

17.X-1 PROBLEMS IN SPACE-GROUP ASSIGNMENTS.  
By R. E. Marsh, A. A. Noyes Laboratory of Chemical Physics,  
California Institute of Technology, Pasadena, Calif. 91125, USA.

Three aspects of a proper space-group assignment will be discussed: finding the correct lattice, determining the appropriate Laue symmetry, and deciding whether or not the structure is centrosymmetric. An incorrect lattice may be chosen if reflections are overlooked, perhaps because they are systematically weak, or are thought to be present when they are not, perhaps because of interference from neighboring reflections. Incorrect Laue symmetry may result if a cell reduction is not carried out correctly, or if errors in cell dimensions are large (perhaps due to absorption or to a poor choice of reference reflections), or if an insufficient sampling of data has been examined. Resolving the centrosymmetric-noncentrosymmetric ambiguity is a more complicated problem and, in terms of molecular structure, a more serious one, as an incorrect choice may lead to large errors in atom positions. Some procedures for reducing the chance of error in all three areas will be suggested.

17.X-2 ERRORS IN ABSOLUTE-STRUCTURE DETERMINATION.  
by G. Bernardinelli and H. D. Flack, Laboratoire de  
Cristallographie, University of Geneva, 24 quai Ernest  
Ansermet, CH-1211 Genève 4, Switzerland.

The term "Absolute Structure" englobes the notions of both chirality and polarity (viz absolute configuration, absolute conformation, enantiomorph). A significant improvement in absolute-structure determination has recently resulted from the use of a single variable parameter which can be refined by least squares.

Absolute structure is a property of any non-centrosymmetric structure and a principal source of error is to ignore it. Systematic errors and effects in intensity data such as: data region, absorption correction, neglect of light atoms and stability constant have been investigated by the use of the refineable parameter. The stability constant causes the major perturbations. Attention will also be drawn to the following error sources in treating non-centrosymmetric structures: (1) Polar dispersion error; (2) Hand of axes; (3) Relation to physical and chemical properties.

In many cases, insufficient attention to the problems of absolute structure is being paid in the determination and publication of non-centrosymmetric structures.

17.X-3 ANALYSIS AND USE OF CRYSTALLOGRAPHIC DATA.  
By Frank H. Allen, Crystallographic Data Centre, University  
Chemical Labs., Lensfield Road, Cambridge, England.

The results of early X-ray analyses had a fundamental impact on the development of theories of chemical bonding in all its aspects. Concepts of ionicity, covalency, H-bonding, van der Waals interactions, etc. were formalized and 'geometrized' by systematic study of these early data. Over the past 25 years it is doubtful if modern inorganic chemistry would have progressed so rapidly had it not been underpinned by some 30,000 crystal structures.

As the number of reported structures rushed towards 100,000 attempts to systematize and interpret this data, beyond the confines of individual studies, abated considerably. The effort to locate and organize original data, against a backdrop of increased demand for more and more crystal structures, was a significant barrier. Increasing availability of crystallographic databases has done much to reduce this barrier: over 100 papers on 'molecular systematics' have appeared in the literature since 1980.

The sheer volume of data now available for analysis has, however, created its own barriers. The urgent need now is for numerical and statistical methods to aid in the extraction of meaningful crystallographic or chemical results. A number of such techniques are now in use, and examples will be given.

In the organic and biological areas considerable use of crystallographic data is now being made by non-specialists. The rapid expansion of molecular graphics facilities, particularly in the pharmaceutical industry, has created a demand for coordinate-based models of both 'known' and 'unknown' molecules. In the latter case a knowledge of likely dimensions and conformational preferences for many common substructural units is of vital importance. The derivation of these quantities, by application of methods noted above, is an important adjunct to purely computational techniques. Prospects for such a 'fragmentary' approach will be summarized.

17.X-4 OVERVIEW OF DIRECT METHODS, WITH ANOMALOUS DISPERSION. By H. A. Hauptman, Medical Foundation of Buffalo, 73 High St., Buffalo, NY 14203.

The electron density function  $\rho(r)$  in a crystal determines its diffraction pattern, that is, both the magnitudes and phases of its X-ray diffraction maxima, and conversely. If, however, as is always the case, only magnitudes are available from the diffraction experiment, then the density function  $\rho(r)$  cannot be recovered. If one invokes prior structural knowledge, usually that the crystal is composed of discrete atoms of known atomic numbers, then the observed magnitudes are, in general, sufficient to determine the positions of the atoms, that is, the crystal structure.

The intensities of a sufficient number of X-ray diffraction maxima determine the structure of a crystal. The available intensities usually exceed the number of parameters needed to describe the structure. From these intensities a set of numbers  $|E_H|$  can be derived, one corresponding to each intensity. However, the elucidation of the crystal structure also requires a knowledge of the complex numbers  $E_H = |E_H| \exp(i\phi_H)$ , the normalized structure factors, of which only the magnitudes  $|E_H|$  can be determined from experiment. Thus, a "phase"  $\phi_H$ , unobtainable from the diffraction experiment, must be assigned to each  $|E_H|$ , and the problem of determining the phases when only the magnitudes  $|E_H|$  are known is called "the phase problem". Owing to the known atomicity of crystal structures and the redundancy of observed magnitudes  $|E_H|$ , the phase problem is solvable in principle.

The values of the individual phases are determined by the crystal structure and the choice of origin. However, there always exist certain linear combinations of the phases whose values are determined by the structure alone and are independent of the choice of origin. These linear combinations of the phases are