

ML.10-H2 QUALITATIVE AND QUANTITATIVE INTERPRETATION OF DIFFUSE SCATTERING, by H.Jagodzinski, Institut für Kristallographie und Mineralogie der Universität München, Theresienstr. 41, D-8000 München 2, FRG

It is generally agreed that the use of averaged intergrated structure factors $|\langle F(h,k,l) \rangle|^2$ results in a periodic structure giving the time and space average over all unit cells of the crystal irradiated during diffraction. On the other hand it may be shown theoretically that this is true only if certain conditions are satisfied. One of them is an unambiguous separation of diffuse scattering from sharp Bragg-reflections. Therefore high resolution techniques are needed especially in those cases where disorder phenomena with long range correlations have to be taken into account. Since three-dimensional diffuse scattering is often very weak, diffraction techniques with low background scattering and lower resolution power are also important. This means in practice that strictly monochromatic, focusing methods have to be used.

It is well known that the diffuse intensities $I(hkl)$ of any disordered crystal may be calculated according to the equation $I(hkl) \sim \langle |F(hkl)|^2 \rangle - \langle |F(hkl)| \rangle^2$ (1)

Since $F(hkl)$ may be calculated with the aid of a classical structure determination, the main difficulty is caused by the first term in equation (1). As has been mentioned above, the calculation has to include time and space correlations of the disordered crystal. In case of short range correlations the cluster method seems to be the easiest approach to the solution of the diffraction problem. In all other cases the method of a periodic modulation of the idealized substructure is more convenient. Unfortunately there are only few examples in literature treating the diffuse scattering of a disordered crystals quantitatively. This may be explained by the large amount of work caused by the experimental and theoretical evaluation of diffraction data. Therefore, an electronmicroscopical study of the disorder phenomena may sometimes be useful. Some examples will be discussed, showing that much more information may be derived from a quantitative treatment of diffraction data. Neutron data of inelastic diffuse scattering play an important role in the study of the dynamic behaviour of disordered crystals.

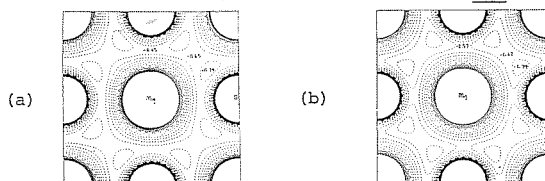
It has been shown by various investigators that diffuse scattering may often be explained using pseudo-kinematical calculations, even if the diffraction problem necessitates a dynamic solution. This could even be shown for crystal surfaces studied by low energy electron diffraction, where diffuse scattering is frequently observed. The influence of anomalous scattering on diffuse scattering will become increasingly important for the determination of defect structures. Since disordered areas of the crystal mainly contribute to diffuse scattering, it should be possible to determine phase relationships of the diffuse scattering in a similar way as known for structure determination. They have to be explained with the aid of a statistical theory which is not yet fully developed. First experiments on this subject will be discussed.

Disorder of domains as well as modulated structures may cause many difficulties in structure determination. A theoretical treatment of a single crystal, consisting of twins of two asymmetric structures correlated by the centre of symmetry can hardly be determined in a classical way. If the mean difference of the two structure factors is less than 20%. Similar results are obtained for other twins or integrown crystals with strictly, or nearly coinciding reflections. In this particular case the study of diffuse scattering alone can lead to a unique solution of the structure. Consequently a qualitative study of diffuse scattering prior to structure determination should be done in order to avoid incorrect structures, although their R-factors are satisfactory.

ML.10-H4 ELECTRON DENSITY AND BONDING, FROM METAL OXIDES TO PROTEINS. By E.N. Maslen, Crystallography Centre, University of Western Australia.

Accurate X-ray diffraction experiments, which enable the structural geometry of crystalline materials to be determined precisely, also provide detailed information on the one-electron density function (obtained by a Fourier transformation from X-ray scattering amplitudes). Many properties of the material are functionally related to the electron density.

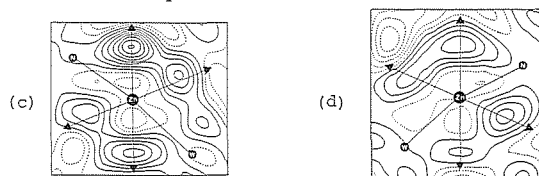
For the electrostatic potential the functional relationship is particularly straightforward. The consistency achieved in favourable cases is shown by results for magnesium oxide, calculated from measurements (a) by P.L. Sanger (1969) *Acta Cryst.* A25, 694 and (b) by P.M. Raccach & R.J. Arnott (1967) *Phys. Rev.* 153, 1028.



Similar consistency cannot be achieved for some quantities (relevant to the chemical behaviour of matter) such as atomic charge and ionicity, because they are not defined uniquely. Their relationships to different types of experimental results are not always compatible. Thus charges used in estimating lattice energies are often smaller formal charges determined by the valence state.

Atomic charge can be related uniquely to the one-electron density function. Neutrality of the atoms in the promolecule (an assembly of undeformed atoms at the equilibrium positions) is essential to the definition. A rigorous specification of pseudo-atom boundaries is also possible.

Consistent results can be obtained even for complex structures as shown by the deformation densities (c) and (d) near crystallographically independent zinc atoms in insulin by N. Sakabe, K. Sasaki & K. Sakabe (1984). *Methods & Applications in Crystallographic Computing*, Oxford University Press.



The interpretation of pseudo-atom deformation densities is simplified if the deformation is dominated by a single term in a perturbation series. Thus the 4d-5p contributions to rare earth densities increase as the energies for the 4d and 5p levels approach each other.

One can identify anisotropic components of experimental pseudo-atom densities associated with the Pauli exclusion principle. Such non-spherical components become progressively more important as the quantum numbers for the valence states increase. Ionic lattices are less polar than is indicated by the formal charge.

The widespread belief that the deformation density is predominantly due to nearest neighbour interactions is not well founded. Whereas covalent bonding is a nearest neighbour phenomenon deformation density is affected significantly by interactions with more distant atoms.