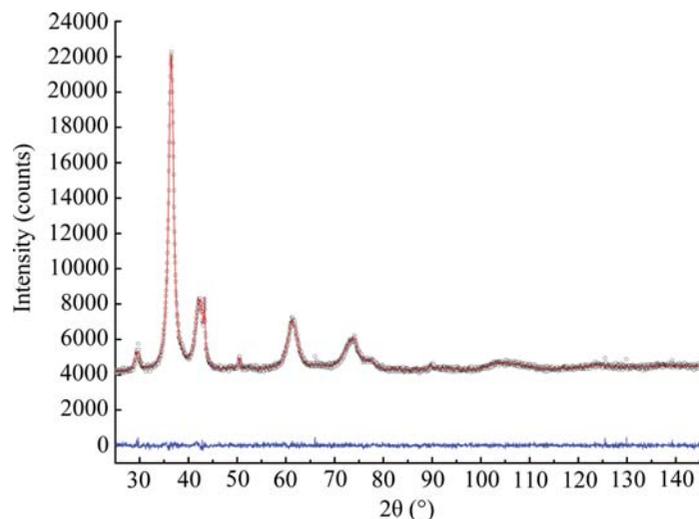3. METHODOLOGY
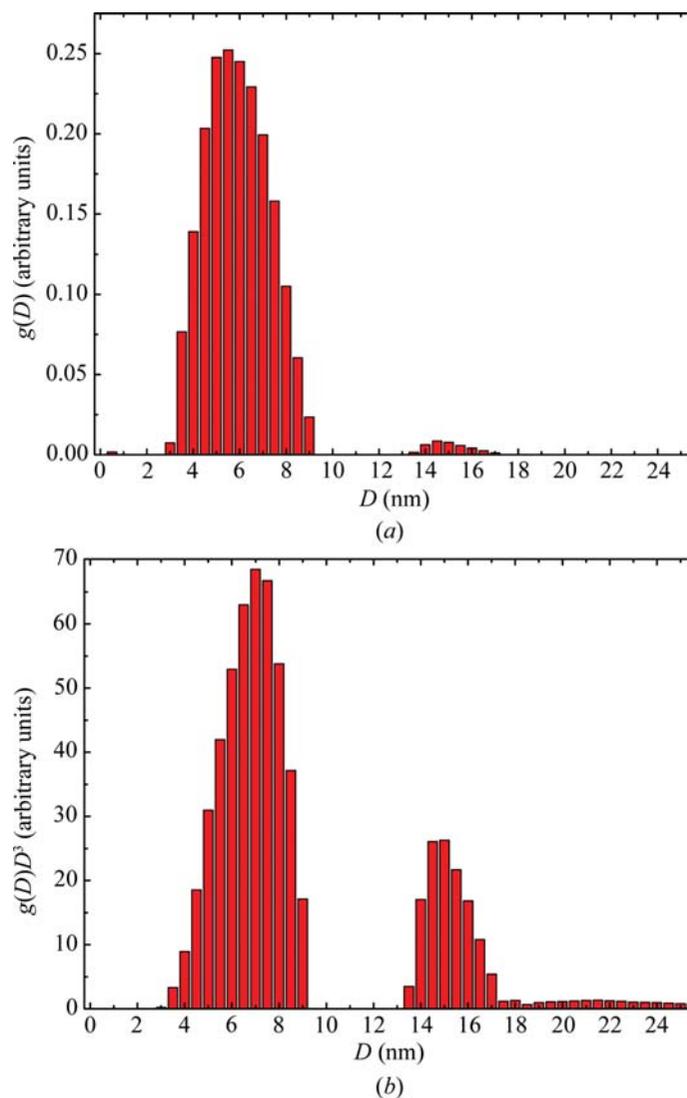

Figure 3.6.5
Result of WPPM of ball-milled Cu_2O: raw data (dots), model (line) and difference (lower line).

Figure 3.6.6
Domain-size distribution of cuprite: (*a*) WPPM result and (*b*) distribution multiplied by D^3.

example by search/match in a large database such as the ICDD Powder Diffraction File): each diffraction peak belongs to a well defined phase and bears information on the microstructure of that phase.

As an example, Fig. 3.6.5 shows the diffraction pattern of a Cu_2O powder specimen obtained by grinding commercial Cu_2O powder (Carlo Erba) in a high-energy shatter mill (Fritsch Pulverisette 9). To limit the heating of the cup that would lead to dynamic recrystallization, milling was performed in 30 steps consisting of 10 s milling followed by 120 s room-temperature cooling (Martinez-Garcia *et al.*, 2007). The powder diffraction pattern was collected on the same diffractometer that was used for the analysis of the ceria powder. To obtain a sufficient SNR, the data were collected in the 18–154° 2θ range with a step size of 0.1° and a fixed acquisition time of 150 s per point. The fluorescence of the Cu present in the specimen is responsible for the large background that was not eliminated by the crystal analyser. From a quick comparison of Figs. 3.6.5 and 3.6.1, we notice a large difference at high angle: high strain effects (due to dislocations) are expected in this specimen as an effect of the extensive cold-work deformation introduced by the milling process.

A search match signals the presence of not just Cu_2O (cuprite, $Pn\bar{3}m$) but also metallic Cu (f.c.c. copper, $Fm\bar{3}m$) and CuO (tenorite, Cc) as minor phases, presumably due to reduction of the higher oxide. WPPM of the diffraction pattern, performed by considering all three observed phases, shows a flat residual (see Fig. 3.6.5). The severe peak overlap and the large broadening at high angle do not help in the analysis: the intensities of tenorite peaks (minor and broadened phase) were then constrained by a structural model (only a scale parameter was refined). Atomic coordinates and Debye–Waller factors for CuO were taken from the ICSD file (FIZ#69094; Brese *et al.*, 1990) and were considered to be constant.

Spherical domains were chosen for all phases. A log-normal distribution was used to model the minor phases. A histogram distribution was chosen for cuprite instead: the peaks clearly have a peculiar shape with a rather sharp tip, possibly indicating a wide, bimodal or odd size distribution (Leoni & Scardi, 2004). The size distribution resulting from the WPPM analysis is shown in Fig. 3.6.6(*a*): in this case it would be impossible for a traditional method to provide a physically sound result. The breadth of the profile is not fully informative: as the diffraction signal is proportional to the volume of matter, the actual distribution

'seen' in the experiment is that of Fig. 3.6.6(*b*), obtained by multiplying the result of Fig. 3.6.5(*a*) by D^3.

The larger size fraction therefore makes a non-negligible contribution to the pattern: as a rule of thumb, the smaller the domains and the wider the distribution, the stronger the contribution of the large domains. This problem of 'visibility' of small domains is attenuated when an analytical distribution (*e.g.* a log normal) can be used as the function goes smoothly to zero at zero size.

Dislocations can also be observed in these specimens: their quantification by TEM is nearly impossible due to the high defect density. The anisotropy term, *i.e.* the average contrast factor, has to be calculated for each of the three phases (Scardi *et al.*, 2007).

The slip system for Cu ($c_{11} = 169$, $c_{12} = 122$, $c_{44} = 75.3$ GPa; Every & McCurdy, 1992*a*) is $\frac{1}{2}\langle 1\bar{1}0\rangle\{111\}$ and the corresponding average contrast factor (for edge and screw dislocations, respectively), is

$$\overline{C}_{Cu,e} = 0.304062 - 0.500211 \frac{h^2k^2 + k^2l^2 + h^2l^2}{(h^2 + k^2 + l^2)^2}, \quad (3.6.56)$$

$$\overline{C}_{Cu,s} = 0.298340 - 0.708805 \frac{h^2k^2 + k^2l^2 + h^2l^2}{(h^2 + k^2 + l^2)^2}. \quad (3.6.57)$$

     references