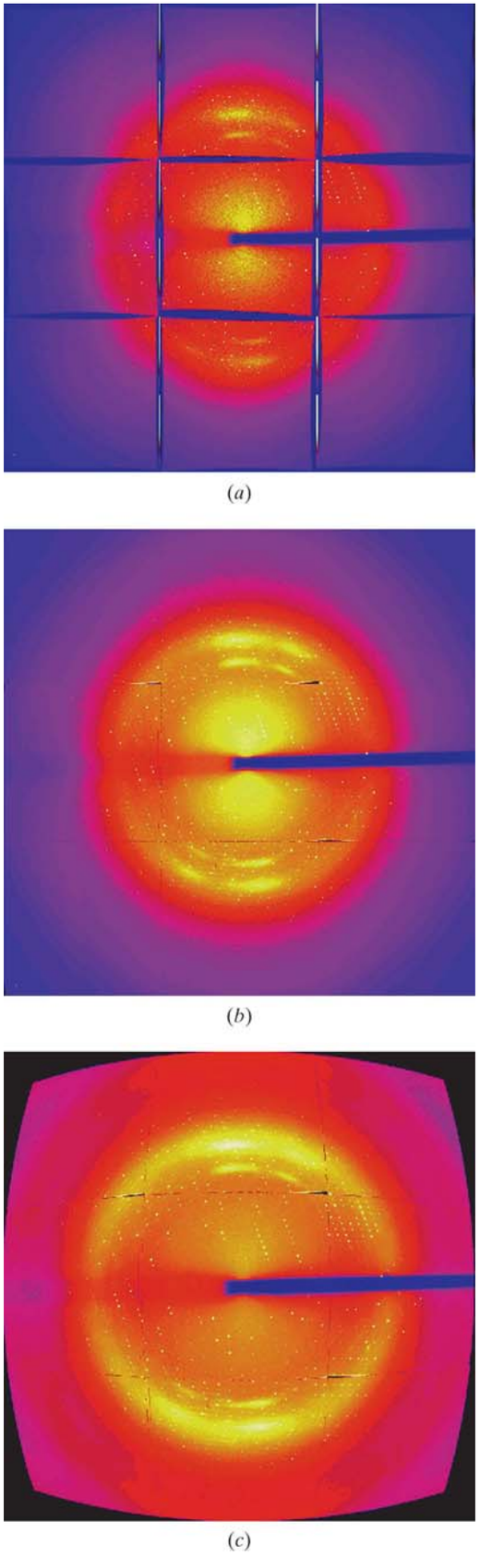

(*a*)

(*b*)

(*c*)

Fig. 11.4.5.1. The transformations in *DENZO* applied to APS-1 detector data. (*a*) Raw data are affected by geometrical distortion introduced by nine fibre-optic tapers; (*b*) the same image converted to planar Cartesian space; (*c*) the same data converted to a virtual spherical detector.

the X-ray beam completes the definition of the detector goniostat in *HKL*.

11.4.5.11. *Crystal goniostat*

The physical goniostat is defined by six angles. Two angles define the direction of the main axis (ω) in the *DENZO* coordinate system. The third angle defines the zero position of the ω axis. The fourth is the angle between ω and the second axis (κ or χ). The fifth defines the zero position of the second axis. The sixth is the angle between the second and the third axes. This type of goniostat definition allows for the specification of any three-axis goniostat (*EEC Cooperative Workshop on Position-Sensitive Detector Software*, 1986). Each type of goniostat is represented by six angles. Misalignment of the goniostat is represented as an adjustment to these angles, which can be refined by the *HKL* system.

11.4.5.12. *Crystal orthogonalization convention*

Crystal orientation specified by the three angles needs a definition of a zero point. Any crystal axis, or its equivalent reciprocal-space zone perpendicular to it, can be used as a reference. The definition of zero point aligns the crystal axis with the beam direction and one of the reciprocal axes with the x direction. The user can specify both axes.

11.4.5.13. *Refinement and calibration*

Both the refinement and calibration procedures determine the properties of the instrument. The principal difference between refinement and calibration is that calibration is performed with data obtained outside the current diffraction experiment, and refinement uses data obtained during the current diffraction experiment. *DENZO* performs both refinement and calibration, and in some cases the difference between calibration and refinement is a question of semantics, as the refined data from one experiment can be used as a reference for another experiment, or even as a reference for a subsequent refinement cycle or for another part of the same experiment.

11.4.6. Prediction of the diffraction pattern

The autoindexing procedure assigns Miller indices only to strong spots, ones that can be found through a peak search. The target of the experiment is to estimate structure factors for all reflections captured by the detector. Therefore, positions of all spots need to be predicted by applying the following equations to all possible triplets **h**. Using

$$\mathbf{S} = [A]^{-1}\mathbf{h}, \qquad (11.4.6.1)$$

we have to find the matrix $[A]$ that generates the vector **S**, which satisfies the diffraction condition [equation (11.4.2.1)], knowing that the matrix $[A]$ is a function of the crystal orientation [equation (11.4.2.6)]. The rotation of the crystal during the experiment creates a straightforward algebraic problem that results in a complex equation defining the angle at which the reflection occurs. This angle also defines the image at which the reflection appears. Knowing this angle, the vector **S** can be calculated, and, from equation (11.4.2.5), the direction of the vector **X** can be found:

$$\mathbf{X}/|\mathbf{X}| = \lambda(\mathbf{S} - \mathbf{S}_0). \qquad (11.4.6.2)$$

Calculation of the length of vector **X** requires knowledge of the detector orientation, which, for flat detectors, is described here by vector **G**, perpendicular to the detector and with length equal to the crystal-to-detector distance:

$$\mathbf{Y} = [R_{2\theta}]^{-1}\lambda(\mathbf{S} - \mathbf{S}_0), \tag{11.4.6.3}$$

$$\mathbf{H} = [R_z]^{-1}[R_y]^{-1}[R_x]^{-1}\mathbf{G}, \tag{11.4.6.4}$$

$$\mathbf{X} = [R_{2\theta}]\frac{\mathbf{H}\cdot\mathbf{H}}{\mathbf{Y}\cdot\mathbf{H}}\mathbf{Y}. \tag{11.4.6.5}$$

Then, by inverting equation (11.4.2.8), the position in pixels, $\{p, q\}$, of the reflection can be calculated:

$$\{p, q\} = [D]^{-1}[K]^{-1}([L]^{-1}([R_{2\theta}]^{-1}([R_z]^{-1}[R_y]^{-1}[R_x]^{-1}(\mathbf{X} - T_D) + T_D) - T_D) + B). \tag{11.4.6.6}$$

11.4.6.1. *Refinement of crystal and detector parameters*

The precision of the integration step depends on precise knowledge of the peak position. The autoindexing step provides only the approximate orientation of the crystal, and the result of that step is imprecise if the initial values of the detector parameters are poorly known. A nonlinear least-squares refinement process is used to improve the prediction (*EEC Cooperative Workshop on Position-Sensitive Detector Software*, 1986). Depending on the particulars of the experiment, the same parameters (*e.g.* crystal-to-detector distance) are more precisely known *a priori*, or are better estimated from the diffraction data. *DENZO* allows for the choice of fixing or refining each of the parameters separately. This flexibility is important to characterize a detector, but when detector parameters are already known, the *fit all* option and detector-specific default values are quite reliable.

DENZO can refine the position and orientation of the detector (six parameters). It can also refine internal parameters of the detector including:

(1) curvature radius and rotation of active surface – *film rotation*, for cylindrical detectors;

(2) x to y scale and x to y skew;

(3) radial/angular distortion for spiral scanners; and

(4) polynomial distortion, separate for each module of multi-module CCD detectors (Naday *et al.*, 1998).

Detector- and crystal-parameter refinement in *DENZO* is achieved by minimizing the sum of the three functions of the type in equation (11.4.5.1). The contribution resulting from the measurement of position p of the reflection is

$$\chi_p^2 = \sum_{\text{hkl}}(p_{\text{pred}} - p_{\text{cent}})^2/\sigma_p^2. \tag{11.4.6.7}$$

The measurement of position q contributes a similar term.

11.4.6.2. *Bragg's law for non-ideal conditions: mosaicity*

The Bragg condition [equation (11.4.2.1)] assumes ideal crystals and a parallel X-ray beam. In reality, crystals are mosaic and the beam has some angular spread. The value of *mosaicity* describes the range of orientations of the crystal lattice within a sample. As the impacts of mosaicity and the beam's angular spread on the angular width of reflections are equivalent, the keyword *mosaicity* describes the sum of both effects.

DENZO assumes the following model of angular shape of diffraction peaks:

$$M = \frac{\text{mos}}{\pi}\left[1 + \cos\frac{\pi(\varphi - \varphi_c)}{\text{mos}}\right] \tag{11.4.6.8}$$

for φ_c in the range $(\varphi_c - \text{mos}/2; \varphi_c + \text{mos}/2)$, otherwise $M = 0$,

$$P_{\varphi_1\varphi_2} = \int_{\varphi_1}^{\varphi_2} M(\varphi)\ \mathrm{d}\varphi, \tag{11.4.6.9}$$

where mos is mosaicity, φ_c is the predicted angle and P is the predicted partiality of data collected by oscillating from φ_1 to φ_2.

Partiality is a number that represents what fraction of the reflection intensity is present in one image. If partiality is 1, such reflections are called fully recorded; otherwise they are called partials. For partials, predictions of partiality can be compared with the observed fraction P_0 of the reflection intensity present in one image. The partiality model contributes the following term to the refinement:

$$\chi_P^2 = (P_{\varphi_1\varphi_2} - P_0)^2/\sigma_{P_0}^2. \tag{11.4.6.10}$$

The combined positional and partiality refinement used in *DENZO* is both stable and very accurate. The power of this method is in proper weighting (by estimated error) of two very different terms – one describing positional differences and the other describing intensity differences. Both detector and crystal variables are uniformly treated in the refinement process.

11.4.6.3. *Detector distortions*

The design of detectors results in pixels not being positioned on an exact square or rectangular grid. A correct understanding of the detector distortions is essential to accurate positional refinement. The types of distortions are detector-specific. The primary sources of error include misalignment of the detector position sensors and optical or magnetic distortion in CCD-based detectors. If the detector distortion can be parameterized, then these parameters should be added to the refinement. For example, in the case of spiral scanners, there are two parameters describing the end position of the scanning head. In a perfectly adjusted scanner, these parameters would be zero. In practice, however, they may deviate from zero by as much as 1 mm. Such misalignment parameters can correlate very strongly with other detector and crystal parameters, particularly for low-symmetry lattices or in the case of low-resolution data. If the distortions are stable, it is better to determine them in a separate experiment optimized for that task.

Fibre-optic tapers used in many CCD detectors have distortion that has to be individually determined for each instrument. The distortion is stable over time and its spatial characteristics are dominated by a smooth component and a small local shear. In high-quality tapers used in X-ray instruments, the small local shear can be ignored. The smooth component can be parameterized in a number of ways, for example by splines (Hammersley, 1998) or polynomials (Messerschmidt & Pflugrath, 1987). *DENZO* uses two-dimensional Chebyschev polynomials (Press *et al.*, 1989) in $\{x, y\}$ or $\{p, q\}$ coordinates, normalized to the range $\{[-1, +1], [-1, +1]\}$. Typically, fifth- or seventh-order polynomials result in a positional error (r.m.s.) lower than 7 μm (about one tenth of the detector pixel). *DENZO* can use either a grid mask pattern or the X-ray diffraction pattern to refine the coefficients of the Chebyschev polynomials. If a grid mask is used, it has to be precisely made and positioned. The use of crystallographic data requires precise knowledge of detector and crystal parameters that are not known *a priori* with the required precision. The crystal and detector parameters can be determined in the same experiment as detector distortion. However, this experiment needs to be designed to minimize the impact of correlations between the parameters involved. The data analysis requires the description of the distortion function and its inverse. In *DENZO*, both are approximated in terms of Chebyschev polynomials. The magnitude of the approximation error is the same for the distortion function and its inverse.

references