Advances in the Parameter Space Concept for Crystal Structure Determination – a maximum resolution study

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Within the last 15 years, the Parameter Space Concept (PSC) was theoretically developed by Fischer, Kirfel and Zimmermann as an alternative approach to solve crystal structures from diffraction intensities without use of Fourier transforms [1-6]. Each experimentally determined reflection restricts the $3N$-dim. parameter space of atomic coordinates for a crystal structure solution (N atoms) by a manifold of $3N$-1 dimensions, equivalent to a unique isosurface, whereas the true solution vector will be the intersection of all isosurfaces. The method has already been tested on numerous, partly challenging problems of X-ray diffraction.

We present a study of the maximum resolution of the PSC. As an example, a split position of La and Sr with $(0, 0, z=0.3584)$ has been investigated in the potential high-temperature super-conductor $(La_{0.5}Sr_{1.5})MnO_4$, I4/mmm. A positional shift of the cations in the order of $\Delta z \approx 0.001_5$ (≈ 0.02 Å) has been suggested in literature [7]. Enhancing the scattering difference of La and Sr by f'_{Sr}, this split was later verified using the PSC within a rather conservative model test [8]. As a result a shift $\Delta z=0.01_3$ had been determined. We now add to the discussion an evaluation based on two additional model data sets, each with $(00l)$ reflections ($l = 2,4…20$) and varied relative errors of up to 20%. A graphical representation of the parameter space revealed an improvement of resolution with a shift of $\Delta z=0.01_2…0.01_6$ ($\approx 0.1_5…0.2_0$ Å). Due to the difference in scattering power of La and Sr, a pseudosymmetric structure solution (z^*_{La}, z^*_{Sr}) exists for approximately interchanged z-positions, which we discuss in conjunction with the accurate solution (z_{La}, z_{Sr}). The two solutions were defined by the intersection of isolines representing $(00l)$ reflection intensities [9]. There is a non-vanishing variance of the pseudosymmetric structure solution, whereas the accurate solution does not vary. Depending on the relative error of the diffraction intensities, we present respective resolution limits for the split position.
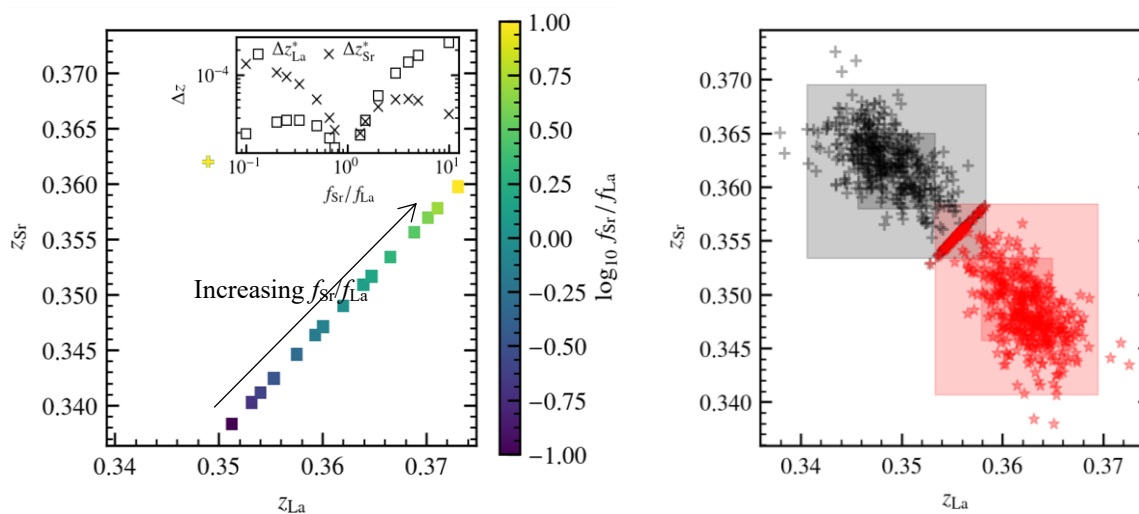

Figure 1. Left: Model study of the real (0.362 | 0.349) and the (broken) pseudosymmetric structure solution (z^*_{La}, z^*_{Sr}) of the PSC model as a function of the relative scattering strength of the La and Sr atom. Inset: Variance of the (broken) pseudosymmetric structure solution $\Delta z^*_{La,Sr}$ as a function of the relative scattering strength of the La and Sr atom. The real solution shows no variance. Right: Monte-Carlo-Study of the structure solution as a function including the single (2.3-times) trust region for 20% intensity error and equal scatterers.

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