TEACHING AND EDUCATION IN CRYSTALLOGRAPHY

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Teaching Diffraction with the Aid of Computer Simulations

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Abstract

A high degree of motivation and very effective learning can be achieved by the combination of multimedia presentations with computer simulations of structures and their corresponding Fourier transforms. Computer simulations of structures offer the unique advantage that students see both the structure and the resulting Fourier transform. Furthermore, since any type of structure can be simulated, a systematic approach to diffraction can be taught with maximum efficiency. The students can simulate their own structures, modify these and observe the corresponding changes in reciprocal space. In the course reported here, students are guided through a series of simulations covering diffraction by individual atoms and small aggregates, reciprocal-space geometry, convolution, modification of a structure, the crystallographic phase problem, inverse Fourier transformation, anomalous scattering, powder diffraction and disordered crystals. The course is supplemented by World Wide Web pages that guide self study and prompt the students to try out their own simulations and observe the effect in reciprocal space.

1. Introduction

A thorough understanding of diffraction and the mathematical formalism involved is a necessity for any crystallographer who has to deal with structure determination from diffraction experiments. In the experience of the authors, the teaching of diffraction techniques is often tedious. Many students face difficulties understanding the intricate mathematics of the Fourier transformation and the abstract concept of reciprocal space. A thorough development of the formulae describing the diffraction process is certainly a necessary part of any crystallography curriculum. This development, however, is abstract by itself and should be accompanied by several different exercises.

The first set of exercises consists of problems that the students have to solve. Standard textbooks list many problems, which we do not review here.

The second set of exercises consists of diffraction experiments themselves. No course can be complete without hands-on experiments with X-ray cameras or diffractometers. Several drawbacks to experiments with actual crystals exist. First, diffraction experiments pose a possible radiation hazard and need to be carried out under the close supervision of a trained member of staff. Second, the experiments are time consuming. Third, and very important, the students get to see only the result of the diffraction experiment. With the exception of high-resolution electron microscopy, the students cannot see the input into the Fourier transform, *i.e.* the crystal structure, directly. They have to accept the diffraction pattern as a result of the unknown structure. Last, not every simple model is available in the form of a crystal structure.

An alternative is offered by a diffraction technique that allows the students to observe both the structure and the corresponding diffraction pattern. Harburn, Taylor & Welberry (1975) and Glusker (1988) have used optical masks for this purpose. Optical masks are, however, not easily produced and represent only a crude simulation of atomic scattering factors. They are, furthermore, strictly two-dimensional sections of a crystal.

Computer applications allow a very different approach to teaching. With a properly interactive program, the students are given a tool to experiment with on their own. Modern multimedia applications allow the combined use of text, images and the spoken word. Some crystallographic teaching tools for diffraction have been described in the literature. Harris & Fitzgibbon (1989) described a program to represent the connection between real- and reciprocal-space geometry in a diffraction experiment in order to plan an optimal strategy for the experiment. *CELLX*, by Rogers (1993), interactively shows the contents of a unit cell and the corresponding intensity in reciprocal space. Programs like those are, however, limited to the geometrical relationship or to periodic structures. Welberry & Butler (1994) used structure simulations to calculate diffuse scattering. Separate programs are used for the structure simulation and the calculation of diffuse scattering to be displayed by plotting programs. The structure simulations are optimized for large crystals with extended defects. Furthermore, a correlation approach is used to create the defects, a concept that is beyond the scope of classes teaching diffraction.

Computer programs for teaching diffraction should be able to simulate both individual clusters of a few atoms and extended crystals. For teaching purposes, it is also desirable to calculate not only the intensity but also the amplitude, real and imaginary parts, and the phase angle of the Fourier transform. The resulting values should be displayed on screen or be written to a file in a format for rapid display by a third program. The program should also be easy to learn and portable to a variety of computers.

In our teaching approach, we provide the students with a systematic course ranging from individual atoms, through small aggregates to periodic crystals and finally powders and diffuse scattering. An important part of our teaching approach is the combined use of World Wide Web (WWW) pages and an interactive program for the structure simulations.

2. Computer simulations of structures

Computer simulations offer excellent teaching tools for diffraction. The students can visualize both the crystal structure and the diffraction pattern. Since any model structure can be simulated, a systematic approach to the different aspects of diffraction is easily possible. A high degree of motivation is achieved if the students can simulate their own structures.

There are two distinct ways of simulating a structure in the computer. Either the program maintains a list of atom positions and explicitly calculates the corresponding Fourier transform according to the standard formula for kinematic scattering,

$$F_h = \sum_{i=1}^{N} f_i \exp(2\pi i h r), \qquad (1)$$

or the electron density of the crystal is simulated within an array and the fast Fourier transform (FFT) algorithm is applied to calculate the corresponding diffraction pattern. Neder & Wildgruber (1989) and Rahman (1989) independently introduced these two approaches. A thorough review of the application of structure simulations to the interpretation of diffuse scattering is given by Welberry & Butler (1994).

The FFT approach has the advantage that the Fourier transform is calculated very rapidly. Several disadvantages remain. Since the scattering factor of each atom is usually represented by a numerical value assigned to a single position within the structure array, this method gives an accurate simulation of neutron scattering yet an unsatisfactory approximation to X-ray structure factors. The size of the array in relation to the unit cell predetermines the extent of reciprocal space calculated and limits the structures to rectangular unit cells. An extreme amount of computer memory is needed if a true three-dimensional structure is to be simulated.

In comparison, the only disadvantage of calculating the explicit Fourier transform is the increased computation time needed for the Fourier transform. There are several advantages. Since the structure is not limited to an arbitrary grid, the atoms can assume any position within the unit cell and the unit cell itself may taken any triclinic shape. The amount of memory needed for each atom is small and no restrictions apply to fully three-dimensional structures. By the use of tabulated form factors for the atoms, their contributions to the Fourier transform are represented accurately for X-ray and neutron scattering, including anomalous scattering. The intensity distribution, the real and imaginary part of the structure factor and its phase angle can be calculated in any section of reciprocal space with any desired resolution.

3. The program

The purpose of the program *DISCUS* (Neder, 1994; Proffen & Neder, 1996; Neder & Proffen, 1996) is to give the user a flexible tool to stimulate any crystal structure. The main purpose is to simulate defect structures and to calculate the corresponding diffuse scattering. It has proven to be a valuable tool in the interpretation of diffuse scattering and for refinement of defect structures. The program is, however, not limited to that task, but can be used to simulate perfect structures and also nonperiodic structures.

To guarantee flexible use of the program, *DISCUS* is controlled *via* a command language. There is no need for a predefined sequence of commands. All commands can be read from macro files and full on-line help is provided. *DISCUS* uses the explicit Fourier transform method to calculate the diffraction pattern. The program initially reads the asymmetric unit of a structure and expands this to one or several cells. Several tools are provided to modify the structure. Individual atoms can be added, deleted, moved, copied or have their chemistry changed. Three predefined defect types can be used to modify the whole crystal. These types are random thermal displacement, wave functions (displacement and density waves) and the introduction of a distribution function for extended defects (microdomains). A Fortran-style interpreter is built into the program and provides several free variables as well as variables that contain data about the structure. One can calculate expressions, program loops and logical expressions. These programming tools can be used to modify the structure to assume any type of defect.

4. Scope of the computer simulations

The following describes several simulations that have been found useful by the authors in teaching diffraction. The simulations have been grouped into:

4.1. *Basics*

The basic examples introduce the students to the program and show the diffraction patterns of individual and small groups of atoms.

4.2. *Reciprocal space*

These examples introduce the students to the concepts and geometry of reciprocal space.

4.3. *Convolution*

These simulations are used to explain the concept of the convolution theorem.

4.4. *Modification*

The structure and the lattice are modified and the differences between variation of the structure and variation of the lattice constants are shown.

4.5. *Phase problem*

The real and imaginary parts of the structure factor and the corresponding phase angles are calculated and the influence of real-space translation on the phase of simulated patterns is demonstrated.

4.6. *Patterson and inverse Fourier calculations*

The students are guided through Patterson, inverse and difference Fourier transforms.

4.7. *Anomalous diffraction*

By including anomalous scattering for a centrosymmetric and an acentric structure, the students learn the breakdown of Friedel's law.

4.8. *Powder diffraction*

Powder diffraction patterns are simulated with different models of the orientation distribution.

4.9. *Diffuse scattering defects*

Several types of defects are introduced to crystals and the corresponding diffuse scattering and satellite distribution are calculated.

In addition to the simulations that the students perform, we offer WWW pages that guide the students throughout the course. They are an excellent possibility for advanced students who need little supersion. The best results, however, are achieved if the students are encouraged to modify the macros of this course and to carry out their own simulations. See the WWW pages (Proffen & Neder, 1996*b*). To fully view these pages, including all the images, you will need a browser like Netscape version 2.0. Earlier versions of Netscape or Mosaic will not enable you to view the images. All simulations are available as macro files together with the source code of *DISCUS*. Most of the structures are kept to very simple two-dimensional examples, so that the students can focus their understanding on the diffraction patterns that result.

5. Intended format and audience

We have used the computer simulations in a variety of teaching formats adapted for the intended audience. Graphical reproductions of the structures and their Fourier transforms work very well as enhancements to lectures on X-ray diffraction, especially in the beginning of the semester. The lecturer can easily create his or her own file of viewgraphs adapted to personal needs. An example of this style may be found in §6.6, one that we used as an introductory example for a class on direct methods. In our present experience, the most successful format is a computer laboratory. Individually or in small groups, the students can be guided to calculate the simulations and to view the WWW pages. They quickly realize the possibilities for modifications or for their own simulations. This creates a wealth of experience with respect to different diffraction conditions that had previously not been achieved by classical lectures. These two formats, personalized viewgraphs and computer laboratory sessions, have been used for undergraduate students in their senior year and for graduate students. A third format is best suited to advanced graduate students or beginning PhD students, who have had some introduction to crystallography. In this third format, we ask the students to work their way through the macros and the WWW pages with little guidance. The students have either applied modifications of the macros offered to research the answers to their own questions or have been able to address specific questions that can be answered in individual sessions with the supervisor.

6. Course notes on teaching

6.1. *Basics*

The first lecture is used to introduce the students to the program and to basic relationships between individual atoms and reciprocal space. The students are asked to use the on-line help of the program to familiarize themselves with the available commands. The first Fourier transforms are calculated by the use of predefined and thoroughly commented macros. The intensity distribution of a single atom is calculated in one and two dimensions. By the addition of further atoms, a small one-dimensional crystal is created. The students are asked to modify the type of atom and the number of atoms in the row, and to switch between X-ray and neutron diffraction and to observe the corresponding changes in the diffraction pattern. At this point, the students are given predefined macros. Later they are asked to write their own macros or to modify existing ones.

6.2. *Reciprocal space*

The second part introduces the students to reciprocal space. The first example modifies the spacing of the row of atoms used in part 1. The further examples calculate the diffraction patterns of cubic, orthogonal and monoclinic structures and illustrate the relationship between direct- and reciprocal-lattice constants.

6.3. *Convolution*

Several examples are presented in the third part covering the concept of convolution and the convolution theorem. In the first example, three Fourier transforms are calculated: (i) of a single atom, (ii) of a row of point scatterers and (iii) of a row of atoms. This example serves to illustrate the convolution theorem. The product of (i) and (ii) yields exactly the same result as (iii). The other examples shown the effect of limiting small crystals by different surfaces (square, rectangle box, circle and a set of $\{110\}$ planes). The Bragg reflections are now convoluted by the familiar Fourier transforms of these shape functions. This is demonstrated again by filling the shapes with a large number of randomly distributed atoms. The Fourier transforms for the shapes result (Fig. 1).

6.4. *Modification*

The fourth set of examples expands the understanding of convolution and shows the effects of structural modifications. A slightly complex structure with several glide planes is used to demonstrate that the structure factor is a continuous function in reciprocal space whose maxima do not necessarily coincide with the positions of the Bragg reflections. By calculation of the Fourier transform of a single unit cell, it is shown that the systematic extinctions are present in this continuous function. The example shows also that other Bragg reflections can have zero or almost zero intensity for structural reasons rather than due to special symmetry elements (Fig. 2). By modifying the structure, the students can learn that the intensities of the Bragg reflections change while their position in reciprocal space remains invariant. If the lattice constants are expanded, the Bragg reflections move closer to the origin of reciprocal space. The size of the unit-cell Fourier transform shrinks at the same rate.

6.5. *Phase problem*

The fifth set of examples covers the phase problem. The first example of §6.1 is picked up again. This time, in addition to the intensity, the real and the imaginary parts of the structure factor are calculated, as well as the corresponding phase. Since the atom is positioned at (0, 0 0), the imaginary part and the phase angle are zero. Next, the atom is moved to (0.5, 0, 0) and the corresponding new values are calculated. Although this structure is still centrosymmetric, the structure factor is no longer real, since the structure is shifted in real space. The students can learn that now the imaginary part is nonzero and that the phase oscillates according to the phase factor:

$$\varphi = \exp(2\pi i a u). \qquad (2)$$

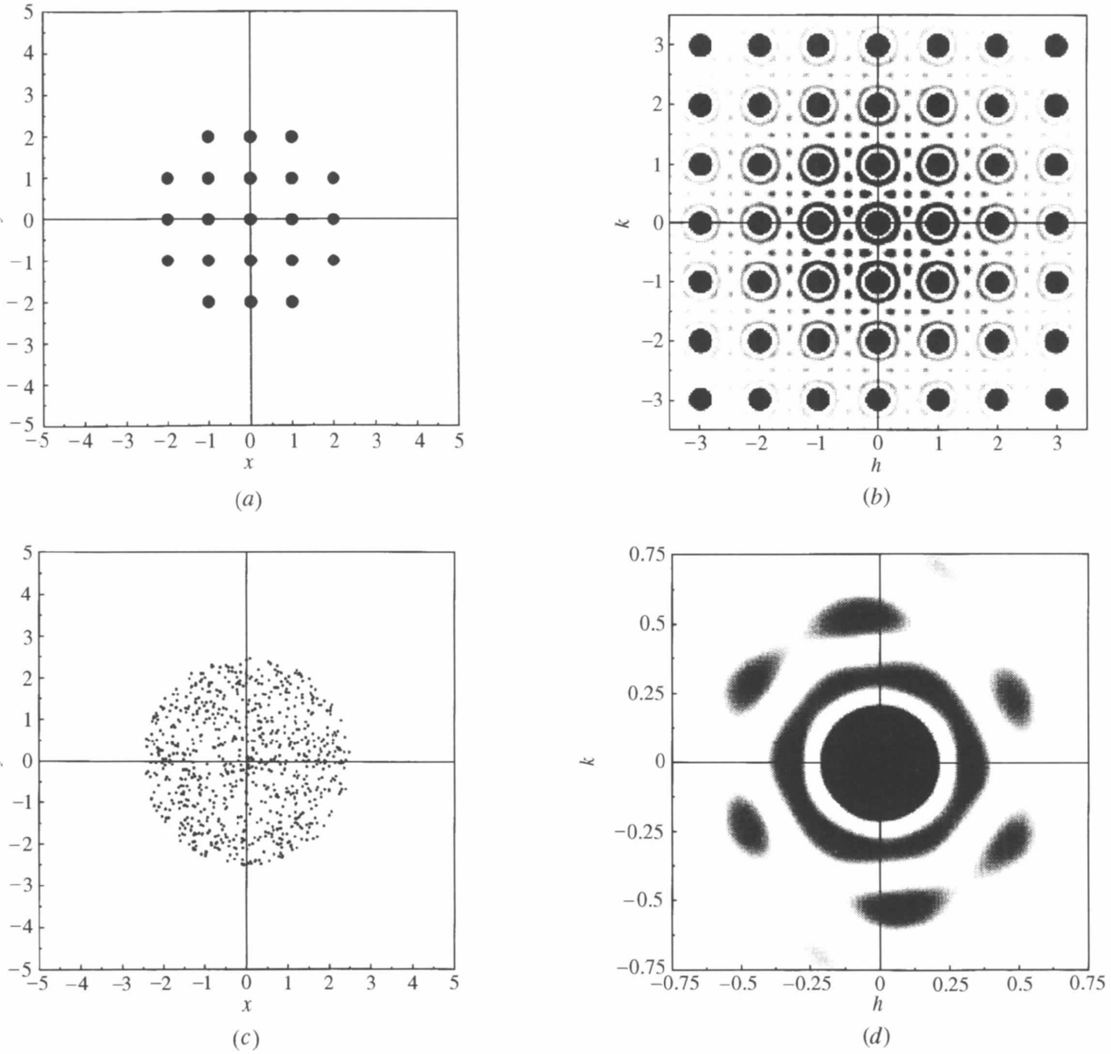
Here, u is the coordinate in reciprocal space and a is the shift in real space. This behavior is well known for the Fourier transform of a function shifted in real space. The intensity, however, is not changed. This gives a good opportunity to explain the crystallographic phase problem.

The next example calculates the intensity and phase for a realistic structure, Al_2O_3. The centrosymmetric structure, space group $R\bar{3}m$, shows a phase angle of zero, as expected. If the Al atom is moved away from the centrosymmetric position, the intensity hardly changes, while the imaginary part and the phase angles show significant differences.

6.6. *Patterson and inverse Fourier calculations*

The students are given the two diffraction patterns for a fictional two-dimensional structure of $ZrTiO_4$ (Fig. 3). These diffraction patterns have been calculated for X-rays and neutrons, respectively. The only information given initially is that the two diffraction patterns are from the same two-dimensional crystal. The students are asked to discuss the information that these patterns contain and any further information that they might need. By guiding the discussion, the supervisor can lead the students to ask for and to deduce the information listed in Table 1. Then they are asked to calculate the Patterson (Fig. 4). With the information from Table 1, the structure is easily solved. Next, the students are asked to calculate the phase angles from the partial structure consisting of the metal atoms only. These phase angles are used to calculate the inverse Fourier and the difference Fourier of Fig. 5, which reveals marked differences for the X-ray and the neutron case. The differences can easily be explained by comparison of the phase angles for the X-ray and the neutron case for the full and the partial structure. In the case of the X-ray diffraction, almost all phase angles are correct, while for neutrons several are wrong, because the X-ray structure factor is dominated by the metals and the missing O atoms do not change the phase angle considerably. This distinction becomes even clearer through the difference Fourier.

At this point, a discussion of partial structure solutions and phase assignments comes naturally. Note that the Ti atom was chosen to demonstrate the basics of direct methods, since its neutron scattering length is negative. Finally, the students are asked to calculate the inverse Fourier using the observed intensities and the phase angles calculated from the atom positions derived from the Patterson and the difference Fourier. Once the students have grasped the concepts of the inverse Fourier and Patterson, the effects of incomplete data sets



(a) (b)

(c) (d)

Fig. 1. (*a*) Atom positions in a finite two-dimensional crystal limited by a circular box. Owing to the small size of the crystal, the resulting boundaries are identical to the {100} and {110} faces. (*b*) Diffraction pattern of the finite crystal. Note that each Bragg reflection is convoluted by the Fourier transform of a circle. (*c*) The circular box is simulated by filling it with a random distribution of 800 electrons. (*d*) The Fourier transform of the 800 electrons from (*c*). 800 atoms are insufficient to fill the circle homogeneously, causing the small deviation from circular geometry.

should be covered. An excellent guide on this subject has been given by Cowtan (1995) and this is not discussed here.

6.7. *Anomalous diffraction*

The students are asked to research anomalous scattering coefficients for an element at its $K\alpha$ edge. A centrosymmetric and an acentric structure containing this element are used to demonstrate the effects of anomalous scattering. By comparing the intensities, and the real and imaginary parts as well as the phase angles, the students will see that Friedel's law still holds for the centrosymmetric structure but not for the acentric structure.

6.8. *Powder diffraction*

Powder diffraction is a very important tool in chemistry. The next set of examples illustrates how a powder pattern is created and shows special problems that arise in powder diffraction. The first example calculates a powder diffraction pattern for a simple cubic structure. The students can vary the number of powder grains that are involved and observe the gradual change from a single-crystal diffraction pattern *via* a coarse grainy powder pattern to a smooth diffraction pattern. The macro provided with the program calculates a two-dimensional powder pattern to save computational time. As an extended task, the students can be asked to expand this macro to calculate a fully three-dimensional pattern.

Next, a powder pattern is created from a powder with preferred orientation. A simple Gaussian distribution is used for the angle of orientation. Have the students modify the sigma of the Gaussian and learn how the pattern can be modified from a nearly perfect single-crystal pattern *via* a crystal with crude mosaic to a random powder pattern.

6.9. *Diffuse scattering/defects*

No crystal is perfect, rather a variety of defects exist that often determine the physical and chemical properties of crystals. Several examples of defect types are provided in this course. They serve to familiarize the students with typical types of defects and the related diffuse scattering.

The first examples, taken from Harburn, Taylor & Welberry (1975), demonstrate the difference between displacement disorder and substitutional disorder. A rigid square molecule is simulated within a primitive lattice. In the first example, the molecules are randomly displaced according to the Debye–Waller factor. A dif-

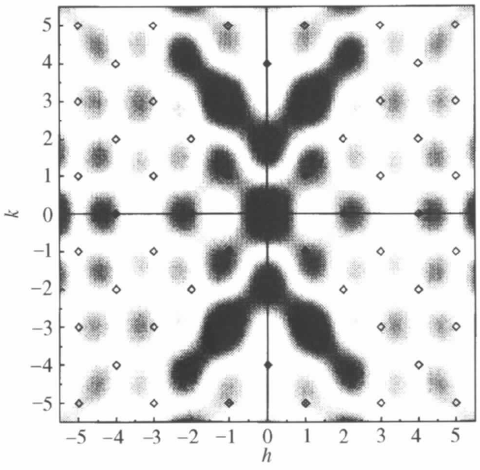


Fig. 2. The diffraction pattern of a single unit cell in *Pnnn* superimposed by the Bragg reflections calculated for a crystal of 10*10*10 unit cells. Note the systematic extinctions for *hk*, $h+k=2n+1$ and the noncrystallographic extinction for *hk*, $h=4$.

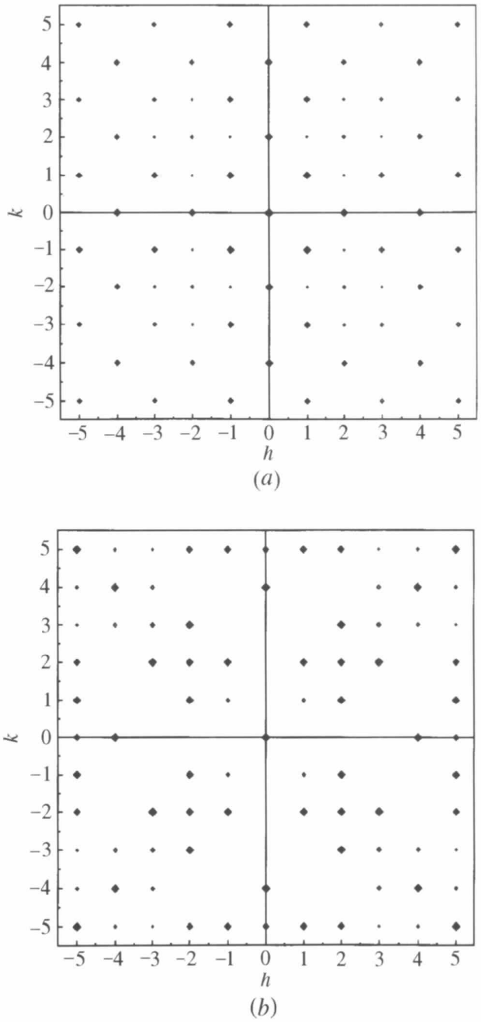


Fig. 3. (*a*) X-ray and (*b*) neutron diffraction patters of the two-dimensional $ZrTiO_4$ structure. Note the pseudo-*c*-centring of the X-ray diffraction pattern.

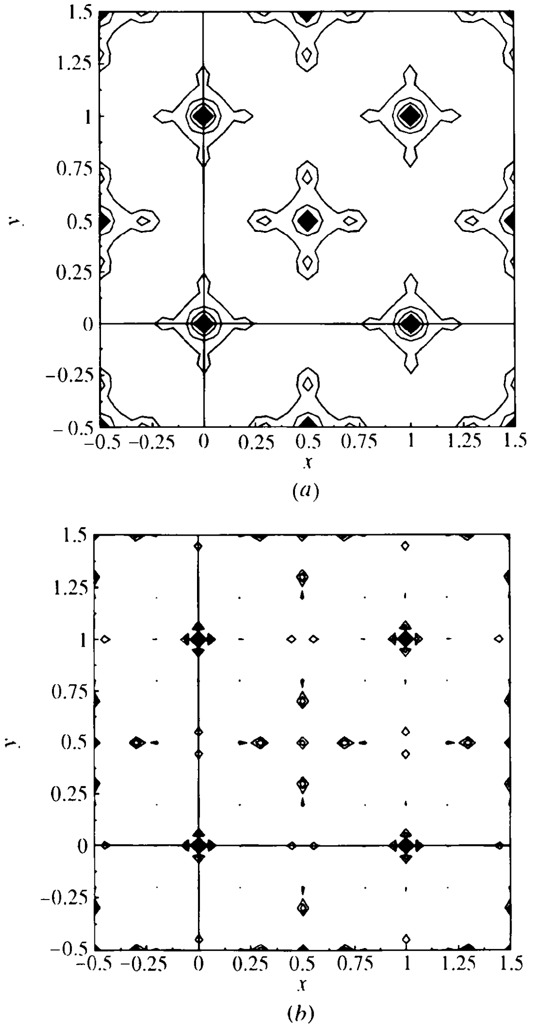
Table 1. *Information deduced from the diffraction pattern and additional information needed*

Chemical composition	$ZrTiO_4$
Plane group	*pmm*4
Lattice constants	$a = 5.0$ Å, $\gamma = 90.0°$
Number of formulae	1
Diffraction technique	Fig. 3(*a*) X-ray Fig. 3(*b*) neutron

fuse intensity that is weak at the centre of reciprocal space and strong at outer sections arises (Fig. 6). This diffuse scattering is modulated by the structure factor of the molecule, as can be seen by calculation of this structure factor. In the second example, the position of the molecule remains unchanged, while 50% of the molecules are removed. Now, the diffuse scattering is strong in the centre of reciprocal space and decreases with increasing scattering angle.

This distinction is commonly observed in diffuse scattering and may serve in some cases as a first indication of the nature of the defect structure.

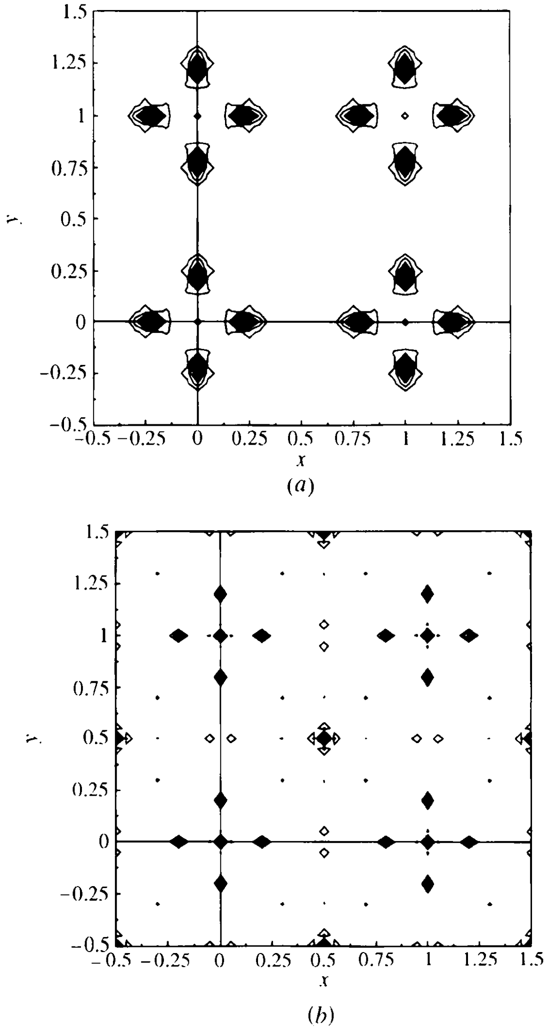
Next, the effect of different waves is demonstrated. Longitudinal and transverse waves are used to displace atoms of a primitive structure. Sharp satellite reflections result. Have the students modify the wavelength, amplitude and direction of the displacement. A few different simulations successfully teach the students the connection between wave vector and oscillation vector and the corresponding position and absence of satellites in reciprocal space.



(*a*)

(*b*)

Fig. 4. Patterson synthesis calculated from the diffraction patterns in Fig. 3. The students learn that a neutron Patterson (*b*) can have significant negative peaks and that the peaks related to oxygen vectors are stronger than those for the X-ray Patterson (*a*). Note that the neutron Patterson peaks at ($\frac{1}{2}$, $\frac{1}{2}$) and at (0.2, 0) are negative.



(*a*)

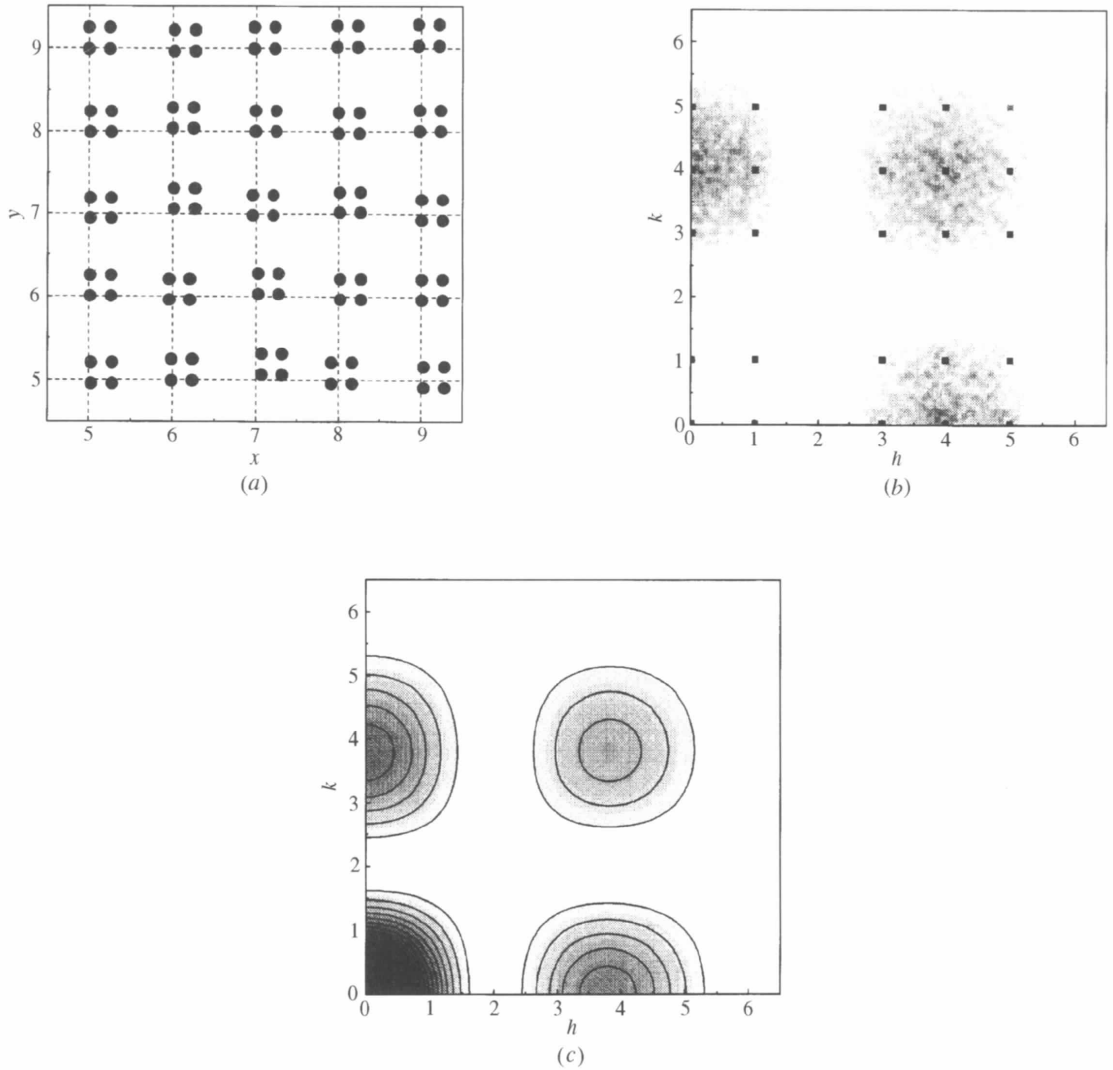
(*b*)

Fig. 5. Difference Fourier transform: (*a*) X-ray diffraction; (*b*) neutron diffraction. The phase angles are taken from the partial structure, with the oxygen positions omitted.

When the displacement wave is replaced by a replacement wave, similar differences in the general intensity distribution throughout reciprocal space are observed as in the first example on diffuse scattering.

7. Availability of teaching materials

All materials needed for the course presented in this paper are available *via* anonymous FTP from three archives. The first archive contains the full source code of *DISCUS* along with installation guides, the documentation, a hard copy of the manual (PostScript file) and some examples on the use of *DISCUS*. The program has been tested on several different platforms (UNIX: Sun, HP, LINUX; VMS: VAX, Dec-Alpha; DOS: LAHEY-F77 compiler). See the WWW pages (Neder & Proffen, 1996; Proffen & Neder, 19906*b*) for further details on downloading and installation of the program. In order to ease portability to different platforms, *DISCUS* does not create any screen output itself. Instead the output is written in several different formats (real bitmaps, integer bitmaps and PostScript) for readily available graphical display and printing programs. The second archive contains the macros used for teaching purposes. Each macro is thoroughly commented. The third archive contains the WWW pages themselves. This archive can be used to install the pages at your institution. With the increasing net traffic, students would



(*a*) (*b*)

(*c*)

Fig. 6. (*a*) Section of a two-dimensional crystal with thermal disorder. The rigid molecules are displaced at random according to a Gaussian distribution function. (*b*) Fourier transform of the crystal from (*a*). The diffuse scattering is modulated and in general stronger at higher *q* vectors. (*c*) Fourier transform of a single square molecule used in (*a*). The multiplication of the Fourier transform of the single molecule with the monotonic Laue scattering causes the modulation of the diffuse scattering observed in (*b*).

benefit from a faster local installation compared to a reference to our servers.

DISCUS source code and documentation. ftp.physik.tu-muenchen.de/pub/science/physics/software/crystal/discus.

Teaching macros. ftp.physik.tu-muenchen.de/pub/science/physics/software/crystal/teach_macros.

WWW pages. ftp.physik.tu-muenchen.de/pub/science/physics/software/crystal/teach_www.

See the README and INSTALL files within the individual archives for transfer and installation guides.

8. Conclusion

The examples presented above cover a wide range of standard diffraction effects. In the experience of the authors they serve exceptionally well to foster the understanding of the students. You can easily modify all examples to adapt to local needs and time available. The exercises are especially efficient if the students are given a chance to modify the macros and perform their own calculations. Compared to classical lectures, they give the students a wider experience and better understanding of diffraction techniques.

With the exception of the inverse Fourier and Patterson examples, the general focus in this course is somewhat unidirectional. A structure is simulated and the corresponding reciprocal space is calculated. The reverse step from reciprocal space to a structure will be treated separately in a complication of examples used to illustrate the principle of direct methods.

References

Cowtan, K. (1995). *Kevin Cowtan's Picture Book of Fourier Transforms*, http://www.yorvic.york.ac.uk/~cowtan/fourier/fourier.html.

Glusker, J. (1988). *J. Chem. Education*, **65**, 474–477.

Harburn, G., Taylor, C. A., Welberry, T. R. (1975). *Atlas of Optical Transforms*. London: Bell & Hyman.

Harris, M. R. & Fitzgibbon, M. (1989). *J. Appl. Cryst.* **22**, 624.

Neder, R. B. (1994). *Z. Kristallogr. Suppl.* **7**, 744.

Neder, R. B. & Proffen, Th. (1966). *DISCUS V2.02*, http://www.kri.physik.uni-muenchen.de/geo/crystal/discus/discus.html.

Proffen, Th. & Neder, R. (1996*b*). *Teaching guide X-ray diffraction*, http://www.kri.physik.uni-muenchen.de/geo/crystal/teaching/teaching.html.

Rahman, S. H. (1989). *Z. Kristallogr.* **186**, 116.

Rogers, K. D. (1993). *J. Appl. Cryst.* **26**, 620–621.

Welberry, T. R. & Butler, B. D. (1994). *J. Appl. Cryst.* **27**, 205–231.