

14.X-4 STRUCTURE ANALYSIS WITH HIGH ENERGY ELECTRONS

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High resolution electron microscopy is becoming an increasingly valuable technique for the determination of the structures of small crystalline regions and also, more importantly, for the study of the local deviations from periodicity in crystals. With the use of higher energy electrons and resolutions of 2Å or better, the range and precision of structural studies is increasing rapidly. At the same time, the requirements for precision in the determination of experimental parameters and the need for care in image interpretation have become much more exacting. For this reason the advancement of techniques for on-line digital analysis of images and computer control of the microscope is considered to be just as significant as the improvement of resolution.

Technical advances made in parallel with the improvements of imaging methods have broadened the scope of high resolution electron beam methods to include microanalysis and microdiffraction. The STEM instrument has introduced the possibilities for combinations of high resolution imaging and nanodiffraction from regions of diameter 3Å or less so that a combination of real space and reciprocal space information may be considered as the basis for a more detailed and complete description of the arrangements of atoms on any desired scale, given only that the specimens are sufficiently stable under electron irradiation. The special advantages of STEM include the choice of detector systems designed to take full advantage of the preknowledge of the specimen to accentuate the information on selected aspects of the structure e.g. to provide preferential information on deviations from periodicity or to detect the presence of particular local atomic configurations.

14.X-5 IMAGING OF DEFECTS IN INORGANIC CRYSTALS.

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Comparison of experimental and computer-simulated images of crystal structures, and their defects, provides a useful technique for structure determination in favorable circumstances. In this paper, the validity of computer simulation techniques, including both the scattering theory and the effect of instrumental electron optical parameters, which allow structural interpretations to be made from experimental images, are illustrated by practical applications. The information obtained is either complementary to that offered by neutron and X-ray diffraction, or cannot, for fundamental reasons, be obtained by other techniques.

Apart from the familiar extended defects - such as dislocations, stacking faults, crystallographic shear planes, Guinier-Preston zones, etc. - small defects having dimensions ~5 Å (called points traditionally) may be readily imaged using appropriate objective lens parameters. Observations of small defects in diamond and nonstoichiometric oxides (e.g. TiO_{2-x} , WO_{5-x} , etc.) will be reviewed, as will recent observations of the interactions between small and extended defects.

14.X-6 STRUCTURE IMAGING IN CHEMISTRY - SOME EXAMPLES

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High resolution electron microscopy (HREM) is now an accepted technique for characterising defects in known crystal structures (Tilley, *Chemica Scripta* (1979) 14, 271, Bursill, these proceedings) and has proved of great value to the solid state chemist in clarifying phase transformations and solid state reactions. Recently HREM has been applied to the determination of completely unknown structures in cases where traditional diffraction methods are inapplicable, such as quasi-crystalline or otherwise defective phases with no long-range order. It is now possible to assess the suitability of HREM for this purpose.

For absolute structure resolution, lens aberrations, instrumental instabilities and beam divergence set a limit for HREM studies in conventional instruments of ca. 2.3Å. At higher accelerating voltages, this can be extended to possibly 1.5Å, but this figure is much poorer than that available from X-ray or neutron diffraction refinement. Furthermore, multiple scattering of electrons is so severe that intuitive image interpretation is rarely possible, and trial and error methods involving the multislice procedure (Cowley & Moodie, *Acta Cryst.* (1957) 10, 609, Goodman & Moodie, *Acta Cryst.* (1974) A30, 280) must be employed. The final structure accuracy is still in no way comparable to that from a normal diffraction refinement.

In spite of these limitations, however, structure determination by HREM is still of crucial importance in solid state chemistry, particularly in the areas of complex solid solutions and heterogeneous catalysis. Knowledge of structural chemistry in these fields is not limited by lack of refined structural data, but by the impossibility of determining trial structures of subsequent refinement. Some of the earliest examples for this type of structure determination arise in the chemistry of tungsten-niobium oxides (Iijima & Allpress, *Acta Cryst.* (1974) A30, 22) and in the alkali-tungsten bronzes. (Husain and Kihlberg, *Acta Cryst.* (1976) A32, 551; Kihlberg, *Chemica Scripta* (1979) 14, 187). The determination of intergrowth structures in the pentasil family of zeolites (Thomas et al. *Faraday Discussion* (1981) 72, 345) also falls into the category. In all these cases some a priori diffraction information was available, but this need not always be the case, as is shown by the determination of the structures of $\text{W}_{18}\text{O}_{49}$ (Sundberg, *Chemica Scripta* (1979) 14, 161) and $\text{Ba}_2\text{Ti}_5\text{O}_{20}$ (Grzanic et al, *J. Solid State Chem* (1983) 47, 151), although the latter was subsequently studied by single crystal X-ray diffraction.

In the field of heterogeneous catalysis, the scope for structure determination by HREM is very great. The materials are generally polyphasic, and rarely at true equilibrium, making the preparation of large single crystals impossible. In the system Bi-Mo-W-O, one complex layered structure has already been established using HREM by the author and co-workers. (*J.C.S. Chem. Comm.* (1983) 594). Trial structures for several phases in the systems Bi-Mo-Nb-O and Bi-Nb-W-O have also been derived from HREM data. Where the Bi content is approximately twice that of the other cations, intergrowths derived from that of Bi_2MoO_6 have been assigned, involving either edge-sharing polyhedra or overlap of oxide layers in a perovskite-like fashion. Where the other cations outnumber Bi, structures with layers based upon pentagonal columns appear to exist, and it seems that there is no limit to the complexity of these phases. In such systems, HREM offers the only possibility of structure elucidation.