How W. L. Bragg Invented X-ray Analysis

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Bragg was a scientific father to me. When Professor J. M. Thomas, the director of the Royal Institution, invited me to speak on the occasion of the centenary of his birth, I thought that Bragg would have liked me to describe to you some of his great discoveries, and to recall how he made them. They were his invention of X-ray analysis for finding the arrangement of atoms in crystals and his determination of the atomic structures of the rocks that make up the bulk of the earth's crust. They revolutionized the foundations of chemistry, mineralogy and metallurgy (W. L. Bragg, 1933, 1937; Sir Lawrence Bragg & Claringbull, 1965; Sir Lawrence Bragg, 1975).

I first met Bragg in Cambridge in the autumn of 1938 when he had just been appointed Rutherford's successor as Cavendish Professor of Experimental Physics. One day I burst into his room announcing proudly: 'I have received an honour that you can't match, I have had a glacier named after me'. 'I have one that you can't match' retorted Bragg, 'I have had a cuttlefish named after me'. He then told me that as a boy in Adelaide he had been a keen collector and found a new species which his seniors promptly named *Sepia Braggi.*

Bragg's father studied mathematics at Cambridge and finished 3rd Wrangler. On the strength of that he was appointed professor of mathematics and physics at the recently founded University of Adelaide when he was only 23, never mind that he had learnt no physics. He read Deschanel's Electricity & Magnetism on the boat going out and remained in Adelaide until 1909, when he moved back to England to become professor of physics at Leeds (Caroe, 1978). Willie Bragg was born in 1890; aged 15, he entered Adelaide University to read mathematics, and graduated there at 18. Next year he entered Cambridge University to read mathematics and physics. One day he wrote to his father at Leeds: 'Dear Dad, I'm so glad you liked the notes on Jeans. I got an awful lot from a Dane who had seen me asking Jeans questions. He was awfully sound, and most interesting, his name was Böhr or something that sounds like it'. That was the start of his lifelong friendship with Niels Bohr. Bragg took his Cambridge degree in 1911. He records in his biography: 'Then came a time of research in the Cavendish. It was a sad place. There

were too many young researchers (about 40) attracted by its reputation, too few ideas for them to work on, too little money, and too little apparatus. We had to make practically everything for ourselves, and even at that the means were meagre. There were a few senior people who had built little kingdoms for themselves with good equipment, but most of us were breaking our hearts trying to make bricks without straw. J. J. Thomson did his best to think of ideas for us all and guide us, but there were too many of us, and he was the only leader of research. C. T. R. Wilson (the inventor of the cloud chamber) liked doing everything on his own, and no other member of the staff was interested in research'. (Unpublished memoirs.)

After a frustrating year he joined his family on the Yorkshire coast for the summer holidays and found his father excited about a paper by Friedrich, Knipping & Laue that had just appeared in Munich. Bragg father had regarded X-rays as 'minute bundles of energy, tiny entities which move like material particles, but with the speed of light'. On the other hand, Max von Laue, a theoretical physicist at the University of Munich, believed that they were electromagnetic waves. It occurred to him that the wavelength of X-rays might be of the same order as the distance between atoms in crystals, in which case crystals would act as diffraction gratings for X-rays. This prediction was verified by W. Friedrich & P. Knipping by the discovery of X-ray diffraction patterns given off by crystals of copper sulfate, zincblende and other simple compounds (Fig. 1) (Friedrich, Knipping & Laue, 1912). Bragg father thought the Germans' X-ray patterns might have been due, not to diffraction, but to neutral particles running down different channels in their crystals. On returning to Cambridge the son continued to mull over von Laue's results and soon convinced himself that they must be due to diffraction. To his father he wrote: 'I have just got a lovely series of reflections of the rays in mica plates with only a few minutes' exposure! Huge joy' and he signed himself: 'Your affectionate son, W. L. Bragg'. Those were formal days. And the father wrote: 'My dear Rutherford, my boy has been getting beautiful X-ray reflections from mica sheet just as simple as the reflections of light in a mirror',

but in Cambridge the son was teased for having disproved his father's corpuscular theory when he focused X-rays by reflecting them from a bent sheet of mica (Fig. 2; taken by Bragg in 1912).

Laue had assumed the atoms in his crystal of zincblende to lie at the corners of a cube; he argued that if these atoms scattered X-rays, the diffracted X-rays would emerge from the crystal in directions where atoms lay an integral number of wavelengths apart, so that their scattering contributions reinforced each other. Laue himself noticed that there was something wrong with this interpretation, because there were many directions where reinforcements of X-rays diffracted by crystals of zincblende should have occurred, but the relevant spots were absent; he tried to explain this by assuming that the X-rays consisted of only five distinct wavelengths that the crystal lattice had picked out.

On 11 November 1912, only four months after he had first heard of Laue's papers, Bragg read a paper to the Cambridge Philosophical Society with the correct interpretation of the German results (W. L. Bragg, 1913a). He describes his success as 'an interesting example of the way in which apparently unrelated bits of knowledge click together to suggest something new. J. J. Thomson had lectured to us on the pulse theory of X-rays, which explained them as being electromagnetic pulses created by the sudden stopping of electrons. C. T. R. Wilson, in his brilliant way, had talked about the equivalence of a formless pulse and a continuous range of 'white' radiation. Pope and Barlow had a theory of crystal structure, and our little group had an evening meeting when Gossling read a paper on this theory. It was the first time that the idea of a crystal as a regular pattern was brought to my notice. I can remember the exact spot in the Backs where the idea suddenly leapt into my mind that Laue's spots were due to the reflection
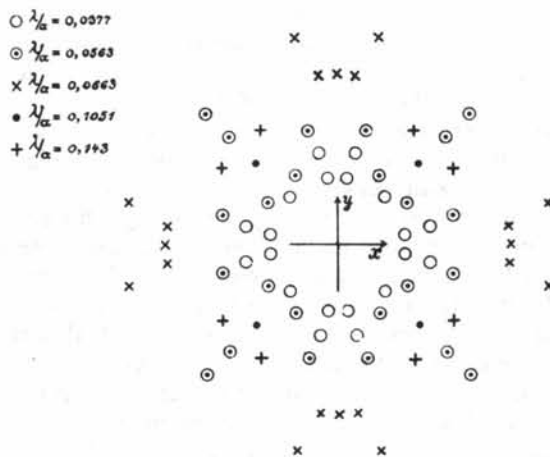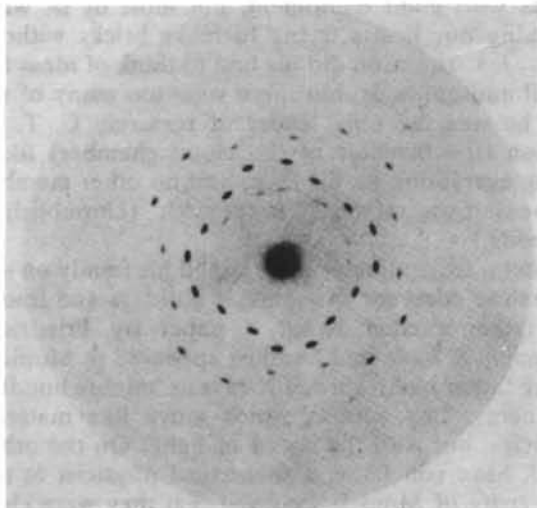

Fig. 1. Friedrich, Knipping and Laue's X-ray diffraction picture of zincblende, taken with the X-ray beam along one of the cube axes, together with their assignment of the spots to five distinct wavelengths (Friedrich, Knipping & Laue, 1912).
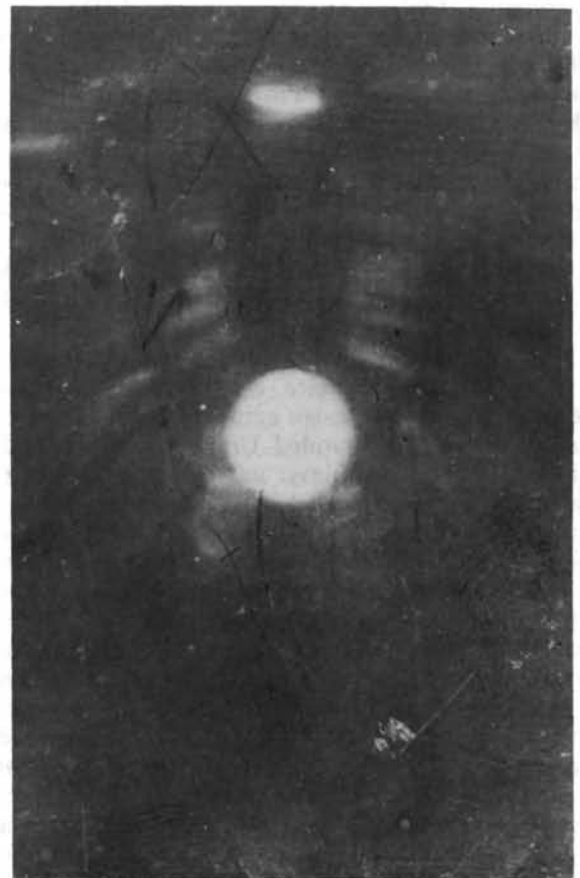

Fig. 2. Focused reflexion of X-rays from a bent sheet of mica taken by W. L. Bragg in 1912. (Courtesy of the Cavendish Laboratory.)

of X-ray pulses by sheets of atoms in the crystal'. (Unpublished memoirs.)

Bragg noticed that spots which were round when his photographic plate was close to the crystal became elliptical as the plate was moved further away. By a remarkable feat of imaginative insight Bragg realized that such a focusing effect would arise if the X-rays were reflected by successive atomic planes (Fig. 3), and he reformulated von Laue's conditions for diffraction into what became known as Bragg's law, which gives a more direct relationship between the crystal structure and its diffraction pattern ($n\lambda = 2d \sin \theta$). He then noticed something else. The German group had tilted the crystal away from its symmetrical position by 3°. If the X-rays had consisted of five discreet wavelengths as Laue believed, then the spots should have disappeared as the conditions for diffraction for the planes from which these wavelengths were reflected no longer held true. In fact the same spots moved by 6° and changed in intensity. This led Bragg to recognize that sets of parallel lattice planes selected from a continuous spectrum (or pulse, as he called it) those wavelengths which corresponded to integral multiples of the path

difference between reflexions from successive atomic planes, so that each Laue spot could be made up of several harmonics of some selected wavelength. Finally, he demonstrated that the presence of spots with certain combinations of indices and the absence of others in the X-ray diffraction pattern of zincblende could be accounted for by assuming a face-centred rather than a primitive cubic lattice. With that assumption the entire diffraction pattern fell into place (Fig 4; W. L. Bragg, 1913a).

Why did this 22 year old student succeed in correctly interpreting the diffraction pattern predicted and discovered by an accomplished theoretician eleven years his senior and two experimental physicists? Bragg himself modestly attributes it to a 'concatenation of fortunate circumstances', but his brilliant paper soon convinces you that its success owed more to Bragg's astute powers of penetrating through the apparent complexities of physical phenomena to their underlying simplicity.

Bragg's first paper was quickly followed by another, written in collaboration with his father, on their newly developed X-ray spectrometer, and a third, written by himself alone, solving the structure of common

L   Lead Screen
C   Crystal
P_1 P_2 Positions of Photographic Plate
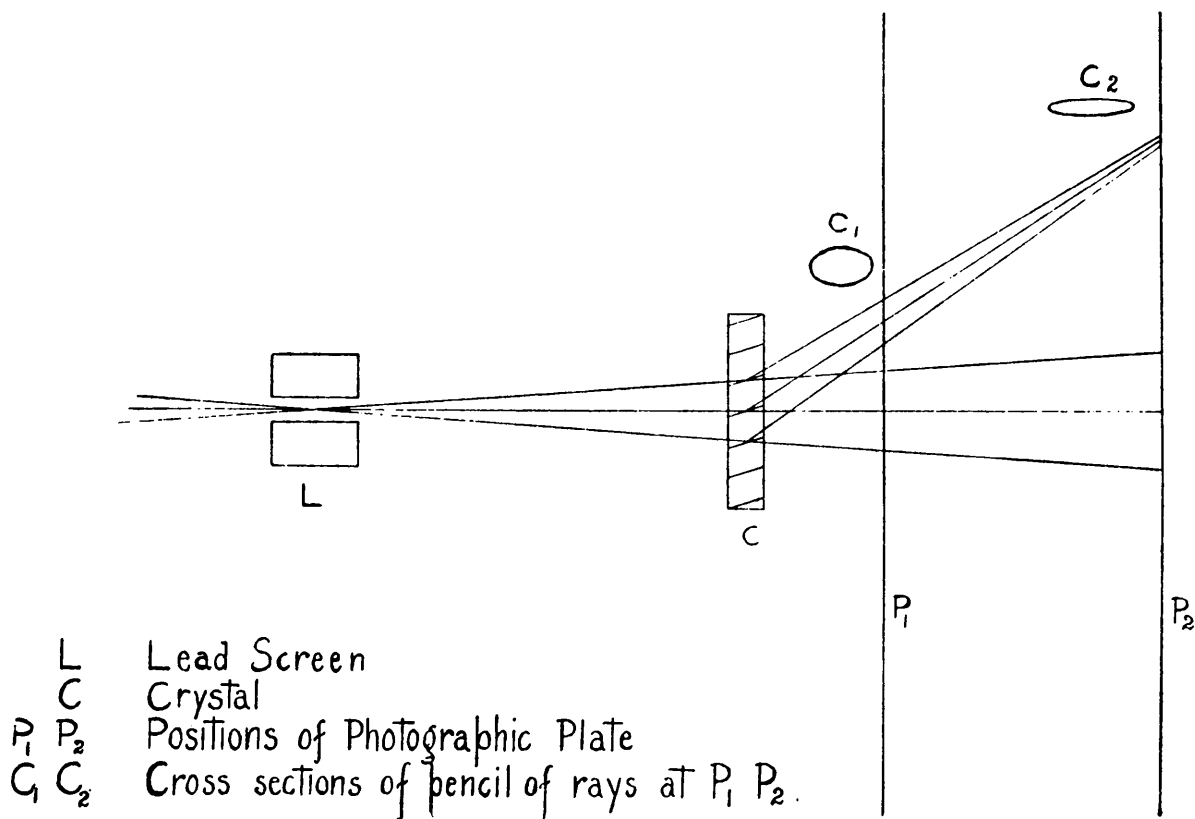C_1 C_2 Cross sections of pencil of rays at P_1 P_2.

Fig. 3. Change of shape of the X-ray reflections as the photographic plate was moved away from the crystal. Reflexions that were round when the plate was near the crystal became drawn out in the horizontal direction further away. Bragg pointed out that reflexion by the lattice planes of an incident cone of X-rays of continuously varying wavelength would come to a focus in the vertical direction, but would spread out in the horizontal direction (W. L. Bragg, 1913a).

salt and showing how the Laue pictures of several simple minerals could be indexed (W. L. Bragg, 1913b). There follows the structure of diamond, solved, as he relates, largely by his father (W. H. Bragg & W. L. Bragg, 1913), and the structures of fluorspar, zincblende, iron pyrites, calcite and dolomite solved by himself alone (W. L. Bragg, 1914a). Finally, on 16 July 1914, he communicated a paper on the structure of metallic copper (W. L. Bragg, 1914b). In view of this published record and the fact that for most of the relevant period the father
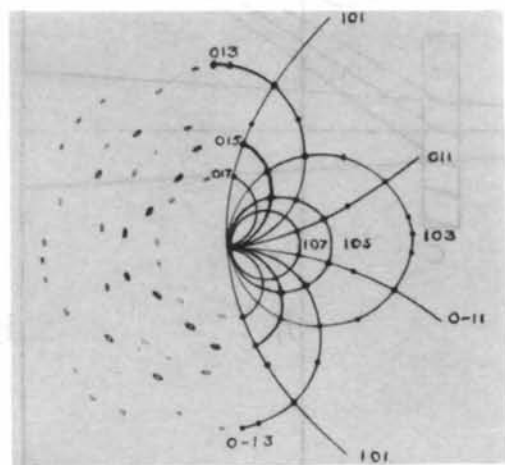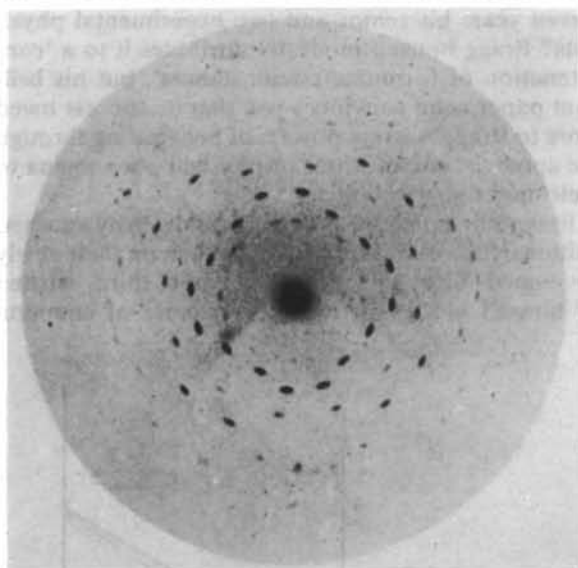

Fig. 4. W. L. Bragg's re-interpretation of the Germans' X-ray diffraction photograph of zincblende. He indexed the reflexions by assigning a face-centred cubic lattice to zincblende and a continuous spectrum to the X-rays. He showed that the reflexions lie on the intersections of the photographic plate with a series of cones, each cone containing the reflexions from planes parallel to a zone axis (W. L. Bragg, 1913a).

was at Leeds and the son at Cambridge, it seems hardly believable that the scientific public tended to attribute most of the credit for these discoveries to the father, sometimes with the undertone that the son had cashed in on the father's success. The son must have suffered a great deal from these thoughtless and lazy judgements. Lazy, because people could not be bothered to read the literature.

Bragg wrote many years later: 'Inevitably the results with the spectrometer, especially the solution of the diamond structure, were far more striking and far easier to follow than my elaborate analysis of Laue photographs, and it was my father who announced the new results at the British Association, the Solvay Conference, lectures up and down the country and in America, while I remained at home'. (Unpublished memoirs.) E. N. da C. Andrade wrote: 'It was always a delight to his hearers to note the affection that came into Sir William Bragg's voice when, in lectures, he found occasion to deal with some one or other piece of work which had been carried out by "my boy" (Andrade, 1943). But the 'boy's' reaction to this patronizing was: 'My father more than gave me full credit for my part, but I had some heart-aches.'

So their great discoveries, which brought them the Nobel Prize for Physics in 1915, are said to have strained relationships between them for the rest of their lives. In his many lectures on the development of X-ray analysis W. L. Bragg was fond of defining the exact roles played by himself and his father, but he never hinted at those strains until a few days before his death when he wrote to me: 'I hope that there are many things your son is tremendously good at which you can't do at all, because that is the best foundation for a father–son relationship'.

In most of the earliest structures of elements or simple compounds solved by the Braggs, crystal symmetry had so restricted the choice of atomic arrangements that only very few atomic parameters were left open. For example, the structure of diamond, published in *Proc. R. Soc. London* by 'Professor W. H. and Mr. W. L. Bragg' in 1913, was determined like this. The crystals were cubic. The presence on the Laue photographs of certain spots and the absence of others showed that the atoms of carbon must lie on a face-centred cube. The length of the cube edges could be measured from the angles at which the diffracted rays emerged. This gave the volume of the cube. The volume multiplied by the density of the crystals showed that it contained eight carbon atoms rather than four. Therefore there must be two sets of four carbon atoms, each occupying the corners and face centres of a cube. How far were they shifted relative to each other? This was the only unknown parameter. The Braggs showed that it can be deduced simply from the orders of reflexion that are reinforced and those that are extinguished by interference (W. H. Bragg & W. L. Bragg, 1913).

The unravelling of the structures of minerals containing several different kinds of atoms presented challenging new problems that could not be solved simply by looking for present and absent reflexions. Bragg described his ingenious new methods for solving such structures in a seminal paper on *A technique for the X-ray examination of crystal structures with many parameters*, published with J. West in *Zeitschrift für Kristallographie* in 1928, and in the following paper on their application to diopside (Bragg & West, 1928; Bragg & Warren, 1928).

In the 20's and 30's most crystallographers recorded the X-ray diffraction patterns photographically, which told them the *relative* intensities of the X-ray reflexions. They were content with qualitative data, but Bragg, together with R. W. James and C. H. Bosanquet, began his postwar research at Manchester with the introduction of quantitative ones. They used an X-ray spectrometer, the forerunner of today's diffractometer, with which they recorded the *absolute* intensities of the X-ray reflections, *i.e.* the fraction of the incident intensity diffracted by the crystal. This provided them with far more meaningful data for solving structures and testing whether they were cor-

rect than those used by most other workers in the field (Bragg, James & Bosanquet, 1921).

Diopside is a silicate mineral that forms crystals believed to contain molecules of $CaSiO_3$ and $MgSiO_3$. In 1928 solution of its structure seemed a more formidable undertaking than anything done before, because it involved the determination of 14 independent parameters. Compare this with the 36 000 atomic parameters of the structure of the photochemical reaction centre for which H. Michel, J. Deisenhofer & R. Huber shared the Nobel Prize for Chemistry in 1988.

Diopside crystals are monoclinic with a face-centred unit cell that contains four molecules of $CaMg(SiO_3)_2$. Crystal symmetry restricts the calcium and magnesium atoms to four alternative positions but does not tell which is the right one; the silicon and oxygen atoms can lie anywhere.

The way to find the silicon atoms may be illustrated by considering the 804 reflexion which is too weak to observe (Fig. 5). There is a contribution of +47 from the four Ca and Mg atoms, another of between +44 and −44 from eight silicon atoms, and another of between +41 and −41 from twenty-four oxygen
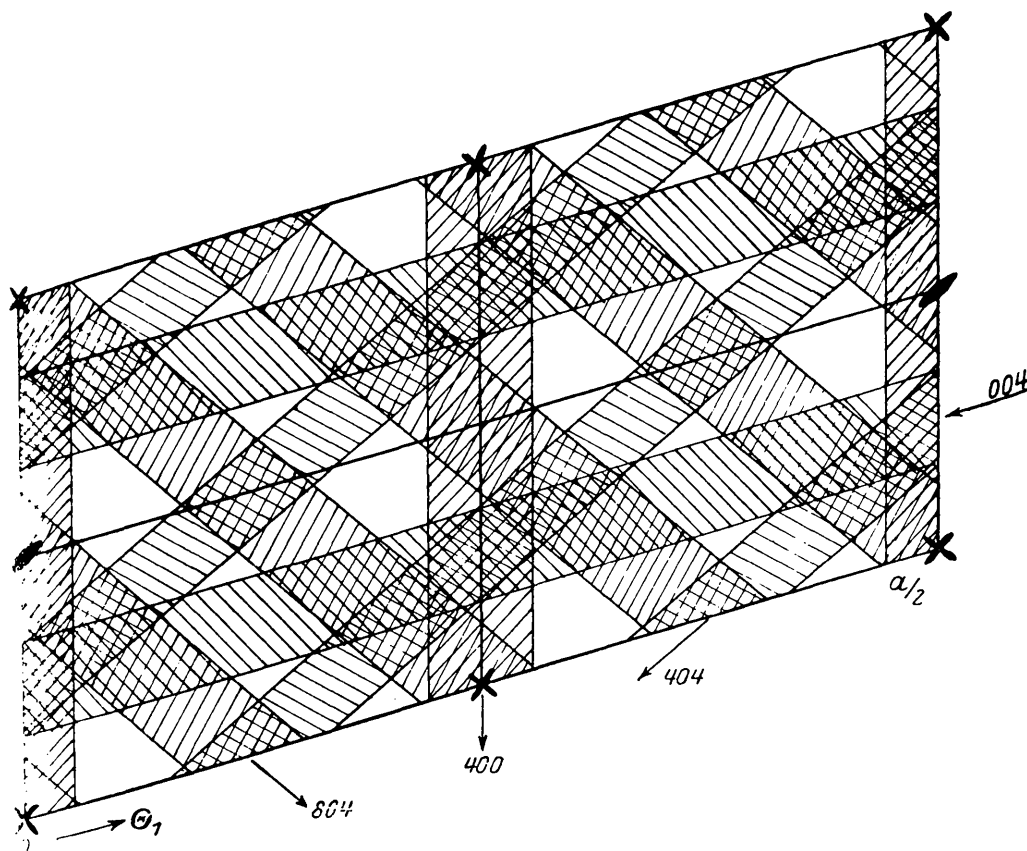

Fig. 5. Unit cell of diopside projected along the *b* axis with shaded areas forbidden to the silicon atoms. The crosses mark centres of symmetry, the ellipse signs twofold rotation axes (Bragg & Warren, 1928).

atoms. The oxygen contribution is unknown within these limits. The silicon atoms cannot be making a positive contribution to $F(804)$, for in that case, even if all the oxygen atoms were making negative contributions, there would be a positive resultant which would be observed. On the other hand, a negative contribution of any amount by silicon is possible. The planes (804) are now drawn and parallel strips are shaded in which atoms making positive contributions might be situated. These areas are forbidden to the silicon atom. Repetition of this procedure for many reflexions led Bragg to the exclusion of all but four possible positions for the silicons (Fig. 6). He then found that, in three of them, neighbouring symmetry-related atoms would be so close together that they would overlap. This left 4 and 4' as the only possible silicon positions. Knowing where the silicons were, Bragg was now able to decide which of the four possible positions for Ca and Mg is the right one. The 14,0,0 reflexion was so strong that all the atoms had to scatter in phase (Fig. 6). If the Ca and Mg atoms were at either B or D they would scatter out of phase with the Si atoms; hence these two positions could be excluded. 406 is equally strong. If the Ca and Mg atoms were at either A or B they would also scatter out of phase with the Si atoms. Hence the only positions not excluded were C which lie on the axes of twofold symmetry.

That was easy! The difficulty began with finding the positions of the six oxygen atoms, so that the sum of their scattering contribution, together with those from the Ca, Mg and Si atoms, equalled the observed amplitude of each of a hundred reflexions. It was an intricate game of chess where every move made to satisfy agreement with the observed amplitude of one reflexion could spoil the agreement with ten others. If the calculated amplitude of only a single one of the 100 reflexions came out radically different from the observed amplitude, then your structure was wrong and you had to start all over again. But Bragg got it right (Fig. 7).

Was the answer worth such exertion? Or did Bragg just play a sophisticated intellectual game, like some of the people working on artificial intelligence or topology today? In the notes that Bragg left me with his collection of reprints, he wrote: 'The analysis of diopside was a turning point in our ideas about silicate structures. I showed that the "SiO₃" which appears in the chemical formula does not represent SiO_3 acid groups but a string of SiO_4 groups joined
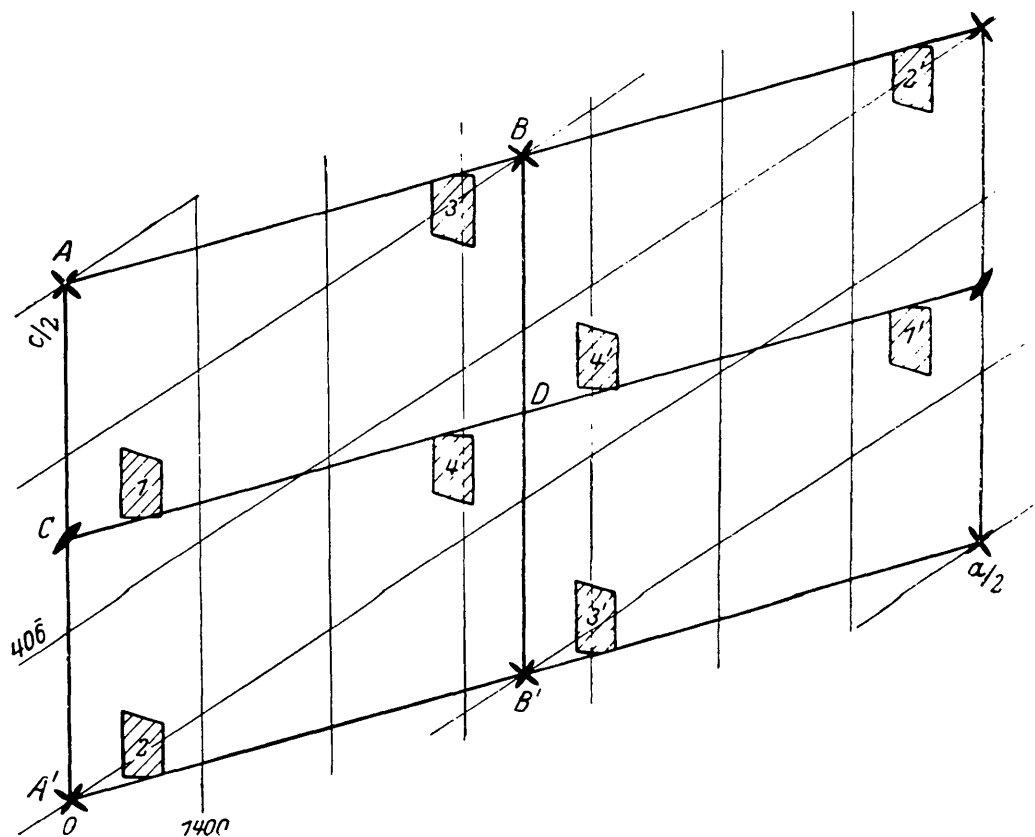

Fig. 6. Unit cell of diopside showing areas allowed to the silicon atoms. A, B, C and D mark positions of the calcium and magnesium ions allowed by the crystal symmetry. The observed intensities of the 40$\bar{6}$ and 14,0,0 reflexions exclude A, B and D (Bragg & Warren, 1928).

by shared oxygen atoms. It was a crucial step in showing that silicon always occurs in a tetrahedral group of oxygen atoms'.

To appreciate the novelty of Bragg's results you have to put your mind back 70 or 80 years and ask what was the body of knowledge in inorganic chemistry and mineralogy in those days. In a lecture at the Royal Institution on 20 May 1927 Bragg said: 'Some of the earliest structures which were analysed caused us to revise our ideas of what was meant by the "molecule" of the chemist. In sodium chloride there appear to be no molecules represented by NaCl. The equality in numbers is arrived at by a chess-board pattern of these atoms; it is the result of geometry and not of the pairing of atoms'. How long did it take for these ideas to be accepted? The publication of Bragg's lecture in *Nature* drew an angry reply, entitled *Poor Common Salt*, from Henry Armstrong, the professor of chemistry at University College London.

'Some books are lies frae end to end', says Burns. Scientific (save the mark) speculation would seem to be on the way to this state! Thus on p. 405 of *Nature* of Sept 17 in a letter on Prof. Lewis's light corpuscles, the statement is made by the writer, that a 'speculation' by Prof. Lewis, about the quantum "is repugnant to common sense." Again, on

p. 414, Prof. W. L. Bragg asserts that "In sodium chloride there appear to be no molecules represented by NaCl. The equality in number of sodium and chlorine atoms is arrived at by a chess-board pattern of these atoms; it is a result of geometry and not of a pairing-off of the atoms." This statement is more than "repugnant to common sense." It is absurd to the nth degree, not chemical cricket. Chemistry is neither chess nor geometry, whatever X-ray physics may be. Such unjustified aspersion of the molecular character of our most necessary condiment must not be allowed any longer to pass unchallenged. A little study of the Apostle Paul may be recommended to Prof. Bragg, as a necessary preliminary even to X-ray work, especially as the doctrine has been insistently advocated at the recent Flat Races at Leeds, that science is the pursuit of truth. It were time that chemists took charge of chemistry once more and protected neophytes against the worship of false gods: at least taught them to ask for something more than chess-board evidence.

Henry E. Armstrong

I looked at textbooks published early in this century and tried to recall the lectures in inorganic chemistry that I attended as an undergraduate in Vienna. In
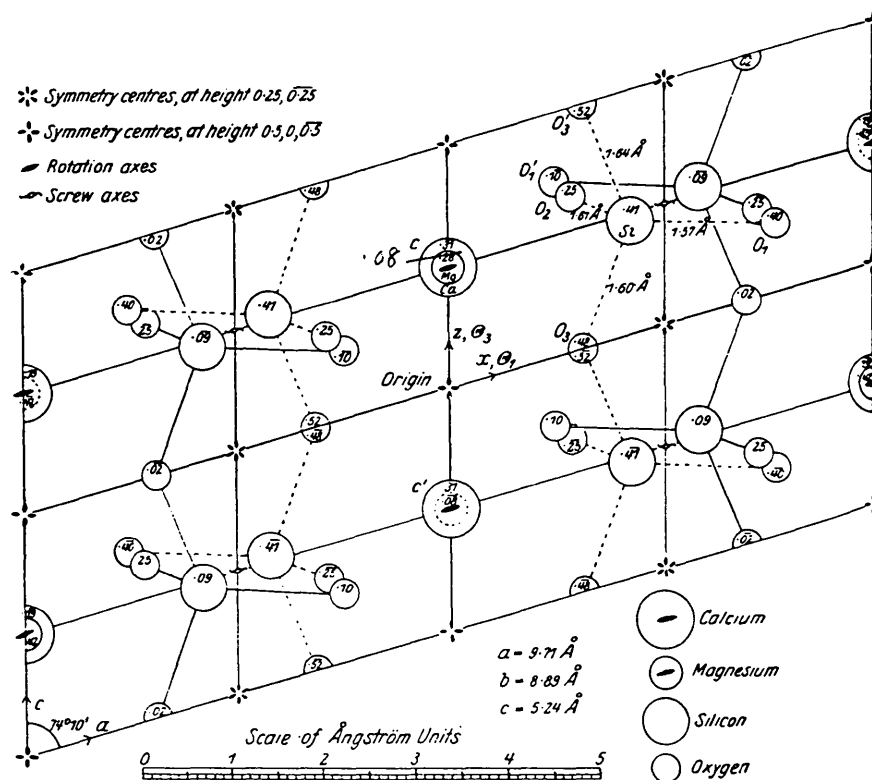
Projection of diopside structure on plane (010).

Fig. 7. Atomic positions of diopside projected along the *b* axis. The numbers give the *y* coordinates of the atoms (Bragg & Warren, 1928).

J. R. Partington's textbook of inorganic chemistry, published in 1925, twelve years after Bragg solved the structure of common salt, the question of the atomic arrangement of the sodium and chlorine atoms, their state of ionization or of the forces that hold the crystal together were never raised. Minerals were described by their morphology, and by their optical and chemical properties, but no one asked what held them together. Bragg said in his lecture: 'Stupendous chemical formulae have to be assigned in order to explain even approximately the proportions of the different elements in some well-known types of minerals'. For example, tourmaline was given the formula $H_6Na_2Fe_4B_6Al_3Si_{12}O_{63}$. Many such chemical formulae given in the textbooks turned out to be meaningless, like that of diopside. Partington's outdated section on silica reminded me of my viva with my Professor of Chemistry in Vienna, the formidable Ernst Späth, at the conclusion of my undergraduate courses. A few days beforehand, I heard that he had failed a girl because she could not tell him the different crystalline forms of silica. I quickly memorized them and duly recited them at the viva: α-quartz, left or right handed, below 575 °C, β-quartz from 575–800 °C; tridymite above 800 °C and crystoballite above 1470 °C. Späth purred contentedly and invited me to become his research student. He never wondered what atomic structures underlay these several forms, and he must have been unaware that X-ray analysis had shown them to be made up of tetrahedra of SiO_4 sharing corners, but stacked in different ways.

Few chemists took much notice of X-ray crystallography's new insights until 1939 when Pauling published *The Nature of the Chemical Bond*, and some ignored them until 1945 when A. F. Wells published his *Structural Inorganic Chemistry*. T. M. Lowry's textbook of inorganic chemistry, published in 1922, was a notable exception. It includes a section on the crystal structures that had been solved and points out that crystals of common salt do not contain molecules of sodium chloride, but ions of sodium and chlorine.

Bragg and his followers showed that most crystals of inorganic compounds do not contain discrete molecules, but a continuum of alternative positive and negative ions. The positive ones are small and surround themselves with the larger negative ones arranged at the corners of polyhedra so they are tightly packed and all electric charges are locally compensated. The silicates that form the bulk of the earth's crust are made up of SiO_4 tetrahedra that are either separate or share corners or edges, and their structures explain each mineral's strength or weakness. Thus Bragg's ingenious and immensely laborious puzzle solving made people understand for the first time the atomic structure of the ground we stand on, and that surely was worthwhile.

Was there an easier way? When Bragg's father delivered the Bakerian Lecture to the Royal Society in 1915, he suggested that the periodic repeat of atomic patterns in crystals could be represented by Fourier series (W. H. Bragg, 1915). 'If we know the nature of the periodic variation of the density of the medium, we can analyse it by Fourier's method into a series of harmonic terms. The medium may be looked on as compounded of a series of harmonic media, each of which will give the medium the power of reflecting at one angle. The series of spectra which we obtain for any given set of crystal planes may be considered as indicating the existence of separate harmonic terms. We may even conceive the possibility of discovering from their relative intensities the actual distribution of the scattering centres, electrons and nucleus, in the atom; but it would be premature to expect too much until all other causes of the variations of intensity have been allowed for, such as the effects of temperature, and the like'.

The American physicist R. J. Havighurst calculated a triple Fourier series to deduce the electron density distribution in a crystal of sodium chloride along the cube edges and the cube diagonals, using the absolute intensities measured by Bragg, James & Bosanquet (1921) (Havighurst, 1927).

Bragg extended the Fourier series to two dimensions. Each of the shaded stripes of his trial-and-error work on diopside now became a sinusoidal wave, *i.e.* a Fourier term. Symmetry dictated that each wave must have either a crest or a trough at the positions of the magnesium and calcium ions, and it was easy to decide which was right. The sum of all the waves took the form of a map that revealed the positions of the oxygen atoms even though these had
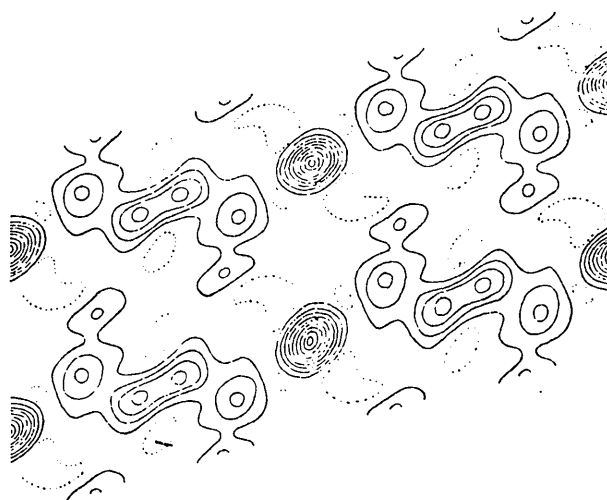

Fig. 8. Comparison of Fourier map calculated from the known positions of the calcium, magnesium and silicon ions alone, and the complete structure solved by trial. The lower peaks in the Fourier map coincide with the oxygens found by trial (W. L. Bragg, 1929).

not been used in deciding whether a crest or trough was to be assigned to any particular wave (Fig. 8; W. L. Bragg, 1929).

The amount of labour Bragg had to perform to calculate the Fourier projections of diopside on three principal planes was gigantic. For the projection on the *b* axis alone he had to calculate the value of each of 26 different terms at 288 separate points and then had to sum 7488 numbers. For the other two projections he had to sum 3360 and 6912 numbers respectively, or 17760 numbers in all. This was the birth of the Fourier projections which were used to solve hundreds of crystal structures for the next 30 years, until the advent of digital computers made it possible to calculate Fourier series in three dimensions.

Bragg's paper on *The Determination of Parameters in Crystal Structures by Means of Fourier Series* is by himself alone. He mentions no collaborators. How did he do all these tedious summations when adding machines had not yet been invented? We shall never know. Incidentally, reports of continual tension between himself and his father are belied by the final paragraph of that paper.

It is with great pleasure that I acknowledge my indebtedness to my father, Sir William Bragg, for

suggestions which materially contributed to the work described in this paper. At the time when I was following up the connection between our usual methods of analysis and the analysis by Fourier series, a connection briefly treated in the paper by Mr. West and myself, my father showed me some results which he had obtained by using relative values of the first few terms of two- and three-dimensional Fourier series to indicate the general distribution of scattering matter in certain organic compounds. It was largely as a result of his suggestions that I was encouraged to make all the computations for this two-dimensional series, using the extensive absolute measurements which we had made on certain crystals.

In notes that he left me, Bragg wrote: 'This paper should really have been written with my father. He produced a crucial idea about two-dimensional Fourier series; I happened to have all the experimental data which showed how much a series could be used. It was the first paper in which Fourier series were used for parameter determination'.

Bragg's application of the Fourier method to diopside required knowledge of the calcium, magnesium and silicon positions to determine whether any

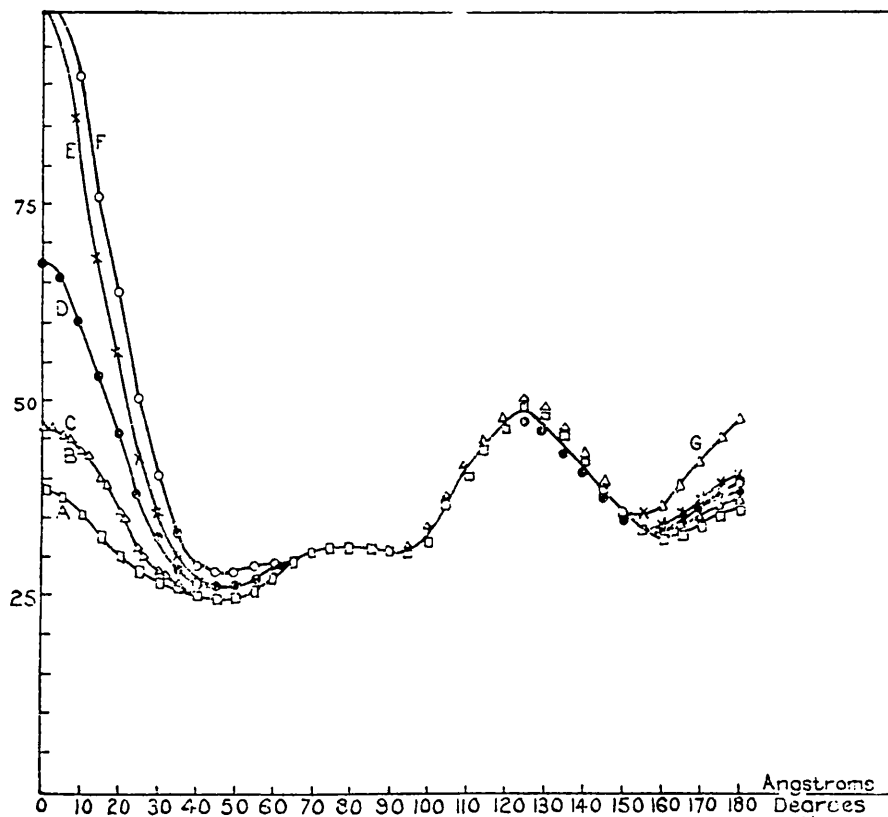Electron Distribution in Planes parallel to the (111) set.

Fig. 9. Fourier projections of the alums on the normal to (111). *A* $(NH_4)^+$; *B* and *C* K^+; *D* Rb^+; *E* Cs^+; *F* Th^+; *G* Cr^{3+}. The overlapping peaks below *G* represent Al^{3+}; the central peak $(SO_4)^{2-}$ (Cork, 1927).

particular Fourier term was positive or negative at the calcium plus magnesium positions. In 1927 Bragg's American postdoctoral student J. M. Cork showed that this ambiguity of sign can be solved by the method of isomorphous replacement with heavy atoms (Cork, 1927). The alums form an isomorphous series of the general formula $AB(SO_4)_2.12H_2O$ where A can be any alkali metal and B can be a trivalent metal such as aluminium. Cork determined the signs of the Fourier terms in a one-dimensional series by analysing the changes in intensity that substitution of one metal ion by another brought about in the reflexions from the (111) planes (Fig. 9). With the solution of the alums Bragg's school laid the foundation for the method of isomorphous replacement that I used 25 years later to solve the structure of haemoglobin.

Peter Medawar wrote that 'Every discovery, every enlargement of the understanding, begins as an imaginative understanding of what the truth might be' (Medawar, 1979). Bragg's success in solving structures was based on a remarkable imaginative insight into the workings of natural phenomena, especially those concerned with optics and the properties of matter. According to Karl Popper and Peter Medawar, research consists of the formulation of imaginative hypotheses that are open to falsification by experiment. This is exactly how Bragg went about finding where the atoms lay, but he combined imagination with a phenomenal amount of hard work. Popper and Medawar argue further that no hypothesis can ever be completely proved, but that it can only be disproved experimentally so that it gradually corresponds more and more closely to the truth. However, Bragg's structures are not preliminary approximations subject to revision; any student setting out to redetermine the structures of calcite, quartz or beryl will be disappointed.

T. S. Kuhn (1970) argued that science advances by a succession of paradigms, but the perusal of old textbooks of chemistry and mineralogy have convinced me that there was no paradigm for the atomic structure of solid matter before 1912. The results of X-ray analysis opened a new world that had not even been imagined before.

When reviewing scientific work I sometimes paraphrase people's papers, but when I tried to paraphrase Bragg's, I always found that he had said it much better. As everyone who has heard Bragg will remember, his superb powers of combining simplicity with rigour, his enthusiasm, liveliness and charm and his beautiful demonstrations conspired to make him one of the best lecturers on science that ever lived.

Bragg united C. P. Snow's two cultures because his approach to science was an artistic, imaginative one. He thought visually rather than mathematically, generally in terms of concrete models that could be either static, like his crystal structures, or dynamic,

like the interaction between crystals and electromagnetic waves or the order–disorder transitions and mobile dislocations in metals. His artistic gifts surfaced in his delicate sketches and water colours, and in his limpid prose (Phillips, 1979).

His scientific output in the 20's and 30's was prodigious, yet I am told that he was never rushed and always had time for his family, because his penetrating intellect and powers of concentration made all work easy. Instead of losing himself in a labyrinth of conflicting evidence which he would rarely bother to read, he would think of the best way interatomic forces could be satisfied to give stable structures.

Nowadays, cynics want us to believe that scientists work only for fame and money, but Bragg slaved away at hard problems when he was a Nobel Laureate of comfortable means. He was driven by scientific curiosity, by a compulsion to solve the problem in hand, and ambition that X-ray analysis which he created should develop to solve increasingly complex structures. He was not a public figure and he liked to do his work at home rather than in aeroplanes. So often men of genius are hellish to live with, but Bragg's was a genial person whose creativity was sustained by a happy home life; typically one would find him tending his garden, with Lady Bragg, children and grandchildren somewhere in the background, and before getting down to crystal structures, he would proudly demonstrate his latest roses.

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Investigation of Surface-Layer Structure of Single Crystals with Triple-Crystal X-ray Diffractometry

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Abstract

The possibilities of the X-ray triple-crystal diffractometry (TCD) method in studying the tails of rocking curves of both a perfect crystal and a crystal with a disturbed surface layer are shown. It was found that at large deviation angles (α) from the Bragg condition the pseudopeak of the TCD curves significantly exceeds the main peak. The thermal diffuse scattering in the monochromator crystal is discussed as one of the reasons for this effect. This phenomenon is also responsible for the violation of the $I(\alpha) \propto 1/\alpha^2$ dependence in double-crystal diffractometry (DCD). By measuring the intensities of the main peaks of TCD curves, it is possible to separate the diffuse and the coherent scattering components in the rocking curves obtained by DCD.

1. Introduction

Much attention has been paid in the last few years to the study of surface-layer structures by X-ray diffraction. It is well known that the shape of a rocking curve (RC) of a crystal with a disturbed surface layer changes with respect to that of an ideal crystal, due to the depth distribution of the lattice strain $\Delta d/d$ and the atomic disorder in the layer.

Several methods have been developed to fit the experimental rocking curves. For example, the method of computing directly the RC by the Takagi-Taupin equations (Burgeat & Taupin, 1968; Fukuhara & Takano, 1977), the method of integral characteristics (Afanasev, Kovalchuk, Kovev & Kohn, 1977; Kohn, Kovalchuk, Imamov & Lobanovich, 1981) and the methods based on the kinematical theory of X-ray diffraction (Kyutt, Petrashen & Sorokin, 1980; Speriosu, Glass & Kobayashi, 1979; Kohn, Prilepsky & Sukhodreva, 1984) are noteworthy. All these methods deal with the analysis of the angular dependence of the coherent-scattering components. However, most of the RC measurements are carried out by a double-crystal diffractometer arranged in the parallel non-dispersive ($n, -n$) setting, in which all the intensity scattered by the sample is collected. This intensity contains not only a coherent contribution but also a diffuse scattering, which modifies the RC shape. As will be shown by an example relating to the study of a surface-implanted layer, this effect can lead to either a distortion or an entire loss of information about the surface-layer structure. The study of samples with surface layers containing a lot of defects can be carried out effectively by the method of triple-crystal X-ray diffractometry (TCD). This method makes possible the separation of the coherent and diffuse contributions by analysis of the angular intensity distribution with the help of the third crystal (analyzer). Successfully used by Iida & Kohra (1979), the TCD method has been widely applied lately (for example, by Afanasev, Aleksandrov, Imamov, Lomov & Zavyalova, 1984; Cembali, Servidori, Solmi, Sourek, Winter & Zaumseil, 1986; Zaumseil, Winter, Cembali, Servidori & Sourek, 1987). Of course, the TCD method is more complicated and difficult in comparison with the double-crystal X-ray diffractometry (DCD) method. It is necessary to measure the entire TCD curve or, at least, the integral intensity of the main peak of this curve to obtain only one