Every few years, my wife ventures down into our dark, grimy basement and returns with a certain cardboard box. After sweeping off the dust, she carefully unloads the precious cargo, piece by piece, onto our dining room table. Here lies the rock collection of her childhood. She is still fascinated by the beautiful crystals, and so am I. The yellowish calcite, whose tiny peaks look like a miniature mountain range. Cut a precipice and you miraculously form a perfectly flat plateau in the shape of a hexagon. Or the dense nugget of galena, lead gray, metallic, heavy to hold. It gives way to the chisel in three different directions, revealing perfect cubes and octahedrons. Cut the stone into even smaller pieces (my wife begins objecting) and you discover still more cubes and octahedrons, octahedrons within octahedrons, and so on. Can this go on? Or the amber-colored topaz, a dozen stubby fingers poking out from a gnarled fist, each finger with a tip shaped like a rhombus. Or the pink halite, which looks like a small cocktail filled with pink, cloudy ice cubes.

How could the inanimate world create such flat surfaces and ordered symmetries? They appear more like human-made buildings than the randomly curving coastlines and clouds and leaf shapes that we associate with nature. Deep, secret forces must be at work.

In 1784, the French mineralogist René-Just Haüy offered the insightful proposal that the visible symmetries of crystals are possibly a consequence of invisible symmetries, an orderly arrangement of the smallest elements of crystals. Those smallest invisible elements would be atoms and molecules, although the idea of the atom was still hypothetical at the time. Certainly no one knew the dimensions of atoms, if they existed at all.

Taking Haüy’s good idea, a nineteenth-century botanist and physicist
named Auguste Bravais found that only a small number of arrangements of atoms could fit together to make a repeating pattern in space. Bravais discovered fourteen such possible arrangements, called unit cells. Four of Bravais’s unit cells are shown in Figure 7.1. The lower left is simply a cube, with an atom at each of its eight corners. Clearly, cubes can be stacked in a repeating pattern that fills up space, as illustrated in Figure 7.2. Here, we have shown only three cubes, to avoid clutter, but the stacking can be continued in all directions indefinitely. The unit cell in the upper left of Figure 7.1 is like a cube, but with skewed angles between the edges at each corner, a kind of Salvador Dali cube. These arrangements, too, can be stacked together in a periodic pattern. The cell in the upper right has some sides that are rectangular, and an additional atom on the top and bottom faces. At the lower right is a cube with an additional atom in the middle. By mathematics alone, Bravais had discovered the language of crystals. But it was the language of a mythical country. No unit cell had ever been seen.

Skipping ahead for a moment beyond the momentous discovery of 1912, Figure 7.3 shows one of the first crystals to be analyzed at the atomic level, sodium chloride, also known as common table salt. Here, the small, light-colored spheres are sodium atoms and the large, dark spheres are chlorine. The lines connecting the spheres are drawn only to help visualize the arrangement. This Tinkertoy structure is, in fact, one of the fancier cells in Bravais’s fourteen-point grammar. The overall shape is a cube, with an atom of chlorine at each of the eight corners, but with an additional atom in the middle of each edge and face. A sing-
gle molecule of sodium chloride, that is, the smallest substance that has the chemical properties of sodium chloride, would be a single atom of sodium bound to a single atom of chlorine. But a unit cell of sodium chloride requires more than two atoms. The unit cell, shown in Figure 7.3, is the smallest unit from which a crystal of sodium chloride can be built up by repetition in three dimensions—that is, by stacking this model on top of itself vertically, horizontally, and outward, over and over, millions of times—in effect creating a tiny city built of sodium and chlorine bricks. Bravais would have been delighted.

Yet Bravais, with his geometrical diagrams, had only begun. For the manner in which atoms arrange themselves in space reveals much more than an explanation of the beautiful symmetries of rocks. These arrangements are fundamental to the physical properties of all solid matter. These arrangements govern how different substances bend and twist and interact in space. Even more profoundly, these arrangements reveal something about the push and pull between atoms, which cause the orderly structures in the first place. The hexagon that appears when I excavate a small mountain peak of my wife’s calcite crystal is quietly whispering about the electrical forces between closely packed atoms of calcium, carbon, and oxygen—a world one hundred million times smaller than the marble-sized piece of rock.

In Gulliver’s Travels, Jonathan Swift imagines a land where people are six inches tall. To such a Lilliputian, the fine stitching in a piece of silk would look like strands of fettuccine, and a chessboard would be a sculp-
The Arrangement of Atoms in Solid Matter

stance that has single atom of cell of sodium cyanide in Figure a chloride can by stacking this ward, over and of sodium and begun. For the als much more These arrange-1 solid matter. send and twist gements reveal which cause the ppears when I ystal is quietly ticked atoms of n times smaller were people are a piece of silk could be a sculp-
ture museum. But Swift’s little people would still be millions of times too big to explore a unit cell of sodium chloride. Even the best microscopes of the nineteenth century could not see anything smaller than a couple of ten-thousandths of a centimeter, still thousands of times larger than an element of Bravais’s grammar. For well over a century after the speculations of Håüy, scientists held little hope of ever peering into the tiny city of crystals.

Then, one wintry evening in February of 1912, a thirty-two-year-old German physicist named Max von Laue, once the star pupil of Max Planck, was “suddenly struck” by a thought: What happens when a beam of X-rays is aimed at a crystal? X-rays, discovered in the late nineteenth century, were believed by some scientists to be traveling waves of electromagnetic energy, like other forms of light, but with very small wavelengths ranging from $10^{-6}$ to $10^{-9}$ centimeters (a millionth to a billionth of a centimeter). In an inspiring vision, von Laue imagined that X-rays would scatter off the neat rows of atoms like water waves scattering off a line of buoys. Downstream, such waves merge, overlap, and produce patterns that reveal the spacings of the buoys. This process, called diffraction, was already known for visible light reflecting off rows of parallel grooves on a flat sheet of glass. Now von Laue hypothesized that waves of X-rays, after flowing through the miniature city of a crystal, would leave periodic patterns on a photographic plate—architectural blueprints of the placement of individual atoms. In effect, X-rays could be used to photograph the inside of a crystal.

Von Laue, a theorist himself, talked excitedly about his predicted effect but had trouble persuading colleagues to do the experiment. At the time, he was a relatively unknown privatdozent, or lecturer, at the University of Munich. X-rays were not waves at all, some physicists said, but rather high-speed particles. Other scientists believed that ambient heat causes atoms in solids to constantly jostle, like an enthusiastic crowd at a football game, and that this movement would blur any attempted photograph. As von Laue recounts in his Nobel lecture of 1915, “the acknowledged masters of our science entertained doubts... A certain amount of diplomacy was necessary before Friedrich [an assistant to the boss, Professor Arnold Sommerfeld] and Knipping [a doctoral student] were finally permitted to carry out the experiment according to my plan.” The experiments began on April 21, 1912. Von Laue worked out the mathematics. Friedrich and Knipping did the experiment, starting with a piece of copper sulfate crystal. They were successful, as can be seen from Figure 2 of their paper.
Wasting little time, Von Laue sent one of his X-ray photographs to Einstein, in Prague, who wrote back to him that "your experiment is one of the finest things to have happened in physics." Two days later, an elated Einstein wrote to physicist Ludwig Hopf: "It is the most wonderful thing I have ever seen. Diffraction on individual molecules, whose arrangement is thus made visible."

Max von Laue was born in 1879, the son of a German military official. Owing to his father's various postings, the young von Laue moved from Pfaffendorf to Brandenburg to Altona to Posen to Berlin to Strassburg. After a year of military service in 1898, he went to the University of Strassburg, and then finished his undergraduate work at Göttingen. In 1902, von Laue made his pilgrimage to the University of Berlin to study with Planck, the greatest European theoretical physicist of the day. There, von Laue applied Planck's ideas of entropy to radiation fields and championed Einstein's new theory of relativity in 1905. A photograph of von Laue from this period shows a very handsome man with strong features and a mustache, a steady gaze, a civilized, almost regal bearing, and a sensitive but determined expression.

From early in his training, von Laue took a special interest in optics and the wavelike behavior of light. As he recalls, "I had finally been able to cultivate what one could almost term a special feeling or intuition for wave processes." What is such a "special feeling" in science? Many of the greatest practitioners, from Einstein to Richard Feynman, have attempted to describe it. In part, this special feeling is a thorough knowledge of the mathematics of a process. It is the ability to comprehend a thing from several points of view. And it is certainly the ability to visualize a phenomenon, even one that is not visible to the eye. In his mind's eye, von Laue was able to imagine a voyage through the tiny city of a crystal.

All of us have some experience with waves. The wave after wave of the ocean, rolling onto a beach. Or the vibrating curve of a plucked violin string. Or the oscillating line on a heart monitor. A critical part of von Laue's "special feeling" for waves was an understanding of how waves overlap, sometimes canceling each other and sometimes reinforcing. This process is called interference. Figure 7.4 illustrates how interference comes about. The waves shown here have the same wavelength, that is,
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length, that is,

the same distance between successive crests and troughs. Waves A and B
are positioned relative to each other so that their crests line up and their
troughs line up. Such waves are said to be “in phase.” When waves A and
B overlap, they will reinforce each other, producing a stronger wave than
either wave alone. Waves C and D, on the other hand, are “out of phase”
with each other. Each trough of wave C lines up with a crest of wave D.

When waves C and D overlap, they will cancel each other and leave still-
ness. Two particles that converge on a point cannot eliminate each other,
but two waves can.

An important application of the interference of waves is a diffraction
grating, which is a row of parallel grooves that scatter incoming light.
The grooves can be carved in glass or in polished metal. The first crude
diffraction grating was built in 1801 by the British physicist Thomas
Young, who was studying the properties of light. Like Mozart, Young
was a child prodigy. He learned to read at age two, had digested the
Bible by six, and was one of the first people to translate Egyptian hiero-
glyphics. With his diffraction grating, Young helped prove the wave
ture of light.

Figure 7.5 schematically illustrates one of Young’s diffraction grat-
ings. Here the vertical row of dots represents a cross section of the
grooves. Parallel beams of light come in from the left, scatter off the
grooves, and then emerge to the right in all directions. In general, even if
the incoming waves are in phase with each other, they will be out of
phase after scattering. However, those waves that scatter in special direc-
tions will be in phase and reinforce each other. The special directions of
reinforcement are determined by the wavelength of light and the spacing
between the grooves. (For example, for a wavelength equal to one-fifth
the distance between grooves, the scattered waves would reinforce in the
directions at angles of 11.5 degrees, 23.6 degrees, and 36.9 degrees relative to the incoming beam.) In these special directions, we would see bright spots of light.

How such magic occurs is revealed in Figure 7.6. Consider waves A and B, initially in phase with each other. These two waves will scatter from the grooves in all directions, as suggested in Figure 7.5, but for purposes of illustration the figure shows just one particular direction of scattering, indicated by the arrow. This direction has been carefully chosen for illustration for a reason: wave B, after it exits the grooves to the right, travels exactly one whole wavelength to catch up to wave A. Consequently, by the time the two waves have reached the dashed line, they are back in phase and will reinforce each other at any further point downstream. Wave B is like a watch that has been stopped for exactly twenty-four hours and then started again, finding itself back in synchrony with another watch, wave A. If all of the grooves are the same distance apart, wave A will likewise be exactly one whole wavelength behind the wave above it (in the direction shown), and those waves will also emerge in phase. And on and on, through thousands of grooves, each scattered wave exactly one wavelength behind the wave above it, with crests and troughs lining up. Thus, all waves scattering in this particular direction will be in phase.

By comparison, consider the smaller scattering angle shown for waves C and D. In this particular direction, wave D, after it exits the grooves to the right, travels exactly one half of a wavelength to catch up to wave C.
Thus, these two waves are out of phase with each other by the time they have reached the dashed line. They will cancel each other out, producing darkness. Indeed, every pair of waves scattering in this direction cancel each other out.

The end result is that the scattered waves will reinforce each other and produce bright spots only at certain angles (directions). As mentioned earlier, these special angles can be calculated simply in terms of the wavelength of incoming light and the distance between grooves. At all other angles (directions), the waves will be more or less out of phase with each other and cancel each other out.

Von Laue’s revelation was that the tiny city of a crystal would act as a diffraction grating in three dimensions. For a crystal, individual atoms substitute for grooves and scatter incoming light. Analogously to the parallel grooves of a diffraction grating, the atoms in a crystal of matter are spaced at precisely repeating intervals, a crucial requirement for diffraction to work. As shown in Figure 7.7, parallel rays of X-rays come in
from the left, scatter within the three-dimensional crystal, and emerge in many directions on the right.

Three dimensions offer new complications. For the standard diffraction grating, interference between waves occurs only in one dimension, along the single row of grooves. But in a three-dimensional lattice, such as is shown in Figure 7.7, waves can interfere with each other along the three perpendicular rows of atoms. Thus full reinforcement requires that scattered waves arriving from atoms above and below each other, right and left of each other, and in front of and behind each other all be in phase when they emerge from the crystal. Depending on the spacing between atoms and unit cells, and the wavelength and direction of the incoming light, there may be no emergent direction for which all of these conditions are satisfied. When such directions do exist, as evidenced by bright spots of reinforced light on a photographic plate, the particular locations and patterns of those spots reveal much detail about the crystal lattice.

But why X-rays? Because only waves of such short wavelengths can probe the tiny distances between atoms in solid matter. A sewing thread can measure the eye of a needle, but a shoestring cannot. It was well known in 1912 that atoms are roughly $3 \times 10^{-8}$ centimeters apart in solid
matter. Visible light has wavelengths ranging from $4 \times 10^{-5}$ to $7.7 \times 10^{-5}$ centimeters, far too large to investigate the tiny spaces between atoms. But X-rays are perfect for the job. As mentioned earlier, X-rays had been measured to have wavelengths ranging from $10^{-6}$ to $10^{-9}$ centimeters. The shorter waves in this range would be roughly one-tenth the space between atoms, the best ratio for a diffraction grating to work.

To fully appreciate von Laue's idea, we must remember that in 1912, X-rays, also called Röntgen rays after their discovery by Wilhelm Röntgen in 1895, were not well understood. The X in the word stood for "unknown." All that was known for sure was that X-rays had extraordinary penetrating power. Experiments by the British physicist Charles Glover Barkla suggested that X-rays were electromagnetic waves of very short wavelength. On the other hand, some scientists believed that X-rays were material particles, like the high-speed electrons called β-rays. Thus, the diffraction patterns observed by Friedrich and Knipping, which could be plausibly produced only by the overlap of waves, not only provided a powerful tool for the study of atomic architecture in solid matter but also gave confirming evidence of the wave nature of X-rays.

Now, the paper itself. It is unusual for it to be rigidly divided into theoretical and experimental sections, with the authors Friedrich, Knipping, and von Laue separately apportioned between these two parts. But it is not unusual to have several scientists jointly author a largely experimental paper. Experiments, unlike theoretical ideas and calculations, often require the varied skills and resources of a team of people.

Von Laue begins by referring to the recent research of Barkla and to the older notions of Bravais that atoms in a crystal may be arranged in an orderly lattice. He then quickly outlines his proposal: by analogy to one-dimensional interference patterns with optical (visible) light, X-rays should produce three-dimensional interference patterns after traversing a crystal.

At the end of this brief introductory section, von Laue announces that "Friedrich and Knipping have tested the above hypothesis at my instigation." By habit, von Laue was a man who gave credit where credit was due. For example, in his Nobel address, he graciously acknowledges the influence of physicist Peter Paul Ewald in his thinking about electromagnetic waves in crystals. But here, in his landmark paper of 1912, von Laue clearly lays claim to the idea of X-ray diffraction. The Nobel committee in Sweden was convinced and awarded the prize to von Laue and
von Laue alone. In an analogous manner, it is Ernest Rutherford who always gets acknowledged for discovering the nucleus of the atom, although the actual experiment was done by his assistants Geiger and Marsden, at Rutherford’s suggestion.

In the next section of his paper, von Laue performs a standard calculation of the interference of electromagnetic waves. What is new about this calculation is that he considers the scattering centers to be distributed in three dimensions rather than one or two. He then specializes to the simple case when the unit cell is a cube, of side \( a \), realizing that this special case will not apply to all crystals but will simplify the analysis. Here and elsewhere, von Laue is more interested in the principles of his ideas than in the details.

The main result is given in the last equation. This equation states that full reinforcement of the scattered waves will occur only if three conditions are satisfied, one for each dimension. The first condition, for example, requires that waves scattering off atoms in a row parallel to the \( x \)-axis travel distances differing from each other by a whole number of wavelengths, so that they are in phase with each other. As in the case of one-dimensional scattering, this condition is true only for certain directions \( \alpha \). The second and third conditions apply to atoms in rows parallel to the \( y \) and \( z \) directions, respectively.

The operational use of these three von Laue conditions is as follows: For each bright spot observed on the photographic film, one can measure its direction from the crystal and obtain the three angles \( \alpha \), \( \beta \), and \( \gamma \). (Technically speaking, \( \alpha \), \( \beta \), and \( \gamma \) are the cosines of the angles the direction makes with respect to the \( x \)-axis, \( y \)-axis, and \( z \)-axis.) One then takes ratios of the angles. These ratios result in the ratios of integers: \( \alpha/\beta = h_1/h_2 \) and \( \alpha/\gamma = h_1/h_3 \). Next, one tries to find small integers \( h_1 \), \( h_2 \), and \( h_3 \) that satisfy these requirements. Once the integers are known, one goes back to the original equations and solves for \( \lambda/a \). If \( \lambda \) is known, one thus derives \( a \). If \( a \) is known, one thus derives \( \lambda \). (Recall that \( \lambda \) is the wavelength of the X-ray and \( a \) is the length of a side of the unit cell.) Each individual spot can be the result of reinforcement of only a single wavelength. But if the incoming beam contains different wavelengths, different spots can be the result of different wavelengths. Evidently, von Laue, Friedrich, and Knipping found from their results, shown in Figures 2 and 3 of their paper, that they required five different incoming wavelengths to fit all of their spots. There may have been other wavelengths as well, but not all wavelengths are able to satisfy the three von Laue conditions.
In the last section of his part, "General Summary," von Laue argues that the observed interference phenomena could not have been produced by particle rays. Essentially, an incoming particle can strike only a single atom at a time and thus not stimulate a coordinated emission from rows of atoms, as can a plane of incoming waves all in phase with each other. Significantly, von Laue was at least as concerned with proving the wavelike nature of X-rays as he was with developing a new tool to measure the atomic spacings of solids. In retrospect, the latter has been far more important.

In the experimental part of the paper, Friedrich and Knipping begin by describing their apparatus. It is extremely important that the incoming X-ray beam be narrow, so that all incident waves travel the same distance to the crystal and thus be in phase with each other upon arrival there. Also important is that the various pieces of equipment be carefully lined up. The experimenters must be assured that the beam of X-rays, which is invisible to their eyes, properly makes its lightning-speed journey through all the collimating shutters and pinholes in order to strike the crystal in the bull's-eye.

I find it surprising and quaint that the crystal is attached to the goniometer (a device that can rotate the crystal) with common wax, although this substance is still used. That the exposure time took as long as hours, and sharp diffraction spots were still seen, seems extraordinary. Any shaking of the apparatus during the long exposure, a slight twisting of the crystal relative to the incoming X-ray beam, would have completely destroyed the delicate interference pattern and produced a dim blur on the films.

Several aspects of Figures 2 and 3, the key results, are worth noting. First, many diffraction spots on the actual photographic film were too dim to show up well in the reproduction of Figure 2 but are indicated in the schematic diagram of Figure 3. Second, the spots have a fourfold symmetry. That is, if we rotate the diagram by ninety degrees, it looks like the original. This high degree of symmetry is both characteristic of the diffraction process in general and also revealing of the particular symmetry of the zinc sulfide crystal under examination. Friedrich and Knipping consider their results to be "beautiful proof" of the orderly arrangement of atoms in a crystal. The positions of the various spots, using von Laue's three conditions, yield information about the incoming wavelengths and size of the unit cell. Von Laue, Friedrich, and
Knipping have achieved humankind’s first glimpse into the atomic world of a crystal.

A mere two years after his paper of 1912, Max von Laue was awarded the Nobel Prize—one of the shortest intervals between discovery and prize of any Nobel. The importance of the work was instantly recognized. As early as 1913, the British physicist William Lawrence Bragg greatly improved upon von Laue’s mathematical method and, with his father William Henry Bragg, used the new calculations and experiments to give the first detailed analysis of crystals. For this work, father and son Bragg also won the Nobel (the only father and son team to do so). In his Nobel Prize lecture, the younger Bragg begins by declaring: “You have already honoured with the Nobel Prize Prof. von Laue, to whom we owe the great discovery which has made possible all progress in a new realm of science, the study of the structure of matter by the diffraction of X-rays.”

The year of his great discovery, von Laue was appointed professor of physics at the University of Zurich, and later, in 1919, the same exalted position at the University of Berlin. As a person, von Laue was highly respected for his character and judgment, and for several decades he had great influence in directing German science. However, he detested the National Socialist Party and Hitler’s regime. In the middle to late 1930s, when Einstein and his “Jewish physics” were denounced by the Nazis, von Laue was practically the only German physicist who continued to support Einstein. During World War II, rather than support the German war effort, von Laue instead wrote a history of physics, which appeared in four editions and seven translations. The father of X-ray diffraction also loved speed. He routinely traveled at high speed on a motorbike to his lectures and, later, at high speed in cars. At age eighty, while driving at high velocity to his laboratory, he had a fatal collision with a motorcyclist.

Because almost all solid matter exists in crystalline form at sufficiently low temperatures, X-ray diffraction has become a far-ranging method of analysis, hailed by chemists and biologists alike as an essential tool for understanding the structure of matter. For example, a crucial step in the determination of the double-helical structure of DNA in 1953 was the X-ray diffraction work of Rosalind Franklin. In 1960, Max Perutz used X-ray diffraction to determine the structure of hemoglobin, the first protein molecule to be unraveled (along with its smaller cousin myoglobin-
bin). Today, almost all biochemical laboratories use X-ray diffraction techniques to uncover the spatial structure of organic molecules.

When I recently visited a laboratory at Brandeis University one morning, a young graduate student rushed up to me, without knowing who I was, and blurted out that he had just decoded the structure of some complex organic molecule with only half of the data. Apparently, he had been working all night. His eyes were bloodshot, his hands trembled. Employing X-ray diffraction and analyzing the interference patterns with a computer, he had an ironclad fit to his molecule after using only a portion of the available information—just as a crossword puzzle can often be finished without the use of all the clues. There is only one way the letters fit together to make words, one inescapable arrangement. "How could this be?" he asked, with confusion, excitement, and awe. And I was equally awed, awed that there is a miniature world underneath our gaze, a hidden world that truly exists, a world of both beauty and logic.
INTERFERENCE PHENOMENA WITH RÖNTGEN RAYS

W. Friedrich, P. Knipping, and M. von Laue

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THEORETICAL PART

M. von Laue

Introduction

BARKLA'S RESEARCH IN THE LAST FEW YEARS (C. G. Barkla, Philosophical Magazine, 2 B. 22, pg. 398, 1911) has shown that Röntgen-rays experience diffraction in matter similar to diffraction of light in translucent materials. Röntgen-rays also, however, induce the atoms of the material to send out spectrally homogeneous fluorescences, which are totally characteristic for the substance.

In addition, in 1850 Bravais introduced into crystallography the theory that atoms in a crystal are ordered in a lattice. If Röntgen-rays are really composed of electromagnetic waves, then one could assume that the lattice would produce interference by free or forced vibrations [of the electrons in the atoms], leading, specifically, to interference patterns of the same nature as those that are known in optical interference spectra. The constants of this lattice [distances between neighboring atoms] can be calculated from the molecular weight of the crystallized compound, its density, the number of molecules per gram equivalent, and crystallographic data. One always finds for these constants an order of magnitude of 10^-8 centimeters, while the wavelength of the Röntgen-rays are of the order of 10^-9 centimeters, as shown by Walter and Pohl (B. Walter and R. Pohl, Annalen der Physik, vol. 25, pg. 715, 1908; vol. 29, pg. 331, 1908), Sommerfeld (A. Sommerfeld, Annalen der Physik, vol. 38, pg. 473, 1912), and Koch (P. P. Koch, Annalen der Physik, vol. 38, pg. 507, 1912). A complication in these observations is that a 3-fold periodicity appears in these lattices, while with optical [one-dimensional] lattices, there is only one direction, and at most two in a [two-dimensional] cross-lattice.
Friedrich and Knipping have tested the above hypothesis at my instigation. They will describe these experiments and results themselves in the second part of this paper.

The Theory and Its Quantitative Comparison with Experiment
We would like to express the above thought mathematically. The midpoint positions of an atom are determined through the rectangular coordinates, \( x, y, z \). We will consider the most common crystal space group, that is the triclinic lattice [unit-cell]. The edges of the elementary parallelepiped could therefore have any length and any angle between them. By choosing particular values of lengths and angles, one can get to any other type of lattice [unit cell]. Let us denote the length and direction of these edges by the vectors \( \mathbf{a}_1, \mathbf{a}_2, \) and \( \mathbf{a}_3 \). Then the midpoint of an atom lies at

\[
    x = ma_1 + na_2 + pa_3,
    
    y = ma_1 + na_2 + pa_3,
    
    z = ma_1 + na_2 + pa_3,
\]

where \( m, n, \) and \( p \) are integers.

For a single atom, we will make the assumption that its vibrations are purely sinusoidal. Needless to say, this assumption may not be any more correct than it is in optics. However, just as in optics, one can describe spectral inhomogeneous rays [not all of the same wavelength] through Fourier analysis. The wave coming from any one atom can then be described at any distance from the atom through the expression

\[
    \psi \exp\left(\frac{-ikr}{r}\right),
\]

where \( r \) is the radius vector from the atom to the observation point, \( \Psi \) is a function of the direction, and \( k = 2\pi/\lambda \), where \( \lambda \) is the wavelength of the Röntgen-ray.

If the direction of the primary [incoming or undeflected] Röntgen-ray is denoted by \( \alpha_0, \beta_0, \) and \( \gamma_0 \) [cosines of the angles made with the \( x, y, \) and \( z \) axes], then the amplitude of the primary ray is the superposition [summed over all atoms]

\[
    \psi \exp\left[\frac{-ik(r + x\alpha_0 + y\beta_0 + z\gamma_0)}{r}\right].
\]
THE DISCOVERIES

If we then let the scattered ray have direction \((\alpha, \beta, \text{and} \gamma)\), then

\[
r = R - (x\alpha + y\beta + z\gamma),
\]

and the scattered ray has the amplitude [summed over all values of \(m, n, \text{and} p\)],

\[
\psi \frac{\exp(-ikR)}{R} \sum \exp[ik[x(\alpha - \alpha_0) + y(\beta - \beta_0) + z(\gamma - \gamma_0)]].
\]

... In the special case where all three edges of the lattice [unit-cell] have the same length and are perpendicular, so that we can align the coordinate axes with these directions, and the incident Röntgen-ray travels in the \(z\) direction, then the equations simplify to:

\[
a_{1x} = a_{2y} = a_{3z} = a,
\]

with all the other \(a\) components zero, and

\[
\alpha_0 = 0, \quad \beta_0 = 0, \quad \gamma_0 = 1.
\]

The condition for maximum intensity [at the observation point] then reads:

\[
\alpha = h_1\lambda/a, \quad \beta = h_2\lambda/a, \quad 1 - \gamma = h_3\lambda/a,
\]

where \(h_1, h_2, \text{and} h_3\) are integers.

On a photographic plate with which the [scattered] rays interact, the curves \(\alpha = \text{constant}\) and \(\beta = \text{constant}\) are hyperbolae whose midpoint lies at the point of impact of the primary Röntgen-ray. If only the first two relations are satisfied [for \(\alpha\) and \(\beta\)], then one sees the well known [two-dimensional] cross-lattice spectrum, in which in every crosssection of two hyperbolae there appears an intensity maximum. The curves \(\gamma = \text{constant}\) choose from the cross-lattice spectrum those points that appear in Figures 2 and 3. ... .

One has to be careful to recognize that any lattice is not uniquely divided into elementary parallelepipeds but can be sorted into an infinite number of these shapes. In a regular lattice, for instance, one can dissect such parallelepipeds into many other [unit cells]. In a cubic array, for example, any side is the diagonal of another cube, and thus the principal directions have a two-fold symmetry axis. The intensity maxima
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(α, β, and γ), then

\( \beta - \beta_0 + z(\gamma - \gamma_0) \).

f the lattice [unit-cell] have

\( \theta = 1. \)

he observation point] then

\( -\gamma = h\lambda/a, \)

cattered] rays interact, the

\( \gamma = h\lambda/a, \)

tercepted. The intensity maxima

must therefore be consistent with different perspectives of a cube. In fact, Figures 2 and 3 show that the spots order themselves in a circle around a two-fold axis. Here, one has irradiated along the axis of a regular crystal and the photographic plate stands perpendicular to the axis.

What we can see is that the theory can be fitted to a four-fold symmetric description under the assumption that there are multiple wavelengths from 0.038a to 0.15a. Since a is equal to \( 3.3 \times 10^{-8} \) centimeters for zinc sulfide, the wavelengths must therefore occur in the interval from \( 1.3 \times 10^{-3} \) to \( 5.2 \times 10^{-3} \) centimeters.

General Summary

Let’s discuss at the end, without any reference to the formulae, the question of how these experiments relate to the wave nature of Röntgen-rays. That the diffracted rays have a wave character is shown by the sharpness of the intensity maxima, which are easy to understand from the interference phenomenon but not easy to understand from the corpuscular assumption [the assumption of the finite size and materiality of the atom]. [The wave character of Röntgen-rays is also demonstrated by] the ease with which the rays go through the material, only possible for the fastest β-rays.

Nevertheless, one could doubt the wave nature of the primary rays. Imagine, therefore, that the atoms of the crystal are stimulated by a particle ray. The particle nature of Röntgen-rays, which is assumed by many researchers, can be included here under the definition of particle rays. Coherent diffraction can only arise from rows of atoms which are hit by the same particle and are parallel to the z direction. Atoms that have a certain offset in the x – y direction are then stimulated from different particles. For these atoms, specific phase differences could not occur [for particle rays].

The breaking of the circle that appears [in Figure 2], therefore, cannot be understood based on the particle interpretation. In addition, the primary [undiffracted] and diffracted rays are so similar that one can deduce the wave nature of the latter from the wave nature of the former. Those diffracted rays that come from the crystal have a spectral homogeneity. The primary ray, instead, as consistent with the Bremsstrahlung experiments of Sommerfeld, must consist of nonperiodic waves [a mixture of wavelengths]. Undetermined at the moment is whether the periodic rays are initially determined by fluorescence in the crystal or whether they are already present in the primary ray and are merely sorted by the crystal.
EXPERIMENTAL PART

W. Friedrich and P. Knipping

For an experimental proof of the previously described theoretical ideas, a definitive experimental protocol was used after a number of attempts with a provisional apparatus, shown in Figure 1. Anticathode A in a Röntgen-ray tube produces Röntgen-rays in a narrow beam of approximately 1 millimeter in diameter passing through the shutters B₁ to B₄. This beam goes through crystal Kr, which is set onto goniometer G. Around the crystal in various directions and at various distances were photographic plates P, on which the intensity distribution was registered from the secondary reflections from the crystal. In order to prevent unwanted diffraction, a lead backstop S was used, and the whole detector was enclosed in a lead box K. We determined the exact line-up optically. Using a cathode meter whose end had a cross hair, we could determine the alignment of all of the pieces, including the beam, the

<table>
<thead>
<tr>
<th>Abstand</th>
<th>mm</th>
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<tbody>
<tr>
<td>Antikathode-Kristall</td>
<td>350</td>
</tr>
<tr>
<td>Kristall-P₁ resp. P₂ resp. P₃</td>
<td>25</td>
</tr>
<tr>
<td>Kristall-P₄</td>
<td>35</td>
</tr>
<tr>
<td>Kristall-P₅</td>
<td>70</td>
</tr>
</tbody>
</table>

Figure 1
lescribed theoretical ideas, after a number of attempts were made. Anticathode A in a narrow beam of approximately 0.1 mm diameter, passed through the shutters B₁ to B₅, is set onto goniometer G. The crystal is rotated at various distances and the distribution was recorded. In order to prevent the screen from being exposed to an X-ray beam, we could rotate the crystal, including the beam, the crystal, and the screen.

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**Figure 2**

○ \( \lambda_a = 0.0077 \)
○ \( \theta_a = 0.0663 \)
× \( \lambda_a = 0.0643 \)
○ \( \lambda_a = 0.1051 \)
+ \( \lambda_a = 0.193 \)

---

**Figure 3**
shutters, and the goniometer axis. A control experiment showed that this optical method translated to Röntgen-rays as well.

When the apparatus was properly aligned, the crystal was attached to the goniometer head with a small amount of wax. It was oriented in the beam with the aid of the cathode meter with cross hair. This very important calibration could be obtained within one minute [an angular measure equal to $\frac{1}{10}$ degree].

After we tried several detectors that were not suitable, we used Schleubner-Röntgen films, which were developed with Rodinal (1:15) and gave the best results. With a power of 2–10 milliamperes in the tube, 1–20 hours were required for exposure time.

Copper sulfate crystals were used as the control. In order to be sure that the reflections originated from the crystal structure of the copper sulfate, the crystals were pulverized, put into a small paper box, and the experiment was repeated.

We assumed that the observation of a regular system with a space group more simple than triclinic would be easier to interpret. Therefore, zinc blende, with which we had already made some attempts, was used and produced more intense secondary reflections.

The positions of the secondary spots [in Figure 2] are completely symmetrical with regard to the through [undeflected, or primary] beam. One can draw two pairs of mutually perpendicular symmetry axes in the figure. There are also two mirror planes. The fact that two symmetry axes and two mirror planes appear on the plate is one of the most beautiful proofs for the space group of the crystal. No other aspect beyond the space group needs to be considered.

If we turn the crystal in the primary beam, we must conclude from the previous experiments that the picture on the plate turns with it. In fact, such experiments are totally conclusive.

During the time of exposure, we noticed that the intensity of the primary beam fluctuated, particularly in older Röntgen-ray tubes, by as much as 6–12 fold. Nevertheless, as shown in the diagrams, the secondary spots remained sharp and unmoved.