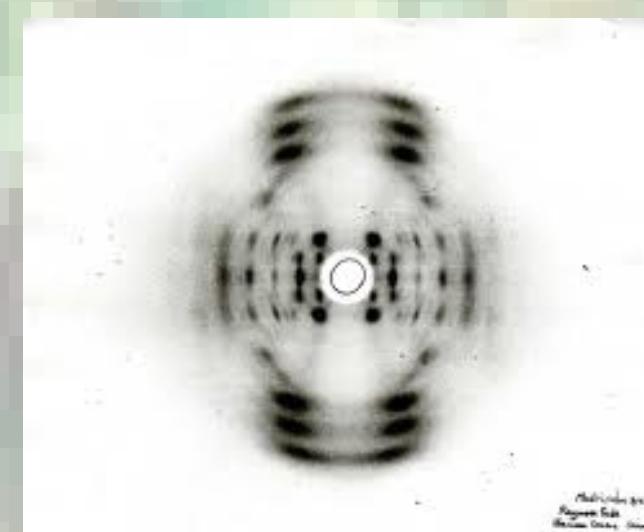
La luce delle stelle subisce diffrazione nel telescopio

Nel micro mondo degli atomi ogni oggetto si comporta anche come un'onda quindi si assiste spesso a fenomeni di diffrazione

Cristallografia e la materia biologica, gli attori della soluzione della struttura del DNA



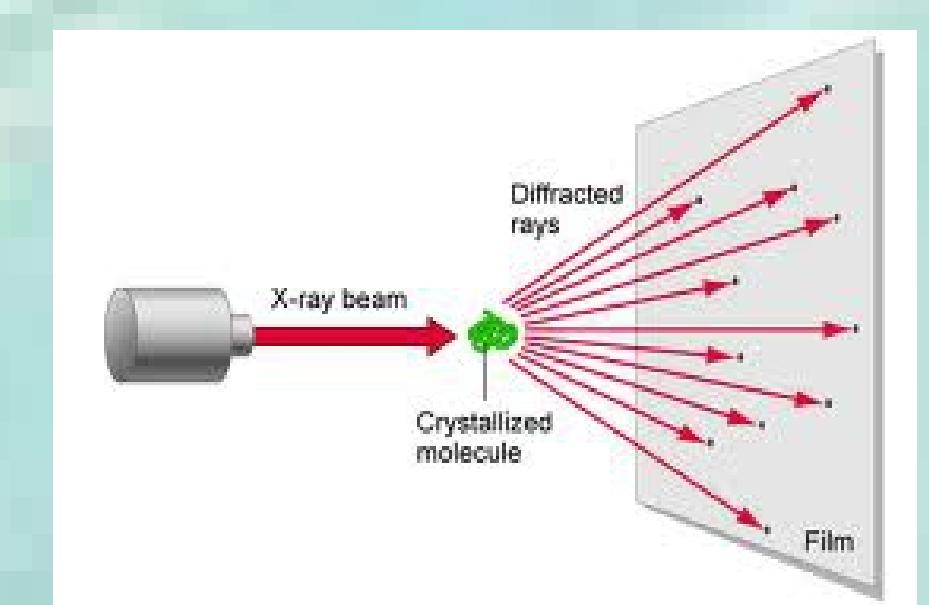
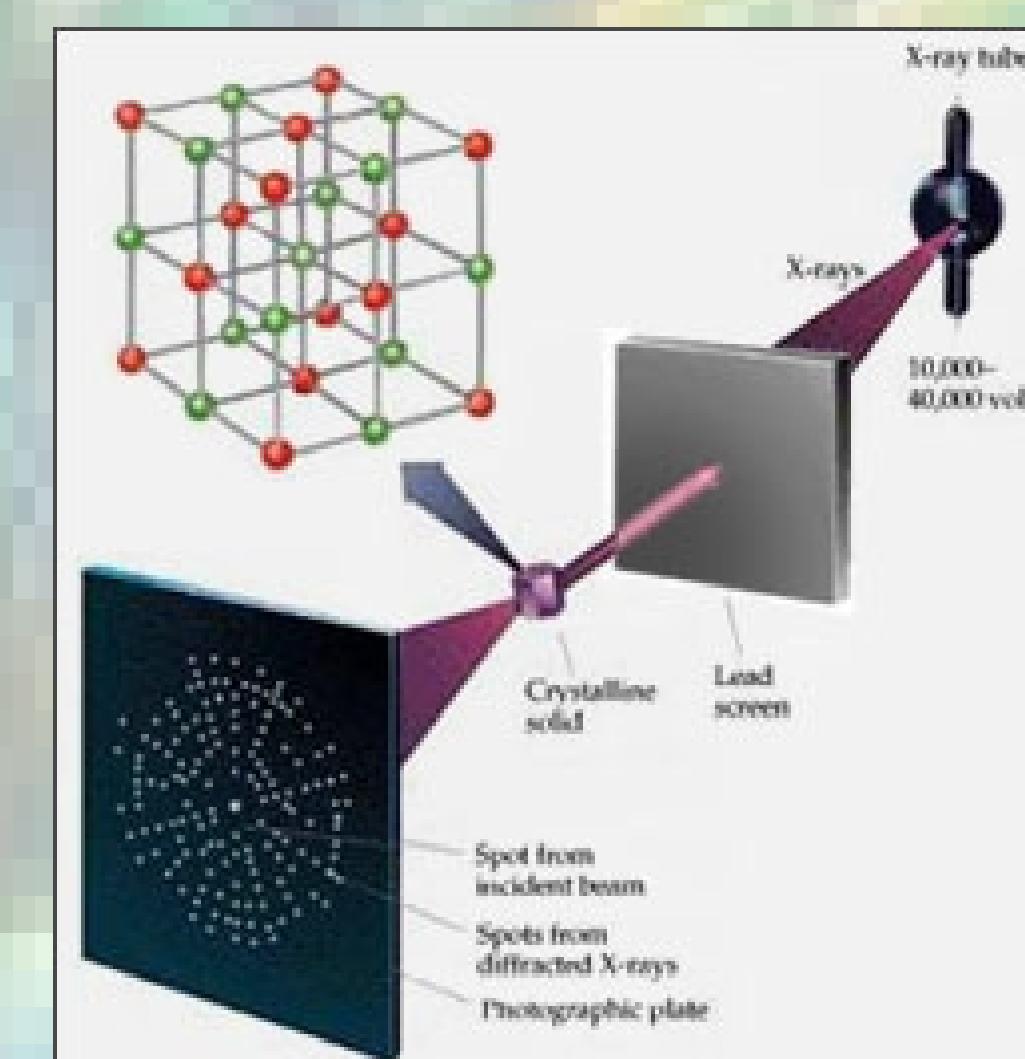
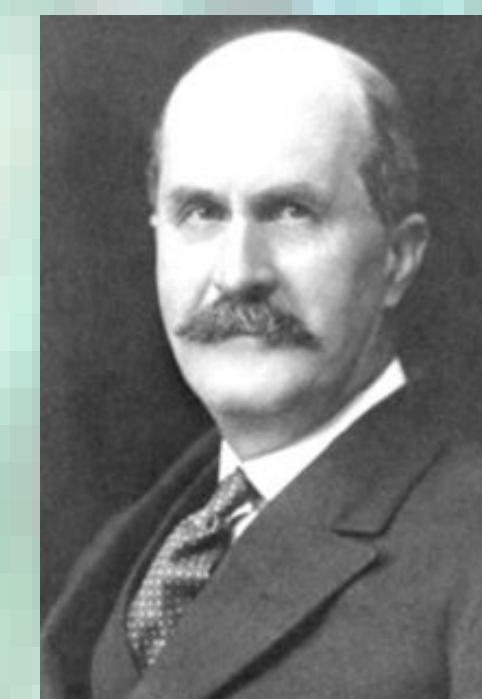
James Dewey Watson
Francis Harry Compton Crick
Biologi, Nobel per la medicina



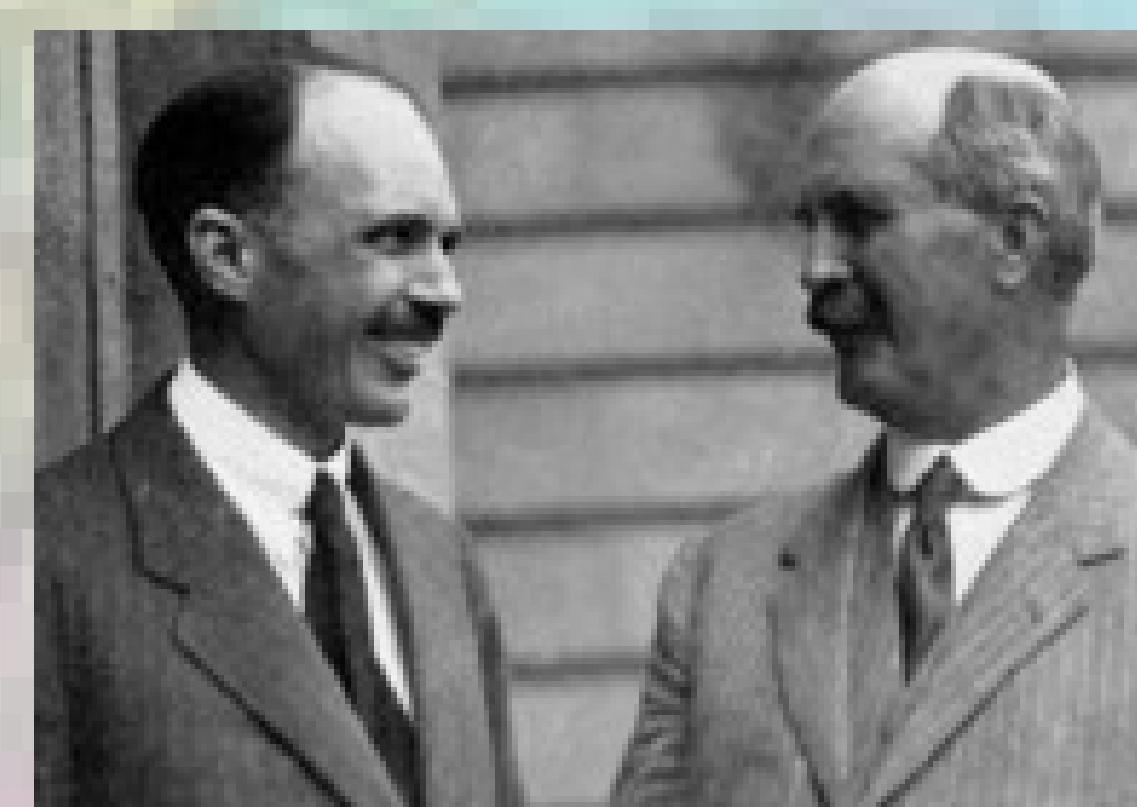
Maurice Hugh Frederick Wilkins, fisico, biologia molecolare, ideatore della struttura a elica, Nobel per la Medicina insieme a Crick e Watson

La diffrazione e i premi Nobel per la fisica

- 1901 Wilhelm Conrad Röntgen (primo Nobel per la Fisica)
1914 Max von Laue
{ 1915 William Henry Bragg
1915 William Lawrence Bragg



Rosalind Elsie Franklin, diffrazione di raggi-x sul DNA, la doppia elica emerge dai suoi esperimenti



La cristallografia delle proteine è un procedimento essenziale per la biologia e la farmacologia



I Bragg

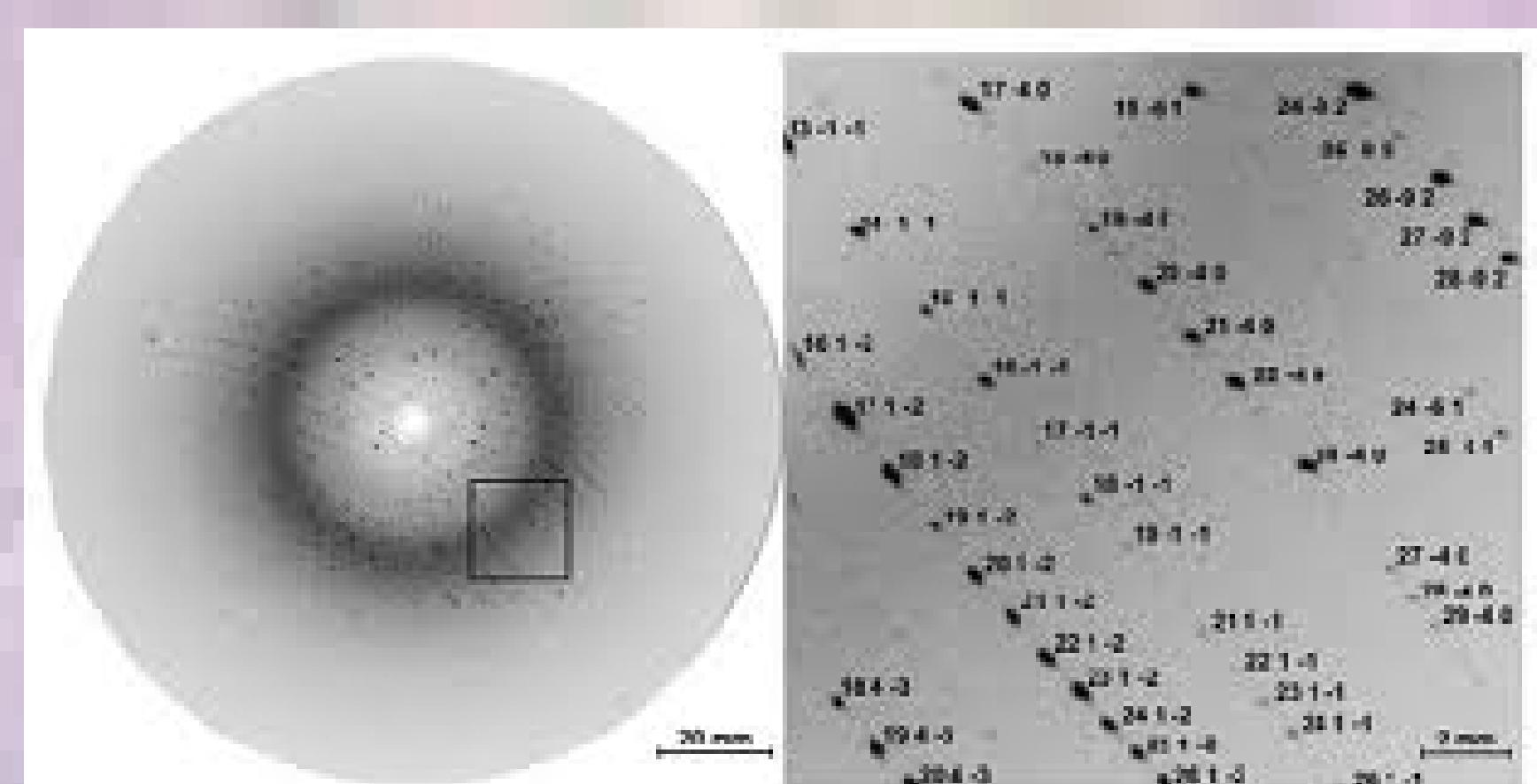
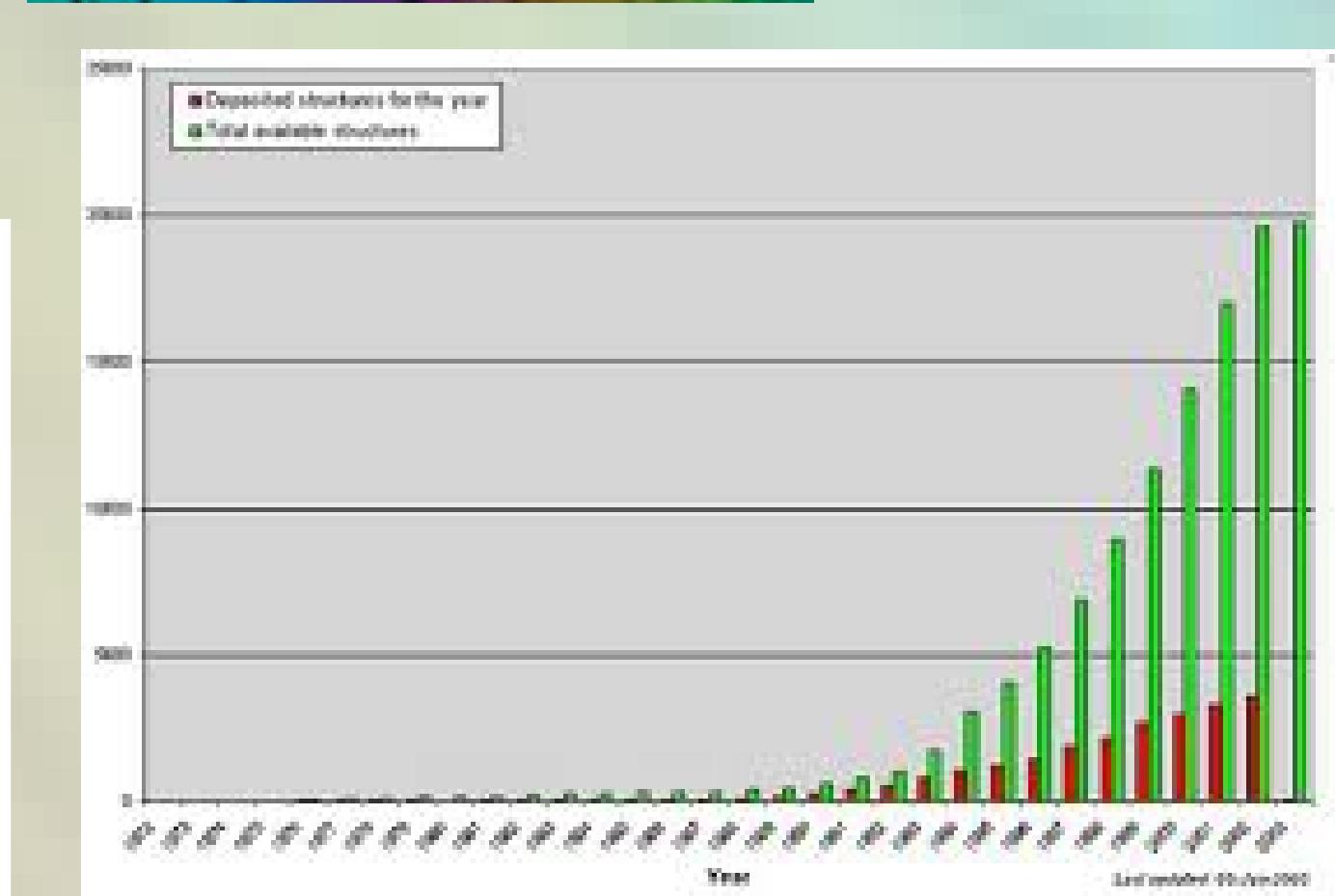
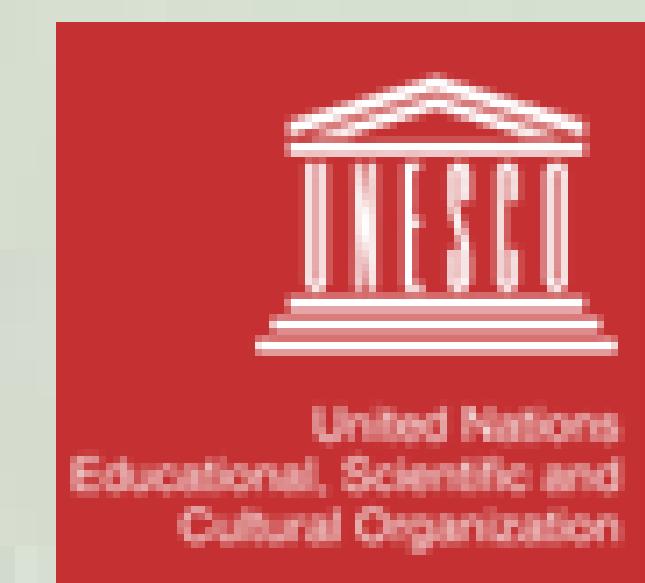


Figura di diffrazione di raggi-X da un cristallo di proteine, il quadrato di lato è un ingrandimento dove si vedono i punti prodotti dalla diffrazione e le terne di numeri (indici di Miller) che li caratterizzano

Protein Data Bank è una raccolta delle strutture dei cristalli di proteine. La crescita del numero di proteine studiate è vertiginosa e continua. Dal 1976 a oggi sono state studiate circa 100.000 proteine, quasi tutte con i raggi-X.

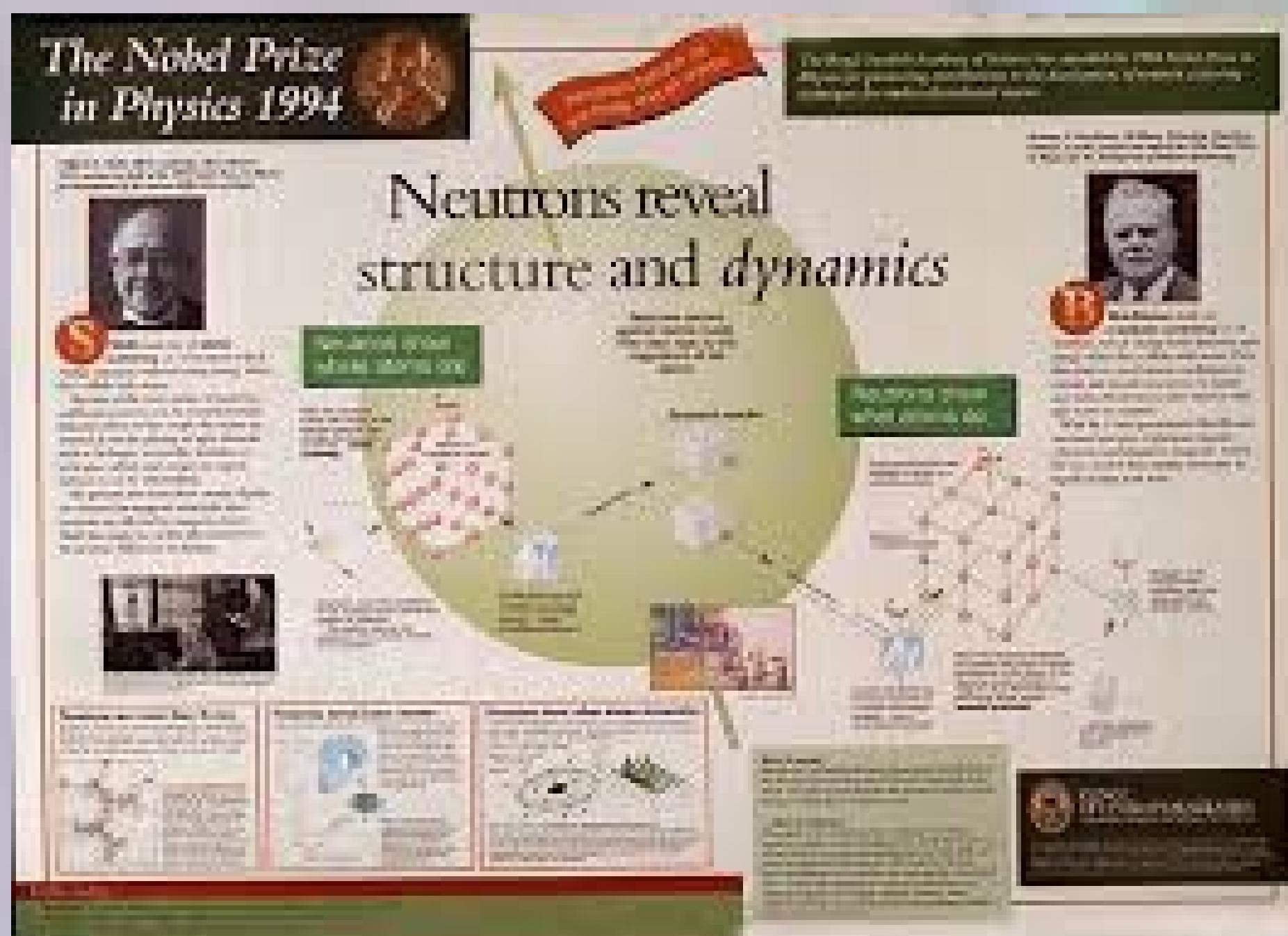




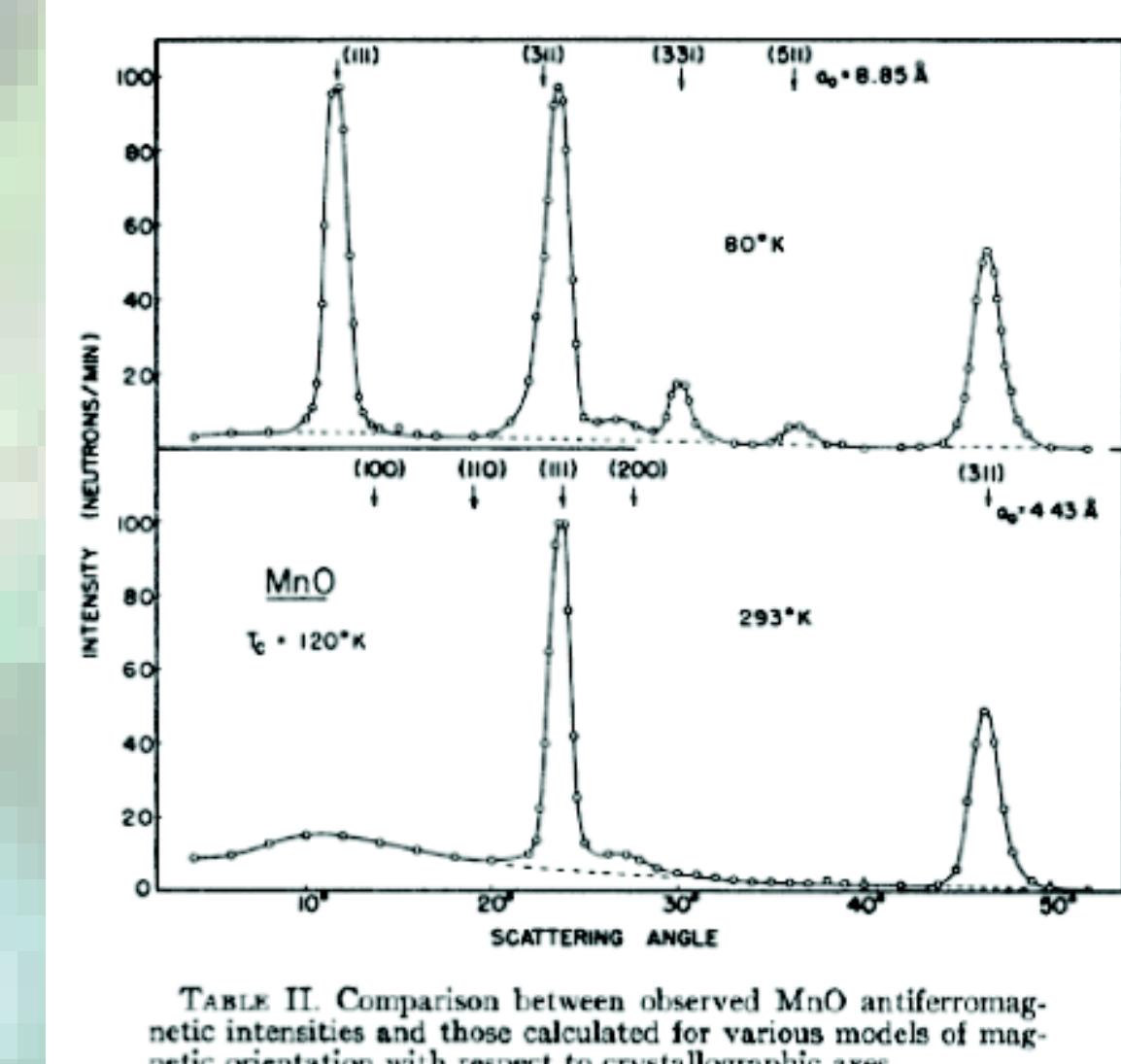
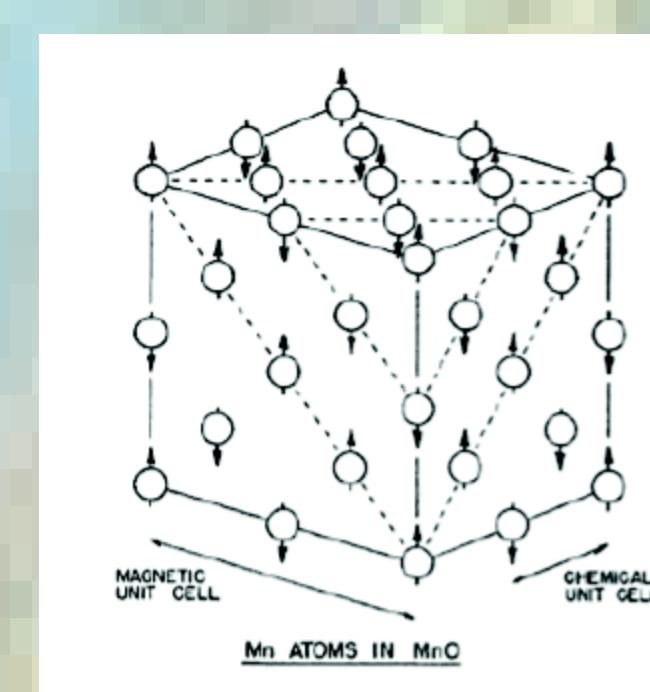
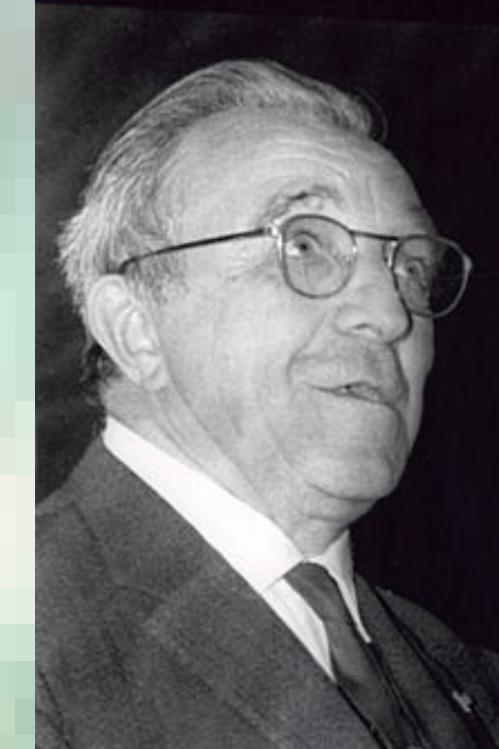
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Diffrazione dei neutroni

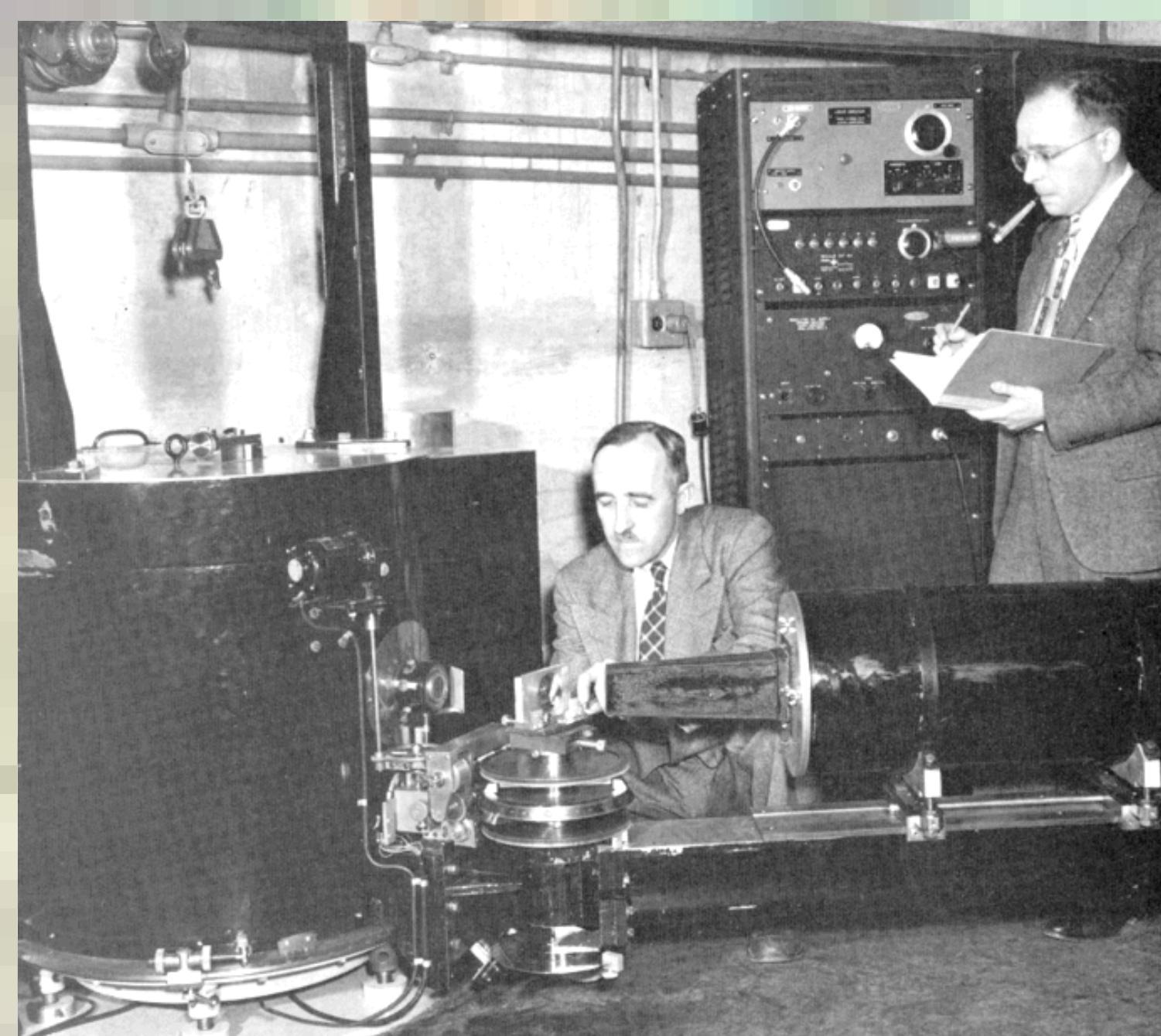
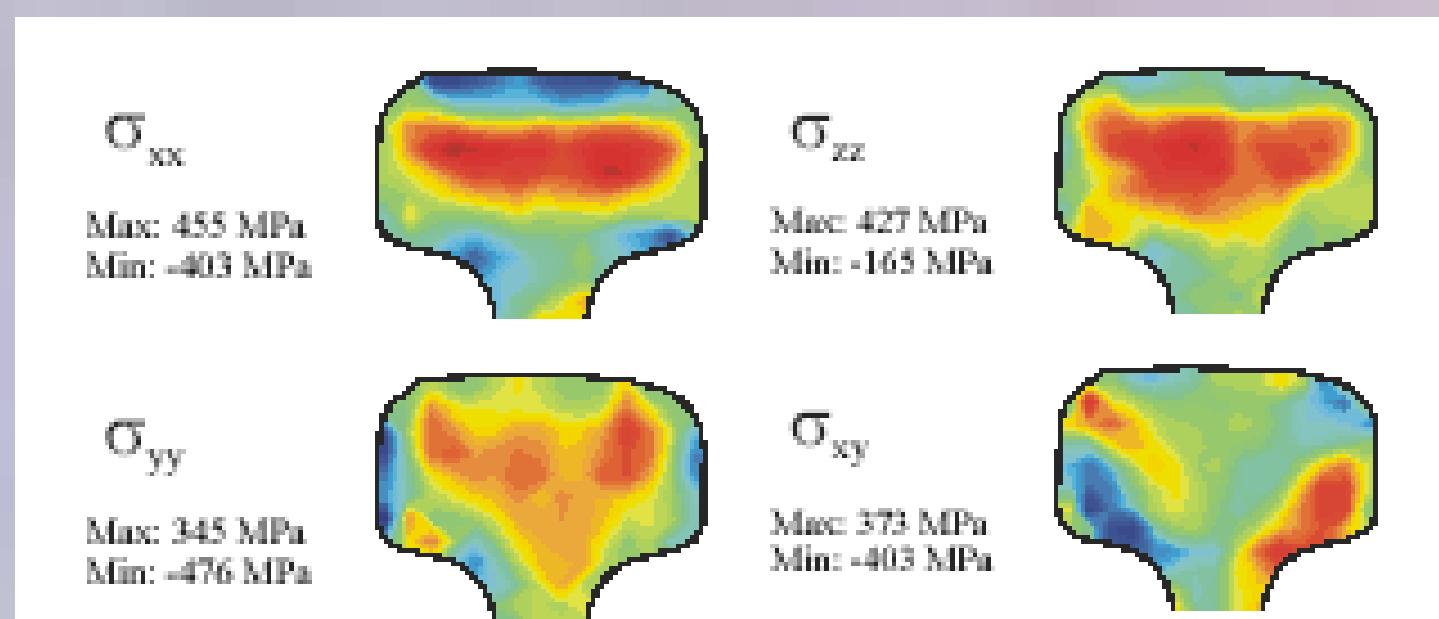
La diffrazione dai cristalli è stata scoperta per mezzo dei raggi-X e la teoria è stata sviluppata per questa tecnica. Nella prima metà del XX secolo, l'avvento della Meccanica Quantistica ha portato a comprendere che i fenomeni di diffrazione possono avvenire con qualunque tipo di particelle microscopiche: elettroni, atomi, protoni e neutroni. I neutroni si sono affermati come tecnica standard grazie all'assenza di carica elettrica che li rende preziosi per investigare materiali di ogni genere anche perché i neutroni sono in grado di vedere gli atomi leggeri che i raggi-X hanno difficoltà ad evidenziare.



1994, premio Nobel per la Fisica



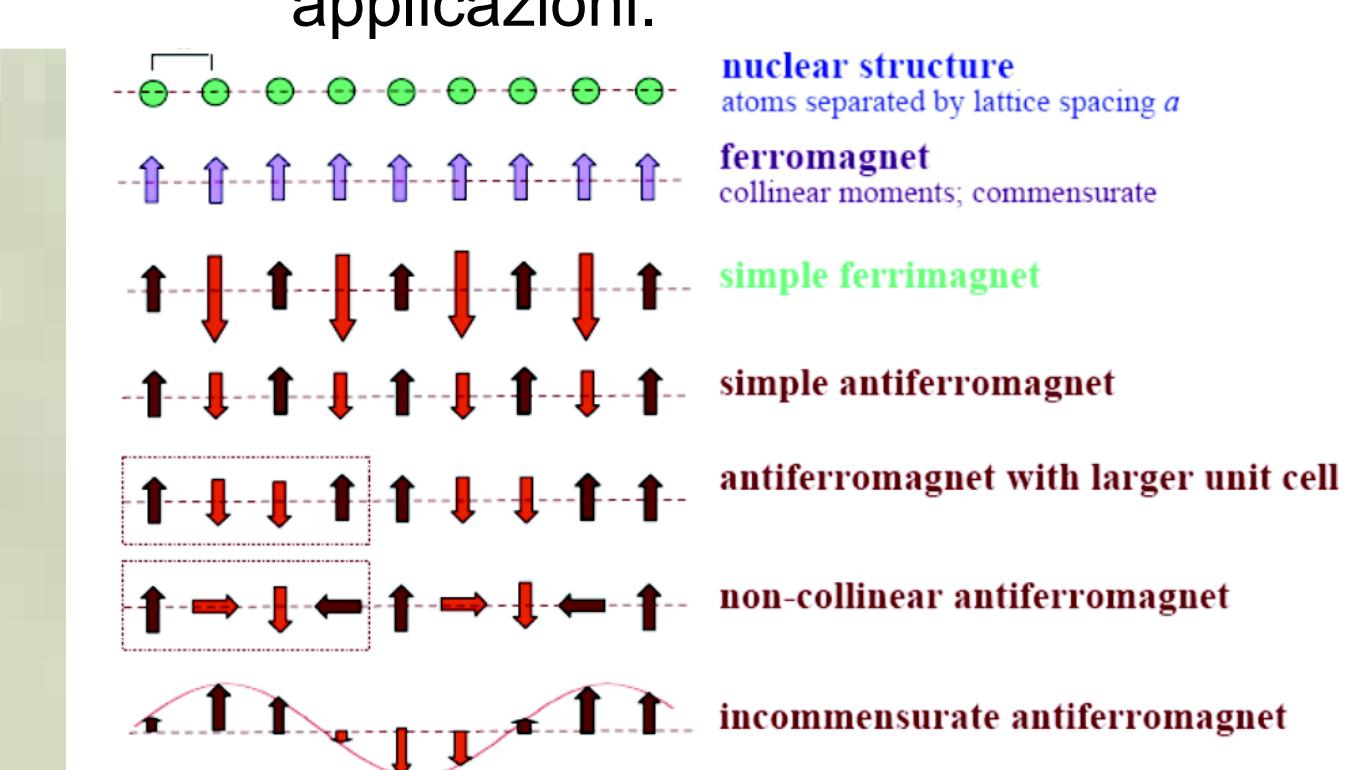
Louis Néel, premio Nobel in Fisica nel 1970 per *fundamental work and discoveries concerning antiferromagnetism and ferrimagnetism which have led to important applications in solid state physics*. La dimostrazione dell'esistenza dell'antiferromagnetismo e del ferrimagnetismo è stata possibile con la diffrazione magnetica dei neutroni.



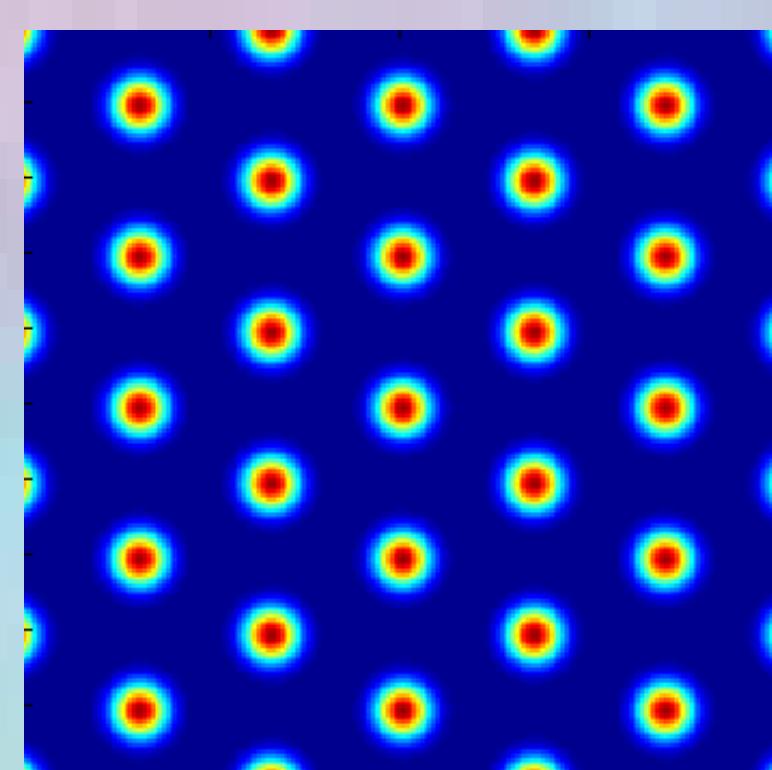
Il magnetismo è un fenomeno complesso che si sviluppa in un numero considerevole di forme schematizzate qui in una sola dimensione. Nei casi reali a tre dimensioni si sviluppano anche distribuzioni a elica e la coesistenza del magnetismo e della supercondutività sono materia di studio in quanto il magnetismo tende a sopprimere la supercondutività. La diffrazione di neutroni è uno dei modi più efficaci per comprendere la natura microscopica di questi fenomeni e governarli anche in prospettiva delle applicazioni.



La diffrazione dei neutroni è molto efficace nello studio degli sforzi residui in parti di apparati industriali. Un esempio importante è quello di componenti soggetti a usura per poter controllare e sostituire i componenti prima che lo sforzo a fatica diventi critico.



Shull (premio nobel 1994, in piedi con la caratteristica pipa) e Wollan nel 1947 al primo diffrattometro per neutroni a Oak Ridge. Notare che si trovano nel laboratorio in giacca e cravatta vicinissimi al fascio di neutroni monocromatici (tutti con la stessa velocità) in uscita dal moncormatatore.



Il campo magnetico non penetra liberamente nei superconduttori ma si organizza in linee dette *flussoidi*. I neutroni permettono di osservare direttamente i flussoidi che sono le zone dove rimane campo magnetico. Il reticolo di flussoidi nel Niobio (uno dei superconduttori più impiegato per produrre i grandi campi magnetici usati ad esempio in diagnostica medica) è qui mostrato come osservato con i neutroni. La zona blu è superconduttrice mentre nelle zone rosse, che sono allo stato normale, c'è il campo magnetico.