

Crystallographic modelling

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SUMMARY

The project on crystallographic modelling aims at extending the application of interactive graphics to inorganic structures. Starting from the available expertise in organic and protein modelling, the symmetry of the crystal structure is used not only to draw fixed models of many unit cells of the structure, which as an entity can be interactively manipulated, but also to change details of the structures interactively with retention of the original symmetry. Real-time shifts of atom positions are automatically applied to all symmetry-equivalent atoms given the symmetry constraints. This also applies to translations and rotations of groups of atoms. In order to get feedback about these structural changes one can simulate powder diffraction patterns in real-time mode and compare them with the experimental powder patterns. These features are crucial in truly crystallographic modelling, but have not been implemented before in other programs. The program can be used in combination with standard molecular modelling programs and is also interfaced to the Inorganic Crystal Structure Database. Before describing the realization of these features on state-of-the-art hardware, we will review the expertise in molecular modelling and discuss an MS-DOS program to study inorganic crystal structures.

INTRODUCTION

This article is based on a lecture which was given by one of us (HS) at the 1987 Shell conference on Computer-Aided Molecular Modelling and dealt with a joint project of the Laboratory of Crystallography of the University of Amsterdam and the Royal Dutch Shell Laboratory Amsterdam.

Through systems such as the E&S PS 300 and the IRIS work stations, interactive graphics has

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proved to be a valuable tool in chemistry. The technique is used to assist chemists in a wide variety of tasks, as can be established from the regular appearance of articles on this subject in the literature. However, most of the graphical applications are oriented towards molecules. Hence there are a great many programs with an interface to the Cambridge Crystallographic Database (CCD) with its 60 000 organic and organometallic structures; there are only a few programs which utilize the Inorganic Crystal Structure Database (ICSD) in which 30 000 inorganic structures have been collected.

Inorganic structures are usually more difficult to visualize than organic ones. Instead of separate molecular entities, atomic clusters have to be studied, often with ranges well beyond one unit cell, and for such studies the classical molecular graphics techniques are inadequate. With inorganic structures it is frequently desirable to emphasize particular atoms or groups of atoms, for instance by drawing nets of non-neighbouring atoms or replacing groups by polygons. Often, to understand an inorganic structure, one has to screen a large number of images, preferably in stereo. With a view to accomplishing this in a relatively short time, a dedicated MS-DOS program has been written, which will be presented in some detail here.

In our fast interactive crystal graphics program PLUVA, which will also be described in more detail, symmetry is incorporated within the display procedure. So when an atom or a group of atoms is interactively shifted, all equivalent atoms will shift while the crystal symmetry is preserved. This system can be used as an aid to find trial models of crystal structures. To judge whether changes in atomic coordinates, applied in an interactive modelling session, correspond to physical reality, powder diffraction patterns are calculated on-line from screen coordinates and compared with the experimental ones.

STATIC DRAWING OF CRYSTALLOGRAPHIC RESULTS

Programs to generate paper plots, and more recently static screen drawings, from crystallographic data have been around for many years, examples being ORTEP [1] and PLUTO [2]. The input consists of crystallographic data obtained by means of diffraction (XRD) experiments, and includes cell constants, space-group specification (symmetry operations and Bravais lattice), fractional coordinates and temperature factors. Further input includes drawing style, view direction, labels and so on. The programs run almost exclusively on mainframes and minicomputers and the resulting pictures are drawn by means of plotters.

Over the last decade, the required crystallographic data have been collected into several databases: protein structures in the Protein Data Bank (PDB [3]), small organic and organometallic compounds in the CCD [4], and inorganic structures in the ICSD [5].

With plotters coupled to large mainframe computers, it may take up to several hours – depending on the local computer configuration – before the results become available. Since it usually takes far more than one attempt to find the optimum view of a structure, the process of obtaining a good presentation is tedious. Therefore some years ago, when small microcomputers with reasonable graphical facilities became available, the group at the University of Amsterdam developed the computer program PLUIT [6] for previewing molecular structures in an interactive way. This program (shareware of the Laboratory for Crystallography of the University of Amsterdam), written for the Commodore 64 and MS-DOS computers, provides for the convenient generation and display of a molecule from any view direction within a few seconds. In this way the optimal

view direction for a particular structure can be found in well under one hour. Subsequently it can be used to plot drawings by means of one of the mainframe programs.

THE MS-DOS PROGRAM INORG

In many curricula, inorganic crystal chemistry is the first subject that brings students in contact with the three-dimensional results of crystallography. However, it is not easy to obtain the right three-dimensional impression of even simple structures. For instance, visualizing octahedral and tetrahedral holes in (pseudo-)closed packed structures is far from being a trivial task. Therefore, models are an essential element in teaching crystal chemistry, and 'hardware' ball models are used extensively.

Another tool by means of which structures can be studied and manipulated quickly in stereo is computer graphics. This technique can well assist in teaching crystal chemistry, provided that an inexpensive facility can be realized. Therefore we changed our molecular graphics program PLUIT to accommodate inorganic crystal structures by incorporating space-group symmetry. Moreover, since in our department inorganic structures are being studied regularly, an attempt was made to construct the MS-DOS program such that it could assist in analyzing research problems. In version 2.0, an interface to the ICSD will be incorporated.

An important feature of the interactive graphics programs is the stereoooption. Stereoimages, more than anything else, assist in providing insight into the architecture of crystal structures. We have opted for split images at half the horizontal resolution in order to preserve colour, as opposed to red/green stereo which gives a colourless image at full resolution.

Right from the start, we have looked for the cheapest possible solutions. Thus we started with CGA graphics in 640×200 monochrome resolution. Now our programs are compiled with Turbo Basic 1.0, and as a result we were able to include the EGA 640×350 colour resolution. Colours are very helpful in visualizing complicated structures. As soon as one of the BASICA-compatible compilers can support Hercules, VGA and other graphical standards, we shall produce new versions with these options.

The INORG program [7] provides for the display of stick, ball, and stick-and-ball models, in mono or stereo view, with or without labels, and with or without colour. The models can be rotated about three orthogonal axes; the view matrix is identical to that of PLUTO and can be displayed in the picture as desired: within the limits of the array sizes there are no limitations on x, y and z, or on search and plot radii. The values of the search radii may be chosen in such a way that the connections between atoms do not represent bonds but some special net, such as the Si net in silicates. Hardcopy images can be made on cheap dot graphics printers.

Another important option is the clipping facility. In a particular view, one can define a backplane which hides all atoms behind it and a frontplane which hides all atoms in front of it. These back and front planes can have any position parallel to the screen. The user obtains information on how many atoms will be displayed between the planes. This option makes it possible to study layered structures layer by layer and to look closely at the packing of layers on top of each other. In addition, it provides a means to remove unwanted atoms. As this clipping is a software facility, it is possible to save a particular clipped set of atoms and use this set as a fresh starting point, e.g. for further clipping in another orientation. In total, 50 successive clipped sets can be stored and played back and forth rapidly in the same orientation in order to show details of the structure.

For teaching purposes, the program is excellent. A limited library of essential structures, with a full description of how to obtain the images, accompanies the program. For research problems, too, the program functions well. A large number of images can be produced and studied in a relatively short time.

Figures 1 and 2 give a few examples of EGA screen dumps of the structure of $\text{Cs}_2\text{Te}_4\text{O}_{12}$ [8], which clearly illustrate the possibilities and advantages of the program. Typically it takes the computer (8086 and 8087) a few seconds to produce a picture and the colour printer a minute to make the hard copy. With a buffer between printer and computer, the latter is quickly available for further manipulations with the graphics program.

REAL-TIME MODELLING

In recent years, hardware and software have become available that enable structures to be displayed dynamically in real time. However, they did not provide the means to model inorganic structures, because none of the modelling systems could handle symmetry during real-time structure manipulations.

The advent of dedicated CAD hardware (e.g., the E&S Picture System) initiated this real-time modelling, in particular in protein crystallography. Protein crystallographers used to build models of their proteins by imaging ironwire models onto electron-density maps by means of special

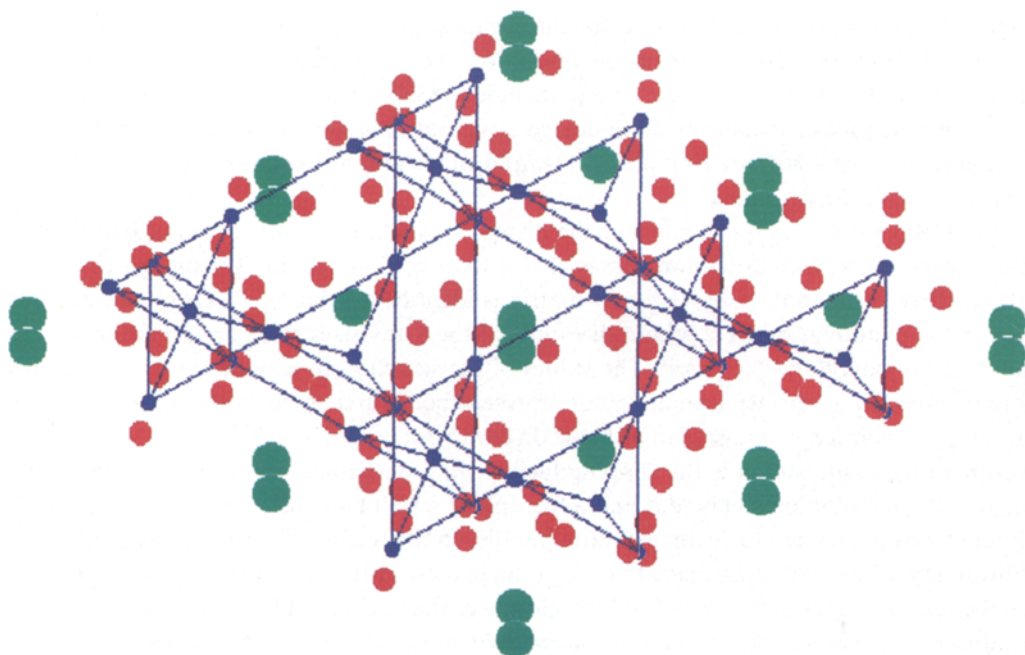


Fig. 1. $\text{Cs}_2\text{Te}_4\text{O}_{12}$, parallel projection. This 166-atom view is the smallest possible starting point for the clipped image of Fig. 2. Green: Cs; Red: O; Blue: Te network.

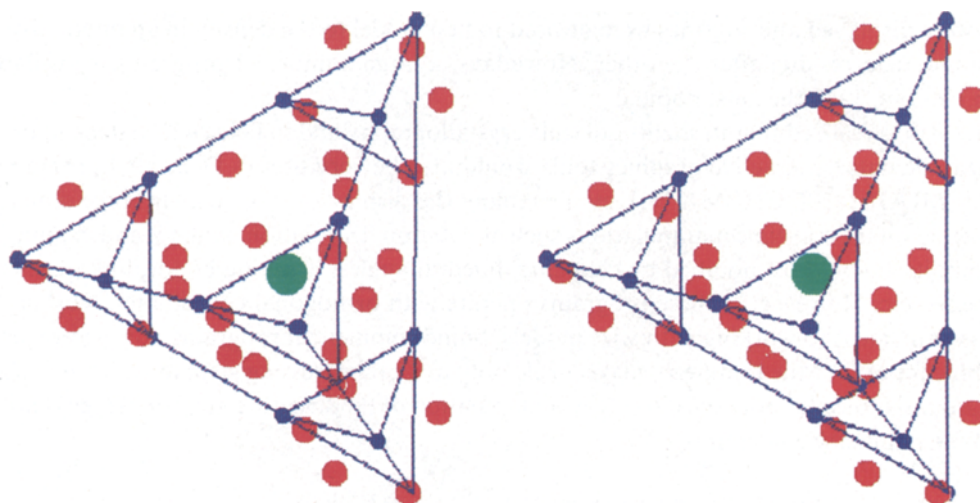


Fig. 2. $\text{Cs}_2\text{Te}_4\text{O}_{12}$, stereoview. The metals have the same arrangement as the metals in spinel. In spinel, the small tetrahedra at the corners of the big tetrahedron carry 4 oxygens, here they carry 6. See also legend of Fig. 1.

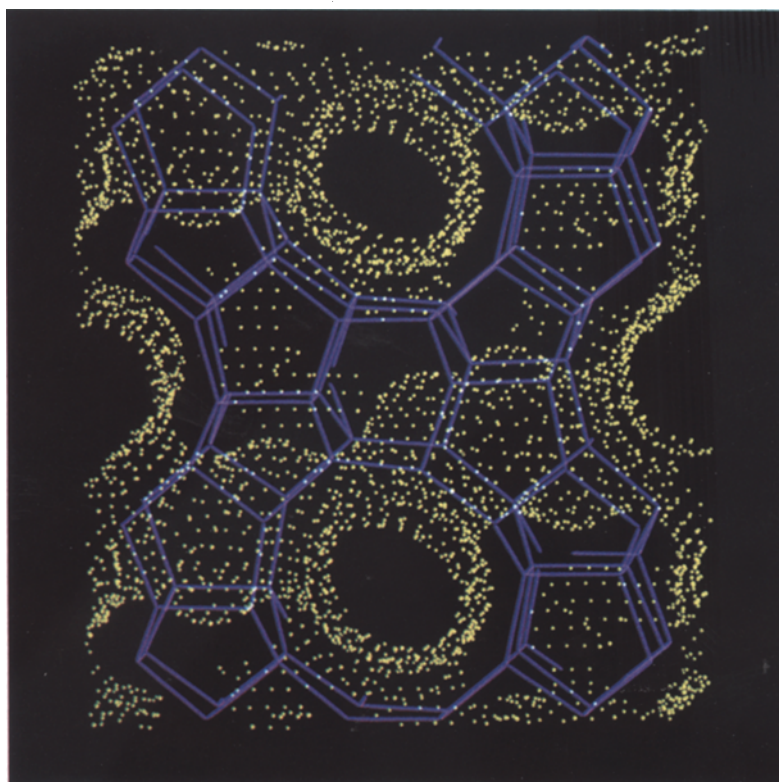


Fig. 3. Connolly surface inside the unit cell of ZSM-5. The Si-net is shown in blue. The surface, generated with a probe size of 2.0 Å, is shown in yellow.

half-mirrors. When the proteins studied became larger, this was no longer feasible and, consequently, some people, like R. Diamond, began to utilize graphics machines. Electron-density maps were displayed and routines were devised to fit a model to the density in an interactive way, one amino acid residue after the other. Nowadays, a large number of programs is available of which FRODO [9] is the most popular.

Later it was realized that in small-molecule crystallography and in fields which depend on crystallographic data, interactive graphics tools would also be very useful. Dedicated programs appeared (MOGLI [10], CHEMX [11], etc.) enabling the display of structures in three dimensions with concomitant real-time manipulations such as rotation, translation, scaling, and clipping. The structure itself could be modified by changing dihedral angles, breaking bonds, linking chemical fragments, etc. However, as these programs operate with orthogonal coordinates, working with them is equivalent to working with wire models. Some commercial programs now accept crystallographic input, but the symmetry plays a role only in a preprocessing step, in which it is used to build a quasi molecule from the data. Any manipulation of the structure at a later stage is not subject to the symmetry constraints.

CRYSTALLOGRAPHIC MODELLING

Crystallographic modelling meets the need to update atomic positions and all symmetry-related ones in real time when one is engaged in interactively modifying inorganic crystal structures on a graphics display. It combines interactive molecular modelling with crystallographic symmetry. In our newly developed program PLUVA, it is of course sufficient to specify the unique atoms ('asymmetric unit'), the cell constants and the symmetry operations (space group) in order to select a part of any size of the crystal structure. This information may also be obtained from the ICSD [5] and loaded into the program through the interface between PLUVA and the ICSD.

On an E&S PS 300 graphics terminal, the program will now generate a wire model, the symmetry information of which resides in the definition of the display structure. As the hardware is able to perform real-time concurrent updating of a picture from user-controlled view specifications, one may subsequently modify this wire model, e.g. by selecting a specific atom and altering its position in real time: at the same time all symmetry-equivalent atoms shift their positions following the symmetry rules. This implies that a shift of an atom has different effects on the displayed structure depending on to which of the 230 different space groups the structure belongs. Of course, the same changes in a structure can be achieved by altering the positional parameters of the particular atom in the input of the first operation and recalculating the display structure; however, this cannot possibly be achieved in real time. Moreover, in the latter alternative, one has to specify the shifts numerically, whilst it is much easier to turn a dial and to watch the immediate shift on the screen, if necessary with numeric feedback.

In addition to moving one atom at a time, groups of atoms may be moved, translated and rotated, and again all symmetry-equivalent groups will move with retention of the space-group symmetry. The controlling network copes with special positions as well. This is necessary since atoms in special positions have a restricted freedom of displacement (e.g. moving an atom out of a mirror plane would create a double atom, thereby changing the elemental composition; moving within the plane is of course allowed).

Thus far, space-group symmetry, cell constants, and elemental composition have been regarded

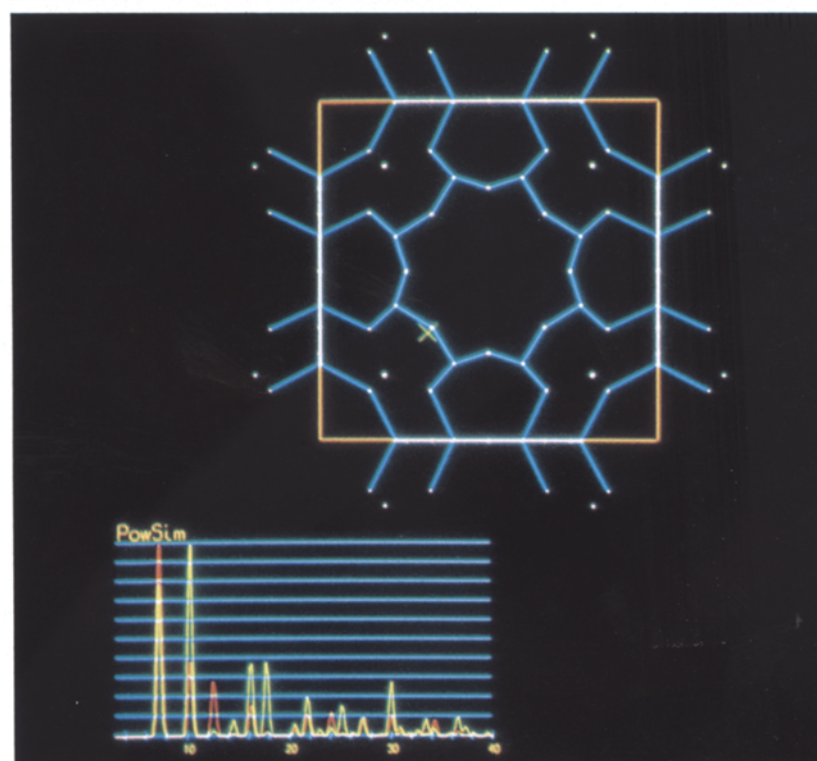
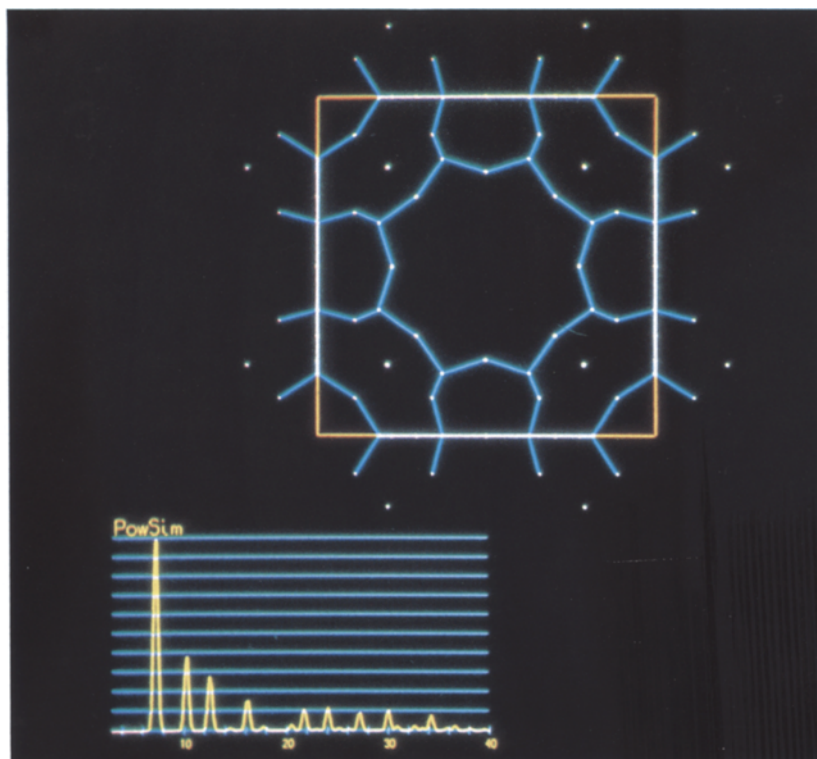


Fig. 4. (A) Unit cell of Zeolite-4A with its simulated diffractogram. (B) A slightly modified structure derived from Zeolite-4A with the simulated diffractogram in yellow, and the original one in red.

as rigid constraints. If symmetry properties, cell constants or the elemental composition have to be modified, one has to start anew with an updated model and calculate a fresh display structure. However, we plan to develop the possibility of including some of these properties in the display structure to facilitate the study of special features such as phase transitions.

The program PLUVA is currently used to study zeolites, which are highly symmetric inorganic compounds built from simple SiO_4 tetrahedrons. Attempts have been made to model their channels using Connolly surfaces [12] in order to visualize which parts inside the structure are accessible to a specific probe molecule. This is shown in Fig. 3 for the zeolite ZSM-5 [13]. For instance, the template of ZSM-5 is easily modelled into the channels by using the zeolite framework as the backbone and moving and rotating the template molecules (utilizing the E&S PS dials) with retention of the symmetry until they fit into the Connolly-surfaced channels.

Furthermore, we are also exploring the display style of atoms, bonds, and surfaces; at the moment a great many options are available. The importance of this aspect should not be underestimated since the perception and hence comprehension of a structure on a graphics display is strongly influenced by the display style. For example, in order to highlight relevant aspects of a structure, an option is needed to de-emphasize distracting details.

It should also be noted that PLUVA can generate input for programs such as MOGLI [10] so that it is possible to switch from PLUVA to MOGLI and continue modelling with a static structure, e.g. to use specific features of MOGLI to study molecules and their interactions with a rigid zeolite.

POWDER DIFFRACTION SIMULATION

An important option that is available in our prototype system is an on-line calculation of powder diffractograms (using the program POWSIM), which provides a feedback to experimental data. Powder diffraction often plays an essential part in the structure elucidation of the vast class of compounds for which single crystals are not available, e.g. polymers, most zeolites, and many inorganic materials. The structure elucidation of such compounds involves the use of several other complementary techniques.

The ability to change a structural model in real time and to calculate one of its analytical data sets opens up the possibility of on-line model verification. In the case of simulating the powder diffraction pattern, it involves the transfer of the updated coordinates of the model from the PS 300 to the VAX, the actual pattern calculation, and finally the transfer of the simulated diffractogram back to the PS 300 display, where it is being displayed in combination with the measured pattern. In this way one can gain an idea of the sensitivity of the relative peak heights to atomic shifts. Figure 4 shows two photographs of Zeolite 4A [14] with its calculated diffractogram obtained during interactive modification of the structure model. One may also put molecules in the cavities, give them appropriate form factors and simulate their powder patterns.

Because of the limited speed of data transfer to the host computer and the speed of the host itself (a MicroVax II), this can be done at present in 'pseudo' real time only (1–10 s per simulation). It is expected that with graphic workstations with faster 'host' processors and comparable graphic processors this can be done in real time. The approach described above involves user-controlled trial and error and so far the trial-and-error process cannot be performed automatically. 'Brute force' automatic trial-and-error routines are still out of reach, because of 'limited' computer

power, problems with local minima, etc. The usual refinement methods, such as Rietveld refinement [15], are also applicable only after a sufficiently close trial structure has been obtained and they do not provide a clue for automation.

The interactive fitting of calculated powder patterns to measured ones is just one example of the coupling of model and experiment. We plan to incorporate simulations of other techniques, such as neutron and electron diffraction, high-resolution electron microscopy, EXAFS, etc., to further constrain the modelling procedure.

FINAL REMARKS

The aim of the described program system PLUVA is to facilitate the study of inorganic crystal structures given their space-group symmetry. Research at KSLA has already demonstrated its great value and potential. However, the project is just one year underway, and the E&S display has been available only during the second half of this period. Many more options are envisaged: to speed up and improve the analysis of inorganic structures, to study surfaces and interfaces, to compare structures, and to study the interaction of molecules with crystal structures, twinning and phase transitions.

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