reduces the reliability with which the structural parameters can be determined. Furthermore, the usefulness of the technique also depends on the satisfactory solution of a number of problems, such as the description of the incident white-beam spectrum in terms of intensity as a function of wavelength, the ability to specify the wavelength dependence of certain systematic effects such as absorption, extinction and thermal diffuse scattering and the ability of the method of analysis to overcome problems arising from correlation between parameters. Our own extensive measurements over the past few years indicate that these prolems are such that structure determination using white-beam techniques is inherently less reliable than that possible using conventional monochromatic-beam techniques.

In order to investigate these basic problems we collected a total of 601 Bragg-intensity measurements from a single crystal of KCl, involving reflexions for neutrons with wavelengths in the range 0·5 to 6·25 Å. Analysis of these white-radiation measurements indicated that the spectrum from the DIDO reactor deviates significantly from a Maxwellian and that the Zachariasen (1967) theory of extinction is not generally satisfactory for neutron-diffraction measurements of this type. The latter problem was overcome by using the modified extinction theory given by Cooper & Rouse (1970) which includes the appropriate angular dependence of the extinction on intensity. With this modified extinction theory and a Maxwellian spectrum we were able to obtain an R value for intensity of about 6%. Use of a more appropriate spectrum would reduce this value somewhat. The fact that systematic effects are relatively less serious for conventional monochromatic-beam techniques is borne out by recent conventional measurements on a single crystal of KCl which have given R values for intensity of less than 1% (Cooper & Rouse, 1972).

The variation of the refined parameters as a function of the spectrum parameter ($P3$), found by Hubbard, Quicksall & Jacobson (1972) in their Table 1 appears to indicate that in their case also there are systematic deviations in the spectrum from a Maxwellian.

Both white-beam and monochromatic-beam measurements on KCl have shown that the basic extinction parameters, r and g (see Cooper & Rouse, 1970), are not well defined individually, even over the wavelength range involved in the white beam case. Similar conclusions have been reached from conventional single crystal measurements on ZnS and ZnTe (Cooper, Rouse & Fuess, 1972). It is therefore difficult, in the white-beam case, to determine the most appropriate model for the extinction. Furthermore, there is also virtually no experimental verification for the wavelength dependence of extinction effects as predicted by these theories.

Further white-beam measurements have been made on single crystals of K_2NaCrF_6 (El Pasolite), urea and hexamethylene tetramine. These have also shown that thermal diffuse scattering and absorption can be serious problems when measurements extend over a large range of wavelength. Although R values for intensity of the order of 10% have been obtained in each case, it is clear that there are still systematic effects to be accounted for and that some further improvement is possible. However, conventional least-squares refinement programs do not appear to be very suitable for this type of data and an existing program (see Cooper, 1970) which uses a search algorithm procedure (Powell, 1965) is being extended for use in this work.

We are hopeful that the problems discussed above can be accounted for adequately in the model used to provide theoretical intensity values. However, it is clear that the magnitude of these problems is such that the reliability of structure determination using white-beam techniques is considerably less than that possible using conventional monochromatic-beam techniques.

Full details of the measurements referred to above will be published when our analysis has been completed.

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An Algol program for crystal-structure illustrations on a digital plotter using a small computer.

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An Algol program for drawing ordinary or stereoscopic-pair views of a crystal on a digital plotter is described. The program is suitable for use on a small computer and plots clinographic projections of ball-and-stick or space-filling models.

Introduction

The object of the program is to produce on a digital plotter normal or stereoscopic-pair views of a crystal unit cell from any angle.

The basis of calculation differs from that used in previous programs of this nature (Johnson, 1965; Cole & Adamson, 1969) in that clinographic projections on crystallographic planes are plotted rather than perspective views from a point specified by polar coordinates. This gives considerable advantages over published programs in both facility of use and in its requirements of computer storage and time.

Data format

The data required are as follows.

(1) Cell constants. (2) Title. (3) Atom parameters: for each atom: (i) number of atom, (ii) fractional coordinates x, y, z, (iii) atomic radius (Å), (iv) label for atom. (4) Bonds to be plotted between atoms [specified by pairs of numbers from 3(i)]. For each view required: (1) the Miller indices h,k,l of the plane normal to the direction of view; (2) the vertical projection axis (a, b or c); (3) overall diagram scale; (4) atomic-radii scaling factor; (5) normal or stereoscopic view and, if the latter, the angular separation, ($2s$), of the two views (usually 6°).

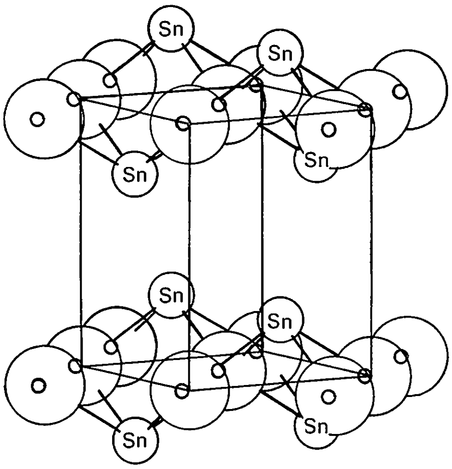

Fig. 1. Unit cell of tin(II) oxide as seen from direction normal to the plane (351). Atomic radius scaling factor 0·5.

Output

The unit cell and its contents are drawn as seen from a direction normal to the specified plane. Atoms and bonds are represented as circles and straight lines respectively. Overlap of atoms with bonds and other atoms is taken into account. The visible portions of partially obscured atoms are drawn and completely obscured atoms are represented by dashed circles. Axes and atoms are labelled. Ball-and-stick or space-filling models may be produced by adjustment of the atomic-radii scaling factor. Perspective diminution of atoms is not considered but since stereoscopic pairs may be calculated automatically this is not a great disadvantage.

Apart from the plotter output, the atoms, bonds and view data are printed, together with the bond lengths as a check that the correct atoms have been specified.

Figs. 1 and 2 show normal and stereoscopic views of the structures of tin(II) oxide (Moore & Pauling, 1941) and caesium tin(II) trichloride (Poulsen & Rasmussen, 1970) respectively, drawn using the program. Plotter output may be traced and photo-reduced so that stereoscopic pairs may be examined with a standard viewer as here. Alternatively, the output may be viewed directly using a simply constructed mirror viewer (Rule, 1938).

Method of calculation

A clinographic projection on the plane specified by h,k,l is calculated by deriving the projected cell constants (a_p, b_p, c_p, α_p, β_p, γ_p) as follows:

$$a_p^2 = a^2 - h^2d^2(hkl)$$

$$\cos\alpha_p = \frac{bc\cos\alpha - kld^2(hkl)}{\{[b^2 - k^2d^2(hkl)]\,[c^2 - l^2d^2(hkl)]\}^{1/2}} \quad etc.$$

The fractional coordinates remain unchanged.

The atoms are sorted according to depth by considering their projections on the $\mathbf{d}^*(hkl)$ vector and plotted starting with the one nearest the eye. Before each atom is plotted, a

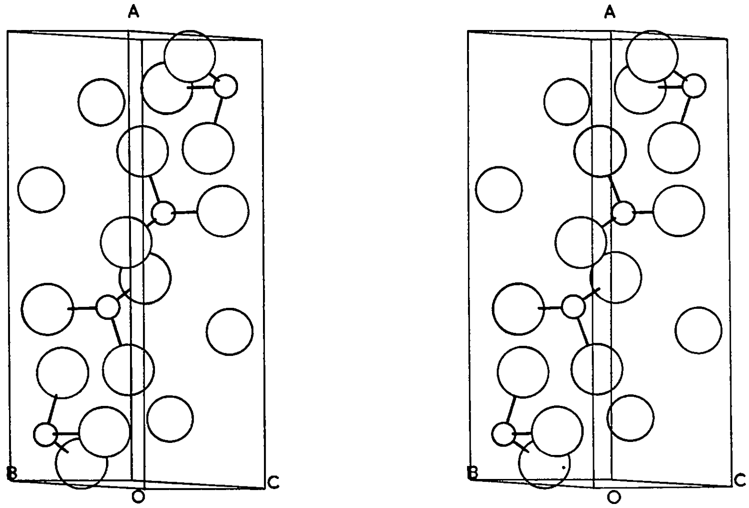

Fig. 2. Stereoscopic view of unit cell of caesium tin(II) trichloride as seen from direction normal to the plane (153). Atomic radius scaling factor 0·5.

check is carried out to determine whether it is hidden by any of the atoms in front of it. Any doing so are stored. Fast plotting procedures are used for unobscured (full circle) and totally obscured atoms (dashed circle). For partially hidden atoms only the unobscured part is drawn. The appropriate atom labels are drawn at the centre of the atoms. When the atom labels lie in an obscured position (see Fig. 1) they may be omitted.

Bonds are drawn as straight lines between atom centres from the edge of the nearer atom to the appropriate point on the further one. The bonds are not plotted at points where they are obscured by other atoms.

Stereoscopic views are obtained by plotting two clinographic projections on planes ($h_1k_1l_1$) and ($h_2k_2l_2$) calculated by rotating the originally specified (hkl) plane through angles of $\pm s°$ (usually 3°). The new projection planes correspond to the left and right eye views as determined by consideration of the angles between the $\mathbf{d}^*(hkl)$ vector and the reciprocal cell axes.

The program has been written in Elliott Algol for the Elliott 503 Computer (8K central processor, 16K backing store) using a Calcomp plotter (100 steps/in, 300 steps/sec). The normal and stereoscopic views shown in Figs. 1 and 2 took $3\frac{1}{2}$ and 8 min respectively. This compares with about 70K storage required for Johnson's *ORTEP* and 60K for Cole & Adamson's program. The program described here is also about twice as fast as the latter.

Further information and copies of the program may be obtained from the authors at the above address.

We are grateful to the staff of Chelsea College Computer Centre for their help in the preparation of this program and one of us (D.C.P.) thanks the S.R.C. for a research studentship.

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Non-rigid-body thermal-motion analysis.

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The usual analysis of thermal-motion parameters, derived from X-ray diffraction data, in terms of rigid-body motions can be extended to include the effect of certain specified internal molecular motions.

Analysis of molecular thermal motion in terms of rigid-body libration and translation (Schomaker & Trueblood, 1968) sometimes leads to excellent agreement between the U_{ij} tensor components derived from X-ray analysis and those calculated from rigid-body thermal-motion analysis ($\langle \Delta U_{ij}^2\rangle^{1/2} \sim 1\text{–}2\times 10^{-3}$ Å^2); sometimes, however, the agreement is not so good ($\langle U_{ij}^2\rangle^{1/2} \sim 10^{-2}$ Å^2). In certain cases the poor quality of the agreement can plausibly be ascribed to internal molecular motions which invalidate the rigid-body assumption.

The general treatment of internal motions, given only the vibration tensors, which are sums of mean-square displacements, is impracticable for most molecules. However, we may sometimes be able to postulate certain kinds of motions and estimate their magnitude by including appropriate parameters in the least-squares equations. Obviously the mere addition of parameters to the least-squares treatment will decrease the value of the usual residual $Q=\sum w(U_{ij}^{\text{obs}}-U_{ij}^{\text{calc}})^2$ but carefully chosen parameters should be more effective than random choices.

Assume, for simplicity, that in Fig. 1, C librates about the axis AB. If the amplitude of libration is not too large the motion is along the unit vector $\mathbf{n}=\mathbf{m}\wedge\mathbf{a}/|\mathbf{m}\wedge\mathbf{a}|$ and its magnitude is the product of the root-mean-square libration amplitude Ω and the perpendicular distance, $R=|\mathbf{m}\wedge\mathbf{a}|/|\mathbf{a}|$, of C from the libration axis AB. We can now describe the motion of atom C in terms of the usual rigid-body contributions *plus* a non-rigid-body contribution. The observational equation for atom C is then, in the Schomaker–Trueblood (1968) notation.

$$U_{ij}=G_{ijkl}L_{kl}+H_{ijkl}S_{kl}+T_{ij}+\Omega^2R^2n_in_j \qquad (1)$$

or, in Cruickshank's (1956) notation the U_{ij} tensor can be expressed as

$$U_{ij}l_il_j=T_{ij}l_il_j+\omega_{ij}(\mathbf{l}\wedge\mathbf{r})_i(\mathbf{l}\wedge\mathbf{r})_j+\Omega^2R^2n_in_jl_il_j\,. \qquad (2)$$

More generally, several intramolecular librational axes $\mathbf{a}_j$ can be chosen so that each of them acts on one or more of the atoms constituting the molecule. The last term in (1) and (2) is then replaced by the appropriate sum over the various axes $\mathbf{a}_j$ which contribute to the motion of that atom. This treatment assumes that the motion of any atom arising from intramolecular motion can be approximated by compounding librational motions about prescribed vectors that have to be chosen by chemical intuition or guesswork.

Although several obvious objections may be raised against this procedure, it should provide in favourable cases a semiquantitative description of the molecular motions in the sense that a large motion should be manifested in a large value of the appropriate Ω and a substantial reduction

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