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valid result. The zero-angle position should be included as a variable parameter in the least-squares calculation.

A precision of a few parts per million in the lattice parameter of NIST silicon has been reached with the high-precision diffractometer in the Daresbury Laboratory (Hart, Cernik, Parrish & Toraya, 1990). This instrument has an accurate gear and an incremental encoder driven by a DC servomotor with a feedback servoloop capable of positioning the detector arm within 0.36″. A large number of repeated measurements showed a statistical accuracy of $0.0001^\circ(2\theta)$, corresponding to 1 in the fifth decimal place of d for $\lambda = 1$ Å and $2\theta = 20^\circ$.

5.2.6. Whole-pattern methods

The recent large increase in the use of powder samples for crystal-structure refinement and analysis has also stimulated interest in lattice-parameter determinations, which are derived during the course of the calculation. The most frequently used method is that of Rietveld (1967, 1969) described in Chapter 8.6. In outline, a profile-fitting function containing adjustable parameters to vary the width and shape with 2θ is selected. The parameters corresponding to the atomic positions, multiplicity, lattice parameters, *etc*. of the selected structure model are varied until the best least-squares fit between the whole observed diffraction pattern and the whole calculated pattern of the model is obtained. There is no detailed published study of the accuracy of the lattice parameters that is attained but the estimated standard deviations quoted in a number of papers (see, for example, Young, 1988) appear to be comparable with those published for simple structures having no overlapped reflections. In this type of calculation, the accuracy of the lattice parameters is tied to the accuracy of the refined structure because it includes the model errors in the least-squares residuals.

An alternative to the Rietveld method is the pattern-decomposition method in which the integrated intensities are derived from profile fitting and the data used in a powder least-squares-refinement program. The reflections may be fitted individually or in small clusters (Parrish & Huang, 1980) or the whole pattern can be fitted (Pawley, 1981; Langford, Louër, Sonneveld & Visser, 1986; Toraya, 1986, 1988); unlike the Rietveld method, no crystal-structure model is required and only the first stage is used for lattice parameters. The Pawley method was developed for neutron-diffraction data and uses slack constraints to handle the problem of least-squares ill-conditioning due to overlapping reflections, and the positions of the reflections are constrained by the lattice parameters. The refinement also determines the zero-angle calibration correction.

Toraya extended the Pawley method to X-ray powder diffractometry. He first determined the profile shapes and peak positions of several standard samples by individual profile fittings to generate a curve relating the peak shifts to 2θ. A pair of split Pearson VII profiles was used for conventional patterns to handle the $K\alpha$ doublets and the profile asymmetries, and a pseudo-Voight function for the nearly symmetrical synchrotron-radiation profiles. The program is set up so that the parameters of the fitting function are varied with 2θ to account for the increasing widths and the peak shifts and the whole pattern is automatically fitted. The positions of the individual reflections are a function of the calculated lattice parameters, which are refined together with the integrated intensities as independent variables. This method also permits simultaneous refinement of several phases present in the pattern. Unit cells calculated from whole-pattern profile fitting and incorporating the peak-shift corrections had estimated standard deviations an order of magnitude smaller than those not using the systematic error correction. It is also possible to use an internal standard and to make the corrections by refining the cell parameters of the sample and holding constant the parameters of the standard.

Good results can also be obtained using selected peaks rather than the whole pattern (Parrish & Huang, 1980). Peak search or profile fitting is used to determine the observed peak positions. The least-squares refinement is used to minimize $\Delta(2\theta)$ (observed − calculated). It also determines the average and the standard deviation of all the d's and 2θ's. In principle, all the aberrations causing shifts can be incorporated in the refinement. There are, however, large correlations between aberrations with similar angular dependencies. In practice, the zero-angle calibration correction is always determined, and the specimen-surface displacement shift is usually included.

The lattice-parameter determination requires an indexed pattern in which the peak angles have been determined by peak search or profile fitting. Reflections known to have poor precision because of very low intensity or close overlapping should be omitted. The estimated standard deviation is dependent on the number of reflections used and it is better to use all the well measured peaks. There is the question of using a weighting scheme in which the high-angle reflections are given greater weight because of their higher accuracy for a given 2θ error. As noted in Subsection 5.2.13, higher-order reflections usually have low intensities and much overlapping. Some judgement and critical tests are often required.

5.2.7. Energy-dispersive techniques

There are now two basic energy-dispersive techniques available. In both, the specimen and detector are fixed in a selectable θ–2θ setting. The method (Giessen & Gordon, 1968) first described and most widely used requires a solid-state detector and a multichannel pulse-height analyser (Section 2.3.2 and Chapter 2.5). The resolution of the pattern is determined by the energy resolution of the detector and is considerably poorer than that of conventional angle-dispersive techniques, thereby greatly limiting its applications. The second method uses an incident-beam monochromator, a conventional scintillation counter, and a single-channel pulse-height analyser. The monochromator is step-scanned to select a gradually increasing (or decreasing) single wavelength (Parrish & Hart, 1987). This method permits much higher count rates, thereby reducing the time required for the experiment. Since the resolution is determined by the X-ray optics, the resolution is the same as in angle-dispersive diffractometry (Subsection 2.3.2.4). The method has, however, the disadvantage that the widths of the profiles vary with energy, and unless care is taken with the step size there may be too few points per reflection to define the profile adequately. The method is particularly applicable to synchrotron radiation, but there have been no publications to date on its use for lattice-parameter determination.

Energy-dispersive techniques (Section 2.2.3 and Chapter 2.5) are not ordinarily the method of choice for lattice-parameter determination. Relative to angle-dispersive techniques, they suffer from the following disadvantages:

(1) lower resolution;

(2) need for absolute energy calibration of the multichannel pulse-height analyser;

(3) need to know the energy distribution in the incident beam;

(4) specimen transparency varies with energy; even tungsten becomes transparent for 35 keV radiation.

Nevertheless, the advantage of stationary specimen and detector may outweigh these disadvantages for special applications.

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