that for the linear combinations given by equation (3) only those which yield the least difference between f_i' and f_i are in general acceptable.

The next step is to establish the true set of numbers which corresponds to the two lines selected initially. This is achieved by testing all sets in the above group in accordance with the 'equivalence' property defined by (7) and (8). Using the values of m_i, n_i obtained previously, equation (4) gives fractional values of y_i for the first three sets, which is inadmissible. Of the remaining sets only $\begin{vmatrix}0&4\\1&0\end{vmatrix}$ fits the data for the hexagonal system in Table 1 and also yields a collection of integers x_i y_i that do not contain a common integral factor. The substance under investigation thus belongs to the hexagonal system and for the first two lines, $x_1=0$, $y_1=4$ and $x_2=1$, $y_2=0$. The values of hkl for each line are then obtained from Table 1. x_i, y_i and hkl are given in columns 6, 7 and 8 of Table 4.

Conclusion

Neskuchaev's method for indexing powder patterns, incorporating the rationalization suggested above, not only becomes more general, but also simpler than other methods employed for systems of intermediate symmetry. The method is therefore recommended as the principal one for patterns in this symmetry range, and as a subsidiary one for patterns of low symmetry. In the latter case, it is possible to establish that the substance under investigation belongs to a low-symmetry system, thus simplifying the application of more general methods of indexing (Ito, 1949, 1950; Peiser, Rooksby & Wilson, 1955; Azároff & Buerger, 1961).

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Parameter Errors in Polar Space Groups Caused by Neglect of Anomalous Scattering

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A simple formula is given for the atomic coordinate error when $\Delta f''$ is neglected. With Cu $K\alpha$ radiation the effect is important for most elements and can reach 0·08 Å.

1

Ueki, Zalkin & Templeton (1966) have recently pointed out the serious coordinate errors which can result from the neglect of the imaginary component $\Delta f''$ of the anomalous scattering in the ten polar point groups. In these groups the position of the origin in one or more dimensions is not fixed by reference to symmetry elements. In Ueki's example of thorium nitrate pentahydrate, space group $Fdd2$, Mo $K\alpha$ radiation, the neglect of $\Delta f''=9$ for thorium caused an error of about 0·05 Å in the z coordinate of Th relative to those of the lighter atoms.

In the present note we consider the problem further and in particular point out that the serious consequences of the neglect of $\Delta f''$ are not confined to heavy elements. As we have remarked elsewhere (McDonald & Cruickshank, 1967) the effect of the inclusion, with Cu $K\alpha$ radiation, of $\Delta f''=0·6$ for the S atoms in S_3O_9, space group $P2_1nb$, was to produce changes of 0·02 Å in some bond lengths.

2

For a centrosymmetric crystal the relation $|F(hkl)|=|F(\bar{h}\bar{k}\bar{l})|$ holds by virtue of the symmetry. For a non-centrosymmetric crystal the same relation is true, provided $\Delta f''$ is negligible (Friedel's law). In consequence

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with non-centrosymmetric crystals it is often the practice to measure, either directly or inferentially with the aid of the symmetry, the reflexions in only half the accessible volume of reciprocal space. In $P1$ the measured reflexions will thus lie in a hemisphere (say with l non-negative).

The contribution of any atom to a structure factor is proportional to

$$\exp[i(2\pi\mathbf{h}\,.\,\mathbf{x}+\varphi)]\,, \tag{1}$$

where $\varphi=\Delta f''/|f|$ is the phase shift due to anomalous scattering. As Ueki *et al.* remark, the fact that $\Delta f''$ is positive always makes the atom seem to lie in front of the plane with normal $\mathbf{h}$ passing through its true position. In $P1$, if the measurements are made for the l non-negative hemisphere, there will be no first-order errors in x and y coordinates from an uncorrected least-squares or electron-density calculation. However, there will be a systematic error in the z coordinate, since part of the phase shift can be simulated by an apparent change in z. The magnitude in Å of this error Δz is governed by

$$2\pi l(z+\Delta z)/c=2\pi lz/c+\varphi\,, \tag{2}$$

so that

$$\Delta z=c/2\pi\,\langle\varphi/l\rangle\,, \tag{3}$$

where the brackets denote an effective weighted average over all reflexions, the details of which will depend on the method of refinement, the least-squares weights and the vibration parameters (see *e.g.* Fig. 1 of Cruickshank, 1960). For an order-of-magnitude approximation we may take $c\langle 1/l\rangle=2/s_{\max}$, so that

$$\Delta z=\frac{1}{\pi s_{\max}}\,(\varphi)_{s=\frac{1}{2}s_{\max}} \tag{4}$$

where $s=2\sin\theta/\lambda$ and the phase shift φ is evaluated at $\frac{1}{2}s_{\max}$, with $s_{\max}$ the effective limit for measurement in the particular problem.

3

Fig. 1 shows Δz as a function of the atomic number Z for both Cu and Mo $K\alpha$ radiation. For Cu $s_{\max}$ was taken as 1·2 Å^{-1} (geometrical limit 1·3 Å^{-1}), and for Mo 1·6 Å^{-1} (geometrical limit 2·8 Å^{-1}). The calculations were based on the f_0, $\Delta f'$ and $\Delta f''$ values given in *International Tables for X-ray Crystallography* (1962), with some assistance from Cromer (1965). The main difference between the two sets of results is that the peaks associated with the various absorption edges are shifted to higher Z values with Mo radiation. The reduced maximum shifts for Mo are due to the assumption of a higher $s_{\max}$ than for Cu.

It can be seen that the errors with Cu radiation reach 0·06 Å at Co ($Z=27$), fall to 0·01 Å for $_{28}$Ni, rise to 0·08 Å for $_{64}$Gd, fall to 0·02$_5$ Å for $_{67}$Ho and rise again to 0·08 Å by the end of the periodic table. With Mo radiation and the assumed value of $s_{\max}$ the errors reach maxima of 0·04 Å at $_{39}$Y and 0·05 Å at $_{84}$Po. If we suppose that the maximum error which can be tolerated in a precision structure analysis is 0·005 Å, we see that for polar space groups the neglect of $\Delta f''$ is only justifiable if the structure contains no elements heavier than oxygen with Cu radiation or sulphur with Mo radiation. The error for carbon with Cu radiation is 0·003 Å.

We have checked the order-of-magnitude formula (4) against the exact shifts in several problems and have found agreement to within 25%. Fig. 1 is not necessarily satisfactory in individual cases as the appropriate values of $s_{\max}$ may not be those assumed in our calculations.

4

We now consider coordinate errors in non-centrosymmetric space groups other than $P1$. Those in the class 2 (b axis unique) will be liable to errors Δy if the data are for non-negative k. With the non-polar class 222 the data are usually collected with all indices non-negative, so that by symmetry the data give the effects of the hkl, $h\bar{k}\bar{l}$, $\bar{h}k\bar{l}$ and $\bar{h}\bar{k}l$ reflexions. A tetrahedral arrangement of the spherical octants is thus involved, and since every index has both positive and negative values there will be no first-order errors in the coordinates.

This tetrahedral arrangement of octants can also be obtained in the class 2 if the hkl and $\bar{h}\bar{k}l$ data are measured, and for $P1$ if hkl, $h\bar{k}\bar{l}$, $\bar{h}k\bar{l}$ and $\bar{h}\bar{k}l$ are measured. In these cases there will be no first-order coordinate errors. In class m (b axis unique) the error can be Δx or Δz according to whether the measurements are for h or l non-negative. As listed by Templeton (1960) the other polar point groups are $mm2$, 4, $4mm$, 3, $3m$, 6 and $6mm$. In these the neglect of $\Delta f''$ can lead to coordinate errors in the direction of the rotation axis. [It may be noted that the polar groups are those in which the piezoelectric effect can occur by hydrostatic pressure alone (Buerger, 1956)].

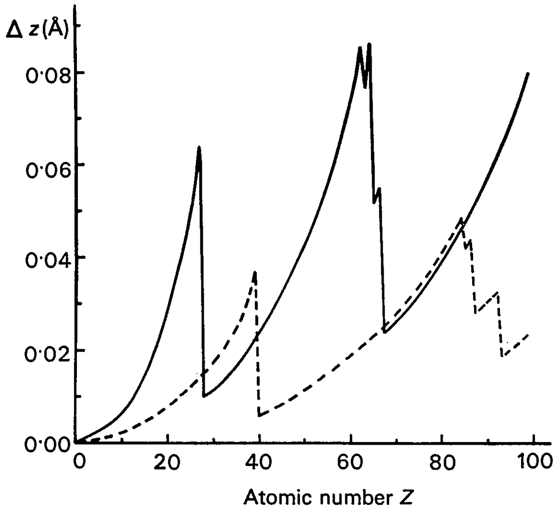

Fig. 1. Typical coordinate errors due to neglect of $\Delta f''$ in polar space groups. Full line: Cu $K\alpha$ radiation. Broken line: Mo $K\alpha$ radiation.

5

In the centrosymmetric space group $P\bar{1}$ the symmetry implies the measurement of both the hkl and $\bar{h}\bar{k}\bar{l}$ reflexions. The apparent shifts Δr will be in opposite directions $\mathbf{h}$ and $-\mathbf{h}$, so that there will be no net coordinate error. However, the atom will appear to be smeared out. Averaging over a sphere of constant $s=\frac{1}{2}s_{\max}$ (for which Δr will be also constant), the mean value of $\Delta|z|$, say, will be $\Delta r/2=\varphi/(2\pi s_{\max})$. Thus the apparent increase in the isotropic mean-square vibration amplitude of the atom will be roughly $\Delta U=(\Delta z/2)^2$, where Δz is given by (4). In the bad case of $\Delta z=0{\cdot}08$ Å, $\Delta U=0{\cdot}0016$ Å^2. This will be usually insignificant.

In a polar space group the coordinate shift, Δz say, will take up most of the U_{33} component of ΔU, together with a part of the U_{11} and U_{22} components.

For many elements the neglect of $\Delta f'$ will have more serious effects on vibration parameters than the neglect of $\Delta f''$, but this is easily taken care of by simple changes in the real part of f.

6

So far we have considered the effects of the neglect of $\Delta f''$, but a still worse situation arises if $\Delta f''$ is allowed for and the structure model is the inverse $(-\mathbf{x})$ of the true structure $(\mathbf{x})$. In this case, quite apart from having the inverse configuration, the anomalous atoms in polar space groups will have relative coordinate errors twice as large as indicated by equations (3) and (4). This can be seen as follows. The refinement processes endeavour to produce $|F_t(\mathbf{h})|$ for the inverse structure which equal the $|F_t(\mathbf{h})|$ of the true structure. Using $|F_t(\mathbf{h})|=|F_t^*(\mathbf{h})|$, we notice

$$\begin{aligned}|F_t(\mathbf{h})| &= |\Sigma \exp\{i[2\pi\mathbf{h}\,.\,\mathbf{x}+\varphi]\}|\\ &= |\Sigma \exp\{-i[2\pi\mathbf{h}\,.\,\mathbf{x}+\varphi]\}|\\ &= |\Sigma \exp\{i[2\pi\mathbf{h}\,.\,(-\mathbf{x})-\varphi]\}|\,. \qquad (5)\end{aligned}$$

Hence an exact fit could be obtained if the inverse structure had phases $-\varphi$. Since the refinement calculations actually take the phase shifts to be $+\varphi$, the equation corresponding to (2) which governs the simulated shifts Δz is

$$2\pi l(z+\Delta z)/c+\varphi=2\pi lz/c-\varphi\,. \qquad (6)$$

Thus Δz is twice as large as in equations (3) and (4).

In the case of a structure in the non-polar class 222, at the end of the refinement to the false minimum, the anomalous atoms will not be displaced relative to the others, but their vibration amplitudes will be too large by roughly $\Delta U=(\Delta z)^2$, where Δz is given by (4). (In 222 and other non-centrosymmetric classes not containing mirror planes, the inverse structure will of course be of opposite absolute configuration to the true structure).

As indicated by Hamilton (1965) the model with the inverse configuration will refine to a slightly higher residual than the true model, and, even when only half the accessible data are used, the slight difference in residual can be used to distinguish the true configuration.

7

In conclusion we note that for polar space groups the error from the neglect of $\Delta f''$ can easily be more important than the well-known systematic errors due to finite-series or rotational effects. Equation (4) is only a guide to the size of the error. The proper way of dealing with it is to include $\Delta f''$ in the calculated structure factors used in the refinement. Our study also indicated that there is a need for more accurate and extensive tables of $\Delta f'$ and $\Delta f''$ as functions of $\sin\theta/\lambda$ than those currently available.

Note added in publication. Zalkin, Hopkins & Templeton (1966) have recently introduced the very appropriate name *polar dispersion error* for the coordinate error caused by neglecting $\Delta f''$ in polar space groups.

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