

**ML.19-B** SUPERSPACE GROUPS IN CRYSTALLOGRAPHY. By A. Janner, Institute of Theoretical Physics, Cath. University, Nijmegen, The Netherlands.

Properties of modulated and of composite crystal structures lead to the concept of an incommensurate crystal-line phase (e.g. van Aalst et al., *Acta Cryst.* (1976) **B32**, 47; Fouget et al., *Phys.Rev.B* (1978) **18**, 3645). This structural phenomenon is very subtle but quite general in nature. It requires a revised definition of ideal crystal and of crystallographic symmetry (de Wolff, *Acta Cryst.* (1974) **A30**, 777; Janssen & the author, *Phys.Rev.B* (1977) **15**, 643). Looking at the diffraction patterns of incommensurate crystals as a projection in the physical space arising from the Fourier transformation of a periodic function (the supercrystal) in a (3+d)-dimensional euclidean space (the superspace), leads to superspace groups. Such a group is a (3+d)-dimensional space group (having some additional properties) with elements leaving the supercrystal invariant. The diffractive and structural properties of incommensurate crystals expressed by these symmetries can be made explicit by a suitable parametrization or by extending the crystal as a supercrystal in the superspace. This approach allows a complete classification of crystallographic symmetries which includes the usual ones (for d=0). A full list of inequivalent superspace groups for d=1, together with the conditions limiting possible reflections has been established (de Wolff et al., *Acta Cryst.* (1981)). A proposal for representing diagrams of equivalent general positions has also been made (de Wolff, *Colloque Pierre Curie*, Paris (1980)). Crystals are known requiring up to d=3 additional dimensions, but the majority of incommensurate crystals involve d=1 only. For a number of crystals superspace groups assignment has been made, permitting an explanation of structural and diffractive properties observed (*Acta Cryst.* (1980) **A36**, 399 and 408). The structure factor of an incommensurate crystal can be expressed in a symmetry adapted form by explicitly using superspace coordinates and superspace group symmetry elements (Yamamoto, *Phys.Rev. B* (1980) **22**, 373).

On the macroscopic level, superspace groups lead to the usual 32 crystallographic crystal classes in 3 dimensions. These classes, therefore, also represent a valid classification scheme for incommensurate crystals. Nevertheless, superspace symmetry does have macroscopic implications. Evidence of this has already been found in crystal growth forms, where a generalization of the Law of Rational Indices is needed, and where an extension to superspace of the Bravais-Friedel-Donnay-Harker rule seems to hold (*Phys.Rev.Lett.* (1980) **45**, 1700). For tensor properties the situation is analogous. The possible non-vanishing coefficients are restricted according to one of the usual crystal classes, but a superspace symmetry adapted tensorial form is possible. This allows a deeper insight into the relationship between microscopic structure and physical properties. As illustration the Lorentz tensor is considered. It is used to describe local electric field gradients and dipole fields in ionic crystals in terms of structural parameters (Colpa, *Physica* (1971) **56**, 185 and 205). This microscopic tensorial field normally has the same superspace group symmetry as the crystal. Once the local polarizability tensor is given in addition, one can derive expressions for the (macroscopic) dielectric tensor (a basic quantity in crystal optics) which are structure and symmetry dependent.

Finally, the possible relevance of superspace symmetries even for commensurate crystals is briefly discussed. All these results allow one to draw the conclusion, that crystal symmetry is still a wide-open field for future investigations reaching down to the foundations of crystallography.

**ML.20-A** FLEXIBILITY AND DYNAMICS OF PROTEIN STRUCTURE. By D.C. Phillips, Laboratory of Molecular Biophysics, University of Oxford, South Parks Road, Oxford OX1 3PS, U.K.

From the earliest analyses of protein structures at high resolution (Kendrew et al., 1960, *Nature* **185**, 422-427) the electron-density maps contained indications of differential flexibility and motion within these macromolecules. In the crystallographic refinement of such structures, as in the corresponding studies of smaller molecules, the effects of systematic errors in the data must be carefully eliminated and there is a fundamental difficulty in distinguishing between the real motion of a molecule in a single conformation and the effects of static disorder that arise when the images of molecules in different orientations and conformations are superimposed.

Crystallographic evidence shows that some proteins adopt widely different conformations under different circumstances and that this variability is related to biological activity (e.g. Huber, 1979, *TIBS*, Dec. 1979, 271-276). Smaller variations in conformation and the effects of complex intramolecular vibrations are observed in all proteins and recent developments in methods of refinement and experimental techniques, including data collection at moderately low temperatures, are making it possible to define them in detail (e.g. Sternberg et al., 1979, *J. Mol. Biol.* **130**, 231-253; Frauenfelder et al., 1979, *Nature* **280**, 558-563; Artymiuk et al., 1980, *Nature* **180**, 563-568). The results are consistent with other experimental evidence and with computer simulations of the dynamic behaviour of proteins (e.g. McCammon & Karplus, 1980, *Ann. Rev. Phys. Chem.* **31**, 29-45; Northrup et al., 1980, *Nature*, **287**, 659-660).

**ML.20-B** THE RENAISSANCE OF POWDER DIFFRACTION: From Ugly Duckling to Beautiful Swan. By J. I. Langford, Department of Physics, University of Birmingham, Birmingham B15 2TT, England.

Many factors have contributed to the spectacular revival of interest in powder diffraction. High intensity sources of X-rays and neutrons, improved instrumentation and new forms of detector have made it possible to collect reliable and accurate data within minutes or even seconds. Powder methods have also benefited from advances in computer technology and programming procedures; more data can be processed in a given time and automatic on-line control is now a matter of routine.

It is in the field of crystal-structure refinement that there has been a marked rejuvenation of powder methods. Following the pioneering work of Rietveld (*Acta Cryst.* 1967, **22**, 151), total-pattern analysis rapidly gathered momentum in the hands of neutron diffractionists (Hewat, *NBS* 1980, Special Pub.No.567,111). Now, with further impetus from synchrotron radiation and energy-dispersive methods (Glazer & Hidaka, *Acta Cryst.* 1978, **A34**, S331), the number of structures refined from X-ray data is increasing steadily (Young, *NBS* 1980, 153).

Less spectacular, but nevertheless important advances have occurred in the indexing of powder patterns and in lattice-parameter determination (Shirley, in 'Crystallographic Computing', Delft Univ.Press, 1978). Given reliable data, a unique cell can usually be obtained for stoichiometric substances, irrespective of the crystal symmetry. One of the principal uses of powder methods is the identification of unknown phases and, with the aid of a small computer and improved data-packing procedures, on-line search-match can be carried out. Development of other traditional applications, such as line-broadening

analysis, has continued. Here the most significant development has been an assessment of the accuracy of powder methods (NBS 1980).

A consequence of the introduction of high intensity sources and position-sensitive detectors is the possibility of time-resolved diffraction. The potential of this technique has yet to be fully realised and it is a field in which important advances of the future may well occur, particularly in the study of phase transitions involving order-disorder phenomena.

For many years, until the late 1960s, workers with single crystals held sway; powder diffraction was almost a fringe interest pursued by a select group of devotees in a handful of laboratories. Now the situation has changed. Single-crystal methods are largely a matter of routine and have been eclipsed by the renaissance of powder diffraction.

#### ML.22-A INTERACTIVE COMPUTER GRAPHICS IN STRUCTURE

ANALYSIS. By W V Wright, IBM United Kingdom Ltd., UK Scientific Centre, Winchester, Hampshire, UK.

Molecular graphics, the application of interactive computer graphics to molecular studies, is established as a useful tool for studying the structure of biological molecules. Scientific results being obtained with these systems are rapidly repaying the investments made for their development. For research which involves the iterative refinement of Fourier synthesis maps, molecular graphics is indispensable.

Mechanical models have always played a central role in the study of molecular structure. The substitution of computer graphics for these began when Levinthal (Scientific American (1966) 214, 42) built a system for folding proteins. This goal proved too difficult, but several members of his group continued the work and developed successful systems for other phases of molecular research.

In 1972 Barry and North (Cold Springs Harbor Symposium on Quantitative Biology, 36, 577) identified the requirements for a system to build molecular models into electron density maps. Successful systems for this application began to emerge about three years later. These systems have also proved useful for molecular refinement, for comparing structures, and for packing studies. Experience indicates that the greatest power of molecular graphics lies in the user's freedom to move easily between the thinking and computational phases of his work.

The development of molecular graphics systems continues, and the area of application is expanding. One emerging use is in the study of the geometry and dynamics of enzyme-substrate interactions.

ML.22-B USE OF LATTICE IMAGING IN THE STUDY OF MINERALS. N. MORIMOTO, Department of Geology and Mineralogy, Faculty of Science, Kyoto University, Kyoto 606, Japan.

The electron microscopic studies of minerals made before 1970 were confined to very special minerals such as clay-like minerals. Since the high resolution imaging technique was first applied on minerals, only several years ago, there has been great progress in the use of transmission electron microscopy for the study of minerals. The appearance of commercial ion-thinning machine has improved mineral specimen preparation techniques for transmission electron microscopy. High quality lattice images have been obtained of mineral oxides, sulfides and many groups of rock-forming silicates. The imaging technique has proved indispensable in elucidating the local arrangement which may not be readily detected using x-ray diffraction alone, such as short-range order, antiphase domain structures, topological transformation, coherent intergrowth, polytypism and stacking disorder.

Current electron microscopic resolution is still insufficient for determining the exact atomic arrangement of minerals. However, the combination of the lattice imaging and x-ray diffraction methods has proved successful in determining the superstructures of the nonstoichiometric and solid solution minerals such as pyrrhotite and plagioclase. The use of in-situ x-ray microanalysis of small structurally characterized area (~30 nm) has offered further invaluable means in the study of minerals. The localized structural perturbation and superstructure in minerals can be used to understand the mechanisms of solid state reactions, and to reveal the past geological conditions in which the mineral was formed.

ML.24-A CRYSTALLOGRAPHIC ENGINEERING, By Robert E. Newnham, Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania, U.S.A.

Crystallographic engineering—the design and construction of non-equilibrium crystal structures—is now a reality. Ion implantation, micro-machining, molecular beam epitaxy, and a host of other techniques developed by the semiconductor industry make it possible to devise miniaturized multiphase composites with a wide variety of connectivity patterns. Some examples of controlled structure-property relations involving the manipulation of conduction paths, mechanical stress configurations, and electric field distributions will be discussed, along with applications to acoustics, electronics, optics and medicine. Scaling down leads to new quantum phenomena and surprisingly large physical effects such as hot electron behavior and composite product-properties. Biological systems often serve as models for devices incorporating self-repair, memory, and membrane effects. Present and future goals for crystallographic engineers will be described.