17.4-3 THE USE OF A WINDOW FUNCTION TO REFINE PARTIALLY OVERLAPPED TWIN DATA. by

A. David Rae, School of Chemistry, University of New South Wales, Kensington, N. S. W., Australia.

Monoclinic crystals of $(5MAP)_2Cu_3Cl_8$ where 5MAP is the 5-methyl-2-amino pyridinium ion have cell dimensions a 3.917Å, b 24.07Å, c 12.18Å, β 104.14°; $P2_1/c$, Z=2. Twinning causes the twin components of 0,k,ℓ data to overlap perfectly but the angle of 89.82° between a*−0.75c* and c* causes h=2n data to partially overlap, while h=2n+1 data is resolved. Mounting a crystal so that c* is approximately normal to the axis of the φ−circle gave maximum values of Δχ 0.083°, Δω 0.36° and Δθ 0.075° to describe the shift in four circle diffractometer angles necessary to locate the twin related h,k,−ℓ−1.5h reflection in the diffracting position rather than the h,k,ℓ of the first component. Mo−K_α data was collected using a θ/2θ scan on a CAD4 diffractometer.The searched reciprocal lattice was for the first component and was accurately determined using h=2n+1 and h=0 data only.

A 4mm high slit at a distance of 173mm implied an angle of Δχ=0.33° to shift a reflection from the centre of the slit to the top edge. A slit width of (1.3 + tanθ) mm implied an angle of Δω = (0.108+0.083tanθ)° to shift a reflection from the centre to the edge of the slit.

This choice of parameters allowed partial resolution of h=2n data and a refineable window function

$$W_\omega(\Delta\omega) = 0.5 - 0.5 \sin\{{}^{\pi}/_{2}\,[|\Delta\omega| - (p_1+p_2\tan\theta)]\,/p_3\}$$

was used to modify the twin ratio to $(1-\alpha)/\ \alpha W_\omega(\Delta\omega)$ where $W_\omega(\Delta\omega)$ =1 if the argument of the sin function is less than $-{}^{\pi}/_{2}$ and 0 if the argument is greater than ${}^{\pi}/_{2}$. Values of p_1=0.116(3)°, p_2=0.090(7)°, p_3=0.118(4)° and (1−α)/α=0.687(5)/0.315(5) were obtained from least squares refinement of the structure using RAELS87. p_1 and p_2 are consistent within the reliability of the cell parameters. A final value of R_1=0.030 was obtained for data considered observed [I>3σ(I)] with R_1 0.024(h=0), 0.028(h=1), 0.034(h=2), 0.029(h=3), 0.041(h=4). The method of data collection increased the distinction between twin related reflections without harming the ultimate refinement.

17.4-4 MAXIMUM LIKEHOOD DETERMINATION OF PARAMETERS FOR POWDER, LAUE AND DIVERGENT BEAM PATTERNS. By

Edmund Ratajczyk and W.A. Keller, Instituto de Fisica, Universidade Federal da Bahia,Salvador, Brasil.

A general approach for any experimental arrangement is developed in which a number of directly measured magnitudes or data is used to calculate a substantially smaller number of parameters, considered as results. A mathematical model of experiment is set up which enables essential reverse calculations of the "theoric" values for the whole data set. Some additional parameters are necessarily introduced to complete the mathematical model.The calculations are realized by a numerical procedure unique for the experiment of interest. Convergence of the procedure is checked by a minimum variance criterium based on the assumption of the normal distribution of all the measured magnitudes. For each particular data set a linear statistical model is postulated. The maximum likehood or "best" values of all the parameters together with their standard deviation are defined under validity of the linear model. The limit value of variance sets the overall precision effectively attained in the particular realization of the experiment. The procedure has been applied for the powder, Laue and divergent beam techniques.

17.5-1 A RATIONAL DEPENDENCE SCREENING TEST. By

J.S Rutherford, Department of Chemistry, University of Transkei, Private Bag X5092, Umtata, Transkei, Southern Africa.

The probability that s points chosen at random on a three dimensional lattice satisfy the primitivity condition is $[\zeta(s)\ \zeta(s-1)\ \zeta(s-2)]^{-1}$, where ζ is the Riemann zeta function. Applied to the reciprocal lattice, this provides a method of estimating whether, for example, such a non-primitive arrangement of strong reflections could occur by chance or represents a genuine case of rational dependence, or of a commensurate superlattice. However, when considering potential sublattices in practice, only those belonging to the same Laue class are of any interest, in which case the formula above only holds for Laue class $\bar{1}$, ie the triclinic space groups P1 and $P\bar{1}$. For all other space groups, we must consider the effect of choosing s points at random together with all the other points related to them through the diffraction symmetry. There are then 24 cases in all, since the expression will be identical for space groups belonging to the same "Patterson symmetry", that is the same Laue class and lattice type. These expressions have been derived, and their form in all cases was found to be A(s)/f(s) where f depends only on the Laue class, and is a product of the sums of infinite series, chiefly zeta functions, but also Dirichlet L functions. A in turn derives from the lattice type, but varies depending on what other lattice types exist in that Laue class, and are therefore available as potential sublattices. It represents a correction to one prime number (p) term in the infinite product form of f(s), the term adjusted being the p=2 term in the monoclinic, orthorhombic, tetragonal and cubic crystal classes, and the p=3 term in the trigonal and hexagonal classes. The various formulae have been evaluated for appropriate values of s and some examples of their application will be given.