1.1. OVERVIEW AND PRINCIPLES
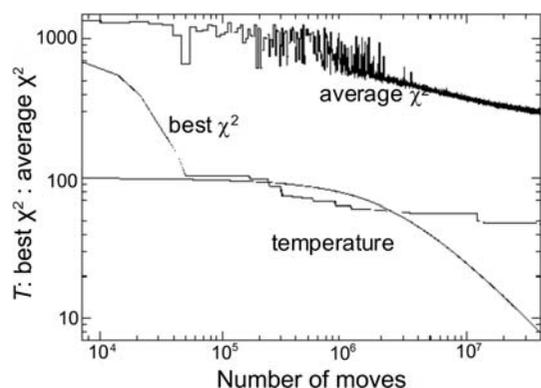

Figure 1.1.26
χ^2 (cost function) and 'temperature' dependence of the number of moves during a simulated-annealing run. [From Mittemeijer & Welzel (2012). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.]

Figure 1.1.27
Screen shot (*TOPAS* 4.1; Bruker-AXS, 2007) of a simulated-annealing run on Pb_3O_4 measured with a D8 advance diffractometer in Bragg–Brentano geometry. [From Mittemeijer & Welzel (2012). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.]

rithm. The most usual implementation is actually as a 'regional' optimizer where the updates to parameters such as atomic position are constrained to be not too far from the previous values in such a way that the algorithm makes a random walk through the parameter space. This algorithm can avoid being trapped in a local minimum by 'walking uphill', since changes to the parameters that produce a worse agreement may be accepted with a probability based on the Boltzmann criterion, $\exp(-\Delta R/kT)$. The temperature in this expression is fictitious (*i.e.*, it does not refer to any real temperature) and ΔR is the change in the agreement produced by the trial update. The temperature plays the role of tuning the probability of accepting a bad move. It is initially chosen to have a high value, giving a high probability of escaping a minimum and allowing the algorithm to explore more of the parameter space. Later in the run the temperature is lowered, trapping the solution into successively finer valleys in the parameter space until it settles into (hopefully) the global minimum (Fig. 1.1.26). The calculation of R can be based on the entire profile, or on integrated intensities. For the latter, the correlation between partially or fully overlapping reflections must be taken into account (as shown schematically in Fig. 1.1.25).

A flow diagram of a typical SA algorithm as used for structure determination from powder diffraction data is shown in Fig. 1.1.25. Parameters that can be varied during the SA runs include internal and external degrees of freedom like translations (fractional coordinates or rigid-body locations), rotations (Cartesian angles, Eulerian angles or quaternions, describing the orientation of molecular entities), torsion angles, fractional occupancies, displacement parameters *etc*. Fig. 1.1.26 shows the results of a typical simulated-annealing run in which the cost function, χ^2, falls dramatically in the first few thousand moves, indicating that the scattering is dominated by the positioning of heavier atoms or globular molecules. Several million trial structures are usually generated before a minimum can be reached. At the end of the simulated-annealing run, Rietveld refinement is used to find the bottom of the global minimum valley.

Special algorithms are not usually used to prevent close contact of atoms or molecules during the global-optimization procedure, as in general these have not been found to be necessary, as the fit to the intensities alone quickly moves the molecules to regions of the unit cell where they do not grossly overlap with neighbouring molecules. A subsequent Rietveld refinement in which only the scale and overall displacement parameters are refined will immediately show whether further
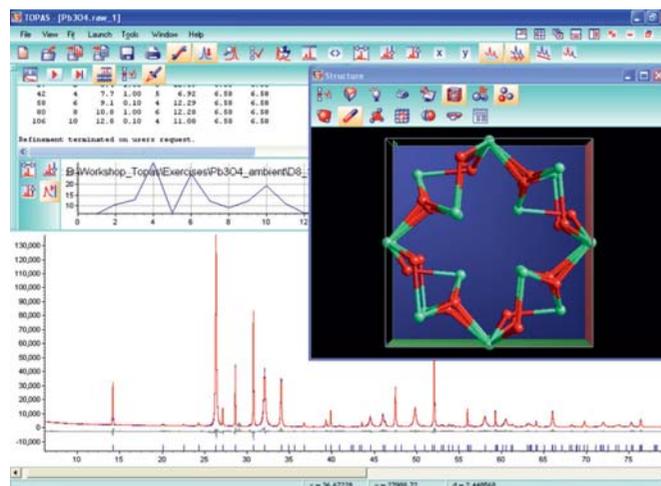
refinement of bond lengths and bond angles is necessary. Since unconstrained refinement often results in severe distortions from the ideal molecular geometry, either rigid bodies or soft constraints on bond lengths, the planarity of flat groups and bond angles can be used to stabilize the refinement. Another advantage of the simulated-annealing technique is that hydrogen atoms can often be included at calculated positions from the beginning if their relative position with respect to other atoms can be anticipated, which is often the case for molecular structures.

For inorganic crystal structures in particular, the identification of special positions or the merging of defined rigid bodies is useful during the final stages of structure solution. This can be accomplished by a so-called 'occupancy-merge' procedure as proposed by Favre-Nicolin & Černý (2004; see also Chapter 4.5). Here, the occupancies of the sites are modified as a function of the fractional coordinates, *i.e.* they are changed when the atoms get 'too close' to a special position. The sites are thought of as spheres with a radius r. In this way any number of sites can be merged when their distances are less than $2r$. As an example, the crystal structure solution of minium (Pb_3O_4) is shown in Fig. 1.1.27. In this example, special positions are identified when two oxygen or lead atoms approach within a distance less than the sum of their respective merging radii, which is estimated as 0.7 Å. The occupancies of the sites then become: 1/(1 + intersection fractional volumes).

The power of the Rietveld approach lies in its ability to extract the maximum information from the region of the data where peaks overlap. Since peak overlap is a significant problem even at moderate d-spacings, this method revolutionized powder diffraction to the point where the quantitative results are often trusted more than those coming from refinements of single-crystal data, since they are less sensitive to factors such as extinction that can affect single-crystal structure refinements. Single-crystal data are still preferred for structure solution, but Rietveld refinement is often the method of choice for obtaining the fine quantitative details of the structure after a solution has been found. However, the Rietveld method has also opened the door to using powder data for structure solution. In structure-solution methods, the structure factors are calculated from the intensities of all the available peaks, and algorithms are used to find the missing phases for each of these peaks and therefore the positions of the atoms in the unit cell. As mentioned above, full

references