Image courtesy of lindenbaum; image source: Flickr

The new definition of crystals – or how to win a Nobel Prize

Why is symmetry so central to the understanding of crystals? And why did 'forbidden' symmetry change the definition of crystals themselves?

By Mairi Haddow

When asked to think of a crystal, you might think of those that are visible to the naked eye, such as:

Common salt (sodium chloride)

Image courtesy of Mark Schellhase; image source: Wikimedia Commons

Gypsum (calcium sulphate dehydrate)

Image courtesy of Tjflex2; image source: Flickr

Cinnamon stone ($Ca_3Al_2Si_3O_{12}$)

Image courtesy of Tjflex2; image source: Flickr

Image courtesy of tlindenbaum; image source: Flickr

Studying crystalline materials is one of the most powerful analytical techniques available to scientists. If it is possible to grow a single crystal of a salt, molecule, protein or even a whole virus, then it is usually possible to identify not only its connectivity (what atoms are bonded to what), but also its bond lengths, bond angles and molecular conformation (what shape a flexible molecule adopts). From the study of protein crystals, it is often possible to elucidate how that protein works in the body and where its active sites are.

Crystals are inherently beautiful, largely thanks to their symmetry. Conventionally, all crystals were thought to have one property in common: translational symmetry in three dimensions. Indeed, this is how crystals were originally defined – as materials in which the constituent atoms, molecules, or ions are packed in a regularly ordered, repeating three-dimensional pattern. Translational symmetry is best illustrated in two dimensions by thinking about patterned wallpaper, which usually has this property – if hung properly. This means that we can draw a parallelogram (tile) containing a certain pattern, and by stacking the tile in two directions, derive the wallpaper pattern (figure 1).

In a similar way, we can derive a 3D crystal structure from a 'box' of atoms, by repeating the box along the

Figure 1: Wallpaper illustrating translational symmetry in two dimensions. The parallelograms indicate the repeating unit

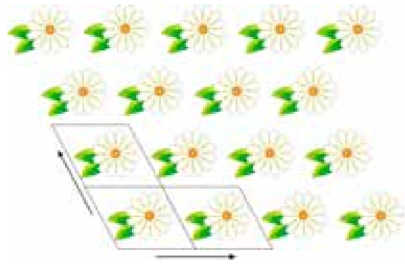
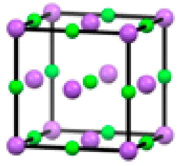


Image courtesy of Mairi Haddow

Figure 2: The unit cell (top) and crystal structure (bottom) of sodium chloride, derived by repeating the unit cell along three directions: x, y and z. Typically, the sizes of unit cells range from a few ångströms (10^{-10} m) for simple salts (the unit cell of sodium chloride is 5.64 Å), to a few tens of ångströms for small molecules, up to several hundred ångströms for protein crystals



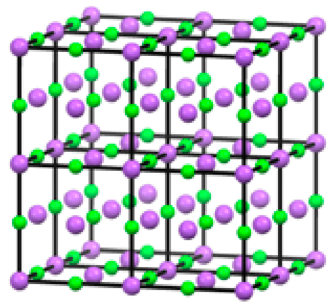


Image courtesy of Mairi Haddow

REVIEW

- Chemistry
- Physics
- Earth science
- Maths
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- Crystallography
- Atomic structure
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- Waves
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As the author writes, "crystals are inherently beautiful," but students often regard crystallography as a difficult and boring subject. For these students and for their teachers, Mairi Haddow's article is a valuable resource to look at crystals with a new and inspiring approach. In this enjoyable article, the topic is explained in clear and precise language, together with beautiful and impressive pictures (for example the one about wallpaper and translational symmetry).

The article could be used in school within chemistry (solid structures), physics (diffraction, waves, atomic structure), earth science (mineralogy, crystallography), and maths (symmetry) curricula. These subjects, with the addition of art history (tiling), offer different interdisciplinary opportunities.

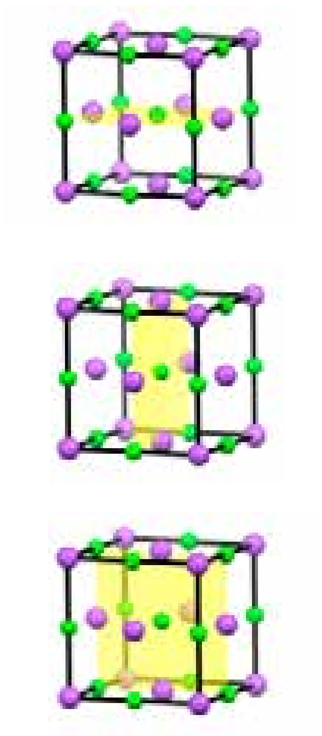
Suitable comprehension questions include:

1. From the article you can deduce that it is possible to grow a crystal of:
   a) A salt
   b) A molecule
   c) A virus
   d) A bacterium
2. With which of the following can diffraction analysis of crystals NOT be performed?
   a) X-rays
   b) Radio waves
   c) Neutrons
   d) Free electron laser
3. With which of the following types of tiles is it possible to completely cover a 2D surface?
   a) Triangles, squares, pentagons, and hexagons
   b) Triangles, rectangles and heptagons
   c) Triangles, squares, rectangles and hexagons
   d) Squares, rectangles and pentagons

Giulia Realdon, Italy

Image courtesy of Mairi Haddow

Figure 3: Unit cell of sodium chloride showing three mirror planes (coloured yellow)



Public domain image (recycling symbol); other images courtesy of Mairi Haddow

Figure 4: Examples of shapes with two-fold or mirror symmetry (two of diamonds), three-fold (recycling symbol), four-fold (Celtic knot) and six-fold symmetry (star)

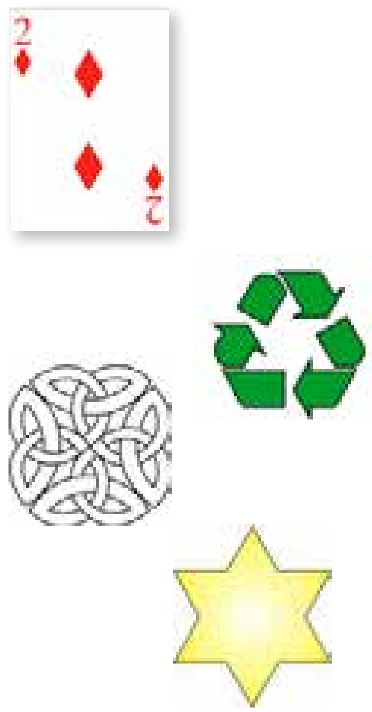
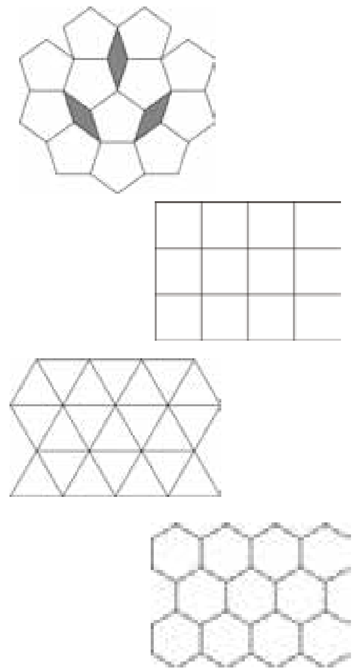


Image courtesy of Mairi Haddow

Figure 5: Packing of polygons: it is not possible for objects with five-fold rotational symmetry (pentagons) to be packed together without leaving gaps (grey shading) between them. In contrast, triangles, squares and hexagons can be packed without gaps



x, y, and z axes. The repeating box is known as the *unit cell* (figure 2).

Symmetry in crystals and quasi-periodicity

Crystals that have such translational symmetry in three dimensions are formally referred to as *periodic crystals* because the structures have a pattern that repeats at a certain distance or *period*. In 2011, however, the Nobel Prize in Chemistry was awarded to Dan Shechtman for his discovery of *quasi-periodic* crystals. These crystals are not periodic – they do not possess translational symmetry – but still have local order. They have the same repeating unit at different points in the crystal, but *not* at periodic intervals. The recent recognition of this work is a triumph of Shechtmann's perseverance over the ridicule that he received when he first published his work (Shechtman et al., 1984). So why was this idea so contentious? Because these crystals seemed to have symmetries that are forbidden in periodic systems.

In addition to translational symmetry, most periodic crystal structures have additional symmetry, such as mirror symmetry. For example, by looking at the unit cell of sodium chloride, we can see that each half is the mirror image of the other (figure 3; see also figure 4).

Image courtesy of Phillip Westcott, National Institute of Standards and Technology

Dan Shechtman explaining the atomic structure of quasi-periodic crystals at a meeting at the National Institute of Standards and Technology, USA, in 1985 – just months after he published his discovery

Rotational symmetry is also possible. This means that if we take an object and rotate it around a central point by a certain number of degrees, it will look the same (figure 4).

When a pattern or crystal has translational symmetry and is periodic, two-fold, three-fold, four-fold and six-fold rotational symmetries are all possible, but five-fold, or indeed seven-fold or higher symmetry, is not. This is because triangles, rectangles, squares and hexagons may all be packed in 2D space without leaving any space in between. In contrast, pentagons, heptagons and higher polygons may not (figure 5).

Image courtesy of Mairi Haddow

Figure 6: Young's diffraction experiment, showing the interference of light passing through a diffraction grating

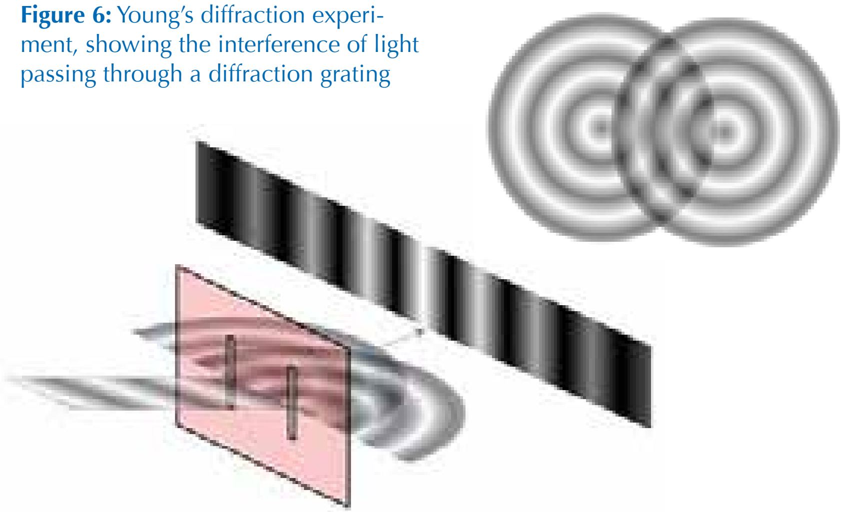


Image courtesy of Mairi Haddow

Figure 7: Layers of atoms in sodium chloride that act similarly to slits in a diffraction grating

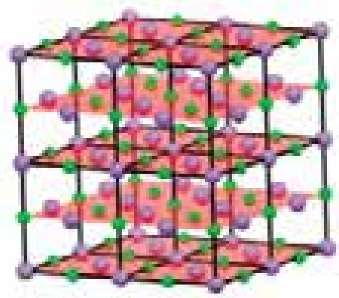
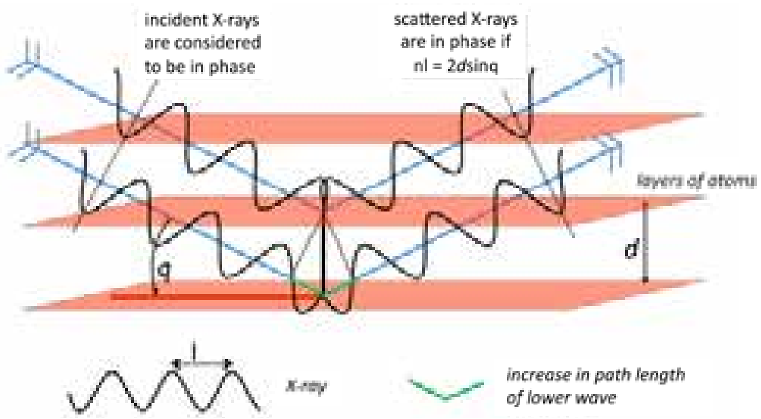


Image courtesy of Mairi Haddow

Figure 8: Derivation of Bragg's law. The extra distance (green path) travelled by the lower X-ray can be shown to be equal to 2d sinθ. The scattered beams will be in phase if and only if the extra distance travelled is equal to a whole number (n) of wavelengths (λ). Thus, a diffraction peak will be visible only if nλ = 2d sinq



How are crystals analysed?

Many students will have performed Young's famous double-slit experiment at school, in which a laser is shone through two slits in a diffraction grating, the spacing between which is comparable to the wavelength of the laser light. An interference pattern can be seen, caused by constructive and deconstructive interference of the waves diffracted by the slits (figure 6).

Crystals are studied using a technique known as X-ray diffraction, the theory of which was developed extensively in 1913 by William Henry Bragg and his son William Lawrence Bragg, who were jointly awarded the Nobel Prize in Physics in 1915 for their work. In a diffraction experiment, crystals act as a complex diffraction grating, where the 'slits' are layers of atoms in the crystal (figure 7).

For diffraction to occur, the wavelength of the radiation interacting with the crystal must be comparable to the distance between the atoms. Commonly in laboratories, the radiation will be X-rays (which are scattered by the electrons in atoms), but there are other possibilities, such as electrons or neutrons[w1].

The crystal is mounted in an X-ray beam of a selected wavelength, and the diffraction pattern is measured as the crystal is rotated. For layers of atoms positioned at an angle θ to the X-ray beam, scattered X-rays will be in phase (i.e. have constructive interference) if and only if the difference between the path lengths of two scattered X-rays is equal to a whole number of wavelengths, resulting in a measurable diffraction peak. This is known as Bragg's law, and the derivation is illustrated in figure 8.

As the crystal is rotated, different layers of atoms will satisfy Bragg's law and produce constructive interference. This results in a diffraction peak with an intensity related to the number and type of atoms in the layer, for example as shown in figure 9. A typical diffraction experiment will measure thousands to millions of *reflections*, and by careful analysis can be used to figure out the exact structure of the crystal.

The diffraction pattern produced by a crystal also has symmetry and this is

Image courtesy of Materialscientist; image source: Wikimedia Commons

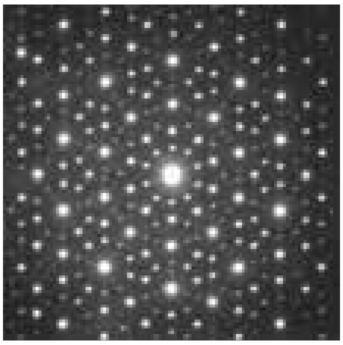
Figure 9: A typical diffraction pattern from a conventional crystal at one particular angle. Each bright spot (reflection) represents constructive interference from a different layer of atoms. (The shape on the right is the shadow of the beam stop, a metal shield which absorbs the unscattered X-ray beam)

Images courtesy of Mairi Haddow (right and left images); central image courtesy of Materialscientist; image source: Wikimedia Commons

Figure 10: X-ray diffraction pattern with two-fold rotational symmetry from a periodic crystal (A) and an electron diffraction pattern from a quasi-periodic crystal, showing 10-fold rotational symmetry (B). For comparison, the X-ray diffraction pattern from a glass fibre (broadly amorphous, i.e. non-crystalline) material (C)

A

B



C

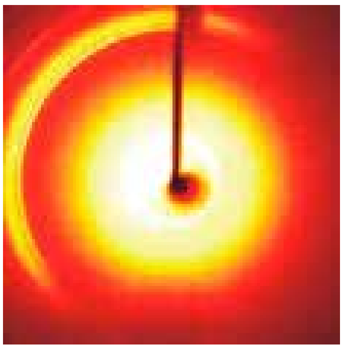
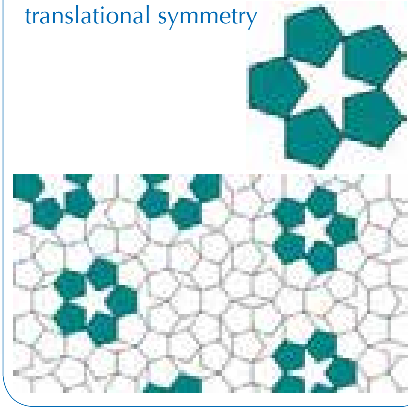


Image courtesy of Mairi Haddow

Figure 11: A single object may possess five-fold rotational symmetry (top) but these objects may not be combined into a periodic system. This occurs, for example, in Penrose tiling (bottom), in which instances of local five-fold symmetry may be found, but which does not have translational symmetry



related to the symmetry of the crystal. The diffraction patterns of quasi-periodic crystals have symmetry that is forbidden in periodic crystals, such as five- or 10-fold rotation (figure 10).

The structures of these unusual crystals are related to Penrose tilings (figure 11). These are structures that possess local symmetry, but not translational symmetry.

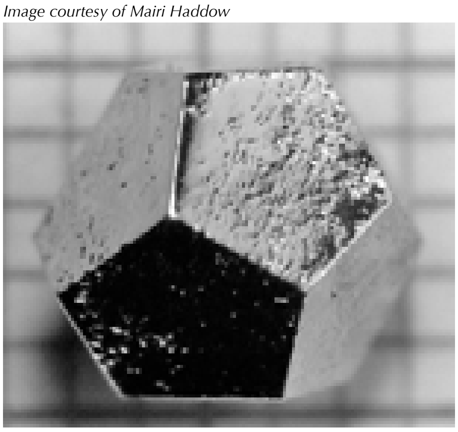
Research in this area led to a change in the definition of a crystal by the International Union of Crystallography in 1991. Crystals now no longer need to have translational symmetry: a material is a crystal if it has a sharp diffraction pattern, which quasi-periodic crystals certainly do.

However, it's unlikely that the school curriculum will be changed any time soon to reflect this new definition. Very few of these quasi-periodic materials have yet been discovered, and the first natural quasi-periodic crystal – icosahedrite ($Al_{63}Cu_{24}Fe_{13}$), a mineral that is probably of meteoritic origin and was found in the Khatyrka river in eastern Russia – was discovered only in 2009. Although more examples have been created since then, and quasi-crystals are now known to exist in many metallic alloys and some polymers, the crystals that school students grow in the lab are unlikely to be anything but periodic, and aside from their unusual and interesting properties, quasi-crystals have no real applications – yet.

Image courtesy of Roger McLassus; image source: Wikimedia Commons

Studying crystals relies on the analysis of the interaction of waves with layers of atoms

Image courtesy of Mairi Haddow



A holmium-magnesium-zinc quasi-periodic crystal

References

Bindi L et al. (2009) Natural Quasicrystals. *Science* **324(5932)**: 1306-1309. doi: 10.1126/science.1170827

Shechtman D et al. (1984) Metallic phase with long-range orientational order and no translational symmetry. *Physical Review Letters*, **53(20)**: 1951-1953. doi: 10.1103/PhysRevLett.53.1951

Web resources

w1 – Diffraction analysis is possible not only with X-rays, but also with neutrons and electrons. This is exemplified by three of the members of EIROforum (www.eiroforum.org), the publisher of *Science in School*.

The European Synchrotron Radiation Facility (ESRF; www.esrf.eu) uses the diffraction patterns of high-energy X-rays to analyse materials. The experiments carried out at ESRF have applications not only in materials science, but also in biology, medicine, physics, chemistry, environmental science and even palaeontology and cultural heritage. See the full collection of ESRF-related articles in *Science in School*: www.scienceinschool.org/esrf

The Institut Laue-Langevin (ILL; www.ill.eu) operates the most intense steady neutron source in the world. Diffraction studies of the neutron beams are used in research into condensed matter physics, chemistry, biology, nuclear physics and materials science.

The European X-ray Free Electron Laser (European XFEL; www.xfel.eu), due to start operation in 2015, will use X-ray flashes to examine samples. The basic idea behind a typical experiment is simple: illuminate a sample by intense X-ray flashes and count the photons that are scattered from the sample in different directions. The result is a diffraction pattern.

Resources

Cornuéjols D (2009) Biological crystals: at the interface between physics, chemistry and biology. *Science in School* **11**: 70-76. www.scienceinschool.org/2009/issue11/crystallography

To learn how to grow your own protein crystals at school, see:

Blattmann B, Sticher P (2009) Growing crystals from protein. *Science in School* **11**: 30-36. www.scienceinschool.org/2009/issue11/lysozyme

More information about Dan Shechtman and his discovery is available on the Nobel Prize website: www.nobelprize.org

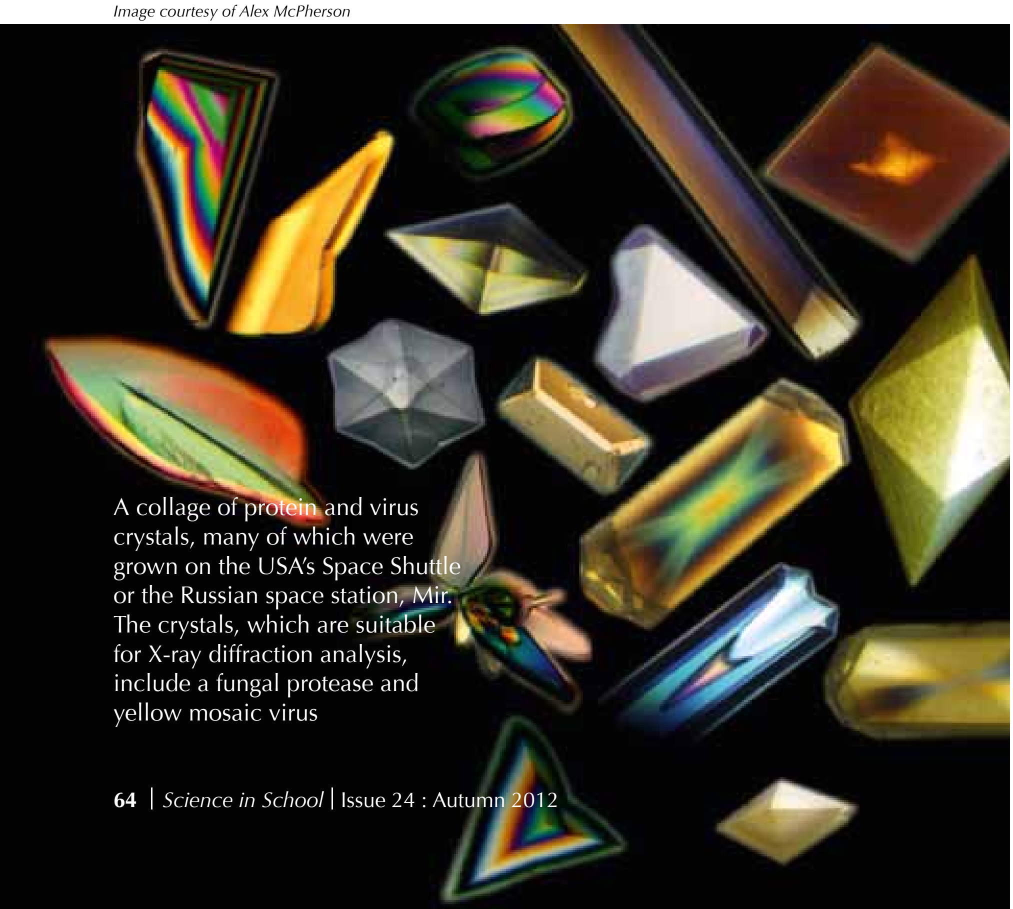
Howes L (2011) Quasicrystals scoop prize. *Chemistry World* **8(11)**: 38-41. www.rsc.org/chemistryworld/Issues/2011/November/QuasicrystalsScoopPrize.asp or use the shorter link: http://tinyurl.com/7ek47aw

For an interview with mathematician and symmetry researcher Marcus de Sautoy, see:

Hayes E (2012) Finding maths where you least expect it: interview with Marcus du Sautoy. *Science in School* **23**: 6-11. www.scienceinschool.org/2012/issue23/dusautoy

If you found this article helpful, you may like to browse the other chemistry articles in *Science in School*. See www.scienceinschool.org/chemistry

Image courtesy of Alex McPherson



A collage of protein and virus crystals, many of which were grown on the USA's Space Shuttle or the Russian space station, Mir. The crystals, which are suitable for X-ray diffraction analysis, include a fungal protease and yellow mosaic virus

Mairi Haddow studied chemistry at the University of Edinburgh, UK, has a PhD in chemistry from the University of Bristol, UK, and now works as a research fellow at the University of Bristol, in charge of the X-ray diffraction facilities in the School of Chemistry. She regularly gives demonstrations of the equipment to A-level students (aged 16-18) who take part in the School of Chemistry's (inappropriately named) 'spectroscopy tours'.

To learn how to use this code, see page 65.