ANALYTICAL METHOD FOR OBSERVED POWDER DIFFRACTION INTENSITY DATA BASED ON MAXIMUM LIKELIHOOD ESTIMATION

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Statistical variations of observed powder diffraction intensity data are mainly ascribed to counting statistics and particle statistics [1]. Even though the fundamental features of particle statistics have been elucidated by the pioneering work of Alexander *et al*. [2], *a priori* estimation of particle statistical errors is still complicated [3]. It is sometimes difficult to justify the analytical methods based on least-squares (LSQ) optimization, because the LSQ method implicitly assumes that the statistical errors are known quantity.

Suppose that the statistical distribution of the observed diffraction intensity data $\{Y_1, ..., Y_N\}$ is described by the normal distribution with average $\{y_1, ..., y_N\}$ and standard deviation $\{\sigma_1, ..., \sigma_N\}$. Then the probability that the intensity data set $\{Y_1, ..., Y_N\}$ should be observed is given by $P(Y_1,...,Y_N) = \prod_{j=1}^{N} \left(\sqrt{2\pi}\sigma_j\right)^{-1} \exp\left(-\Delta_j^2 / 2\sigma_j^2\right)$, where $\Delta_j \equiv Y_j - y_j$ is the deviation at each sampling point. Maximum likelihood estimation (MLE) is the maximization of the probability $P(Y_1,...,Y_N)$ by adjusting $\{y_j\}$ and $\{\sigma_j\}$, which is equivalent to the minimization of the quantity: $S = \sum_{j=1}^{N} \left(\ln\sigma_j^2 + \Delta_j^2 / \sigma_j^2\right)$. We have obtained more reliable crystal structures by the MLE method with a theoretical model for statistical errors, as compared with the results of a traditional LSQ method, from powder diffraction data of $Ca_5(PO_4)_3F$ and $BaSO_4$ [4].

Projections shown in Fig. 1 demonstrate another example, the structure of a $La_xSr_{1-x}MnO_3$ ($x \sim 0.03$) phase optimized by LSQ and MLE methods. The bond valence sums (BVS) about the Mn1 and Mn2 atoms estimated at 3.82 and 3.92 for the structure optimized by the MLE method are more likely than the values 2.97 and 4.39 estimated by the LSQ method applied to the same intensity data.

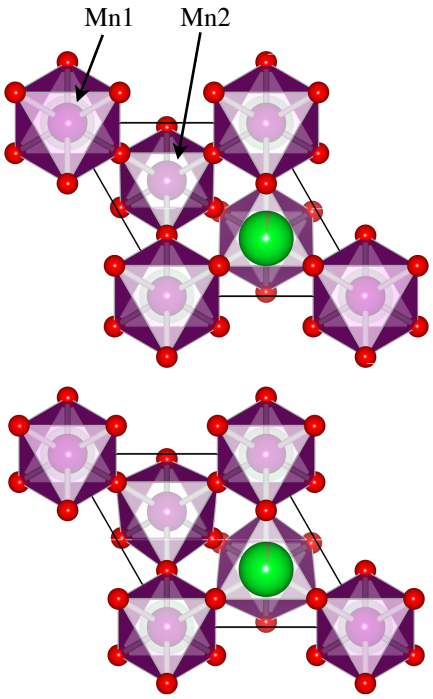

Fig. 1 Structures of $La_xSr_{1-x}MnO_3$ optimized by LSQ (upper) and MLE (lower) methods. Sr(La), Mn and O atoms are colored by green, purple and red, respectively.

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