Poster

Finding the Bravais lattice of a "1/N" size supercell from error-containing lattice parameters

Y. Hinuma[1], H. Ozaki[1]

[1] *National Institute of Advanced Industrial Science and Technology, 1-8-31,Midorigaoka,Ikeda,Osaka 563-8577, Japan*

y.hinuma@aist.go.jp

Identifying the crystal structures that govern their properties is essential when developing new materials. Rietveld analysis is commonly used to identify the crystal structures, namely the symmetry, lattice parameters, atom sites, and the occupancy rates. This analysis involves deciphering crystal structures from powder X-ray or neutron diffraction profiles. Finding lattice parameters and the Bravais lattice is a critical first step in Rietveld analysis.

Sometimes the provided lattice parameters should be regarded as those of a supercell and a smaller cell represents a Bravais lattice of higher symmetry. In other words, finding a cell with size 1/N-times the original cell, or "1/N"-supercell, could be important.

As an example, a class of Li battery cathode materials have very similar structures (see Figure 1). $LiCoO_2$ is a prototypical Li battery cathode material. The crystal structure type is α-$NaFeO_2$, its space group is $R\bar{3}m$ (number 166), and the lattice parameters are a=2.8128 Å and c=14.0272 Å. This takes a disordered rocksalt (NaCl) structure (space group type $Fm\bar{3}m$, number 225) where Li and Co layers alternate along the (111) direction of the cubic lattice. Li_2MnO_3 (space group $C2/m$, number 12, a=4.937 Å, b=8.532 Å, c=5.03 Å, and β=109.46°) is a compound related to $LiCoO_2$ where the Co layers are replaced by ordered $Li_{1/3}Mn_{2/3}$ layers. The Li_2MnO_3, $LiCoO_2$, and rocksalt structures are therefore closely related.

The key question is, how can we judge that monoclinic Li_2MnO_3 is a disordered structure of rhombohedral $LiCoO_2$, or even of the cubic NaCl structure, just by looking at the lattice parameters of Li_2MnO_3 and the number of atoms in the unit cells of these crystals?

We define the 'augmented lattice' as a lattice with N^3 lattice points than the original lattice and where all lattice points of the original lattice are included in the lattice points of the augmented lattice, or in other words, the space group of the original lattice is a k- subgroup of the augmented lattice. In the above example, the primitive cell of Li_2MnO_3 is a supercell of the NaCl lattice and the augmented lattice contains six times more lattice points than the original lattice because the primitive cell of Li_2MnO_3 contains six anions while that of NaCl contains one anion. N^2-supercells of the augmented lattice that further satisfy certain conditions are 1/N-supercells of the original lattice.

We developed an algorithm to find 1/N- supercells of an arbitrary crystal when N is given. Bravais lattices of the 1/N- supercells can be obtained by considering tolerances on interaxial angle and basis vector lengths. The algorithm can be used in data analysis to provide an additional layer of information for structure analysis.

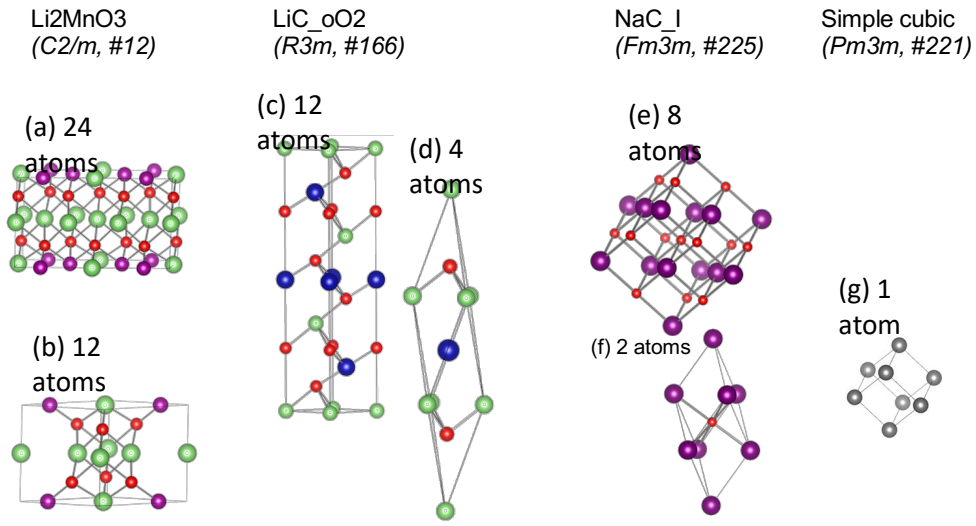

Figure 1. Illustration of the problem discussed in this study. The (a) conventional and (b) primitive cells of Li_2MnO_3, (c) conventional and (d) primitive cells of $LiCoO_2$, (e) conventional and (f) primitive cells of NaCl, and (g) a simple cubic crystal all has very similar structures where the difference is the element species at each site and minor deformation. Finding a unit cell with fewer atoms, which is the opposite of finding a supercell, is difficult because lattice points need to be interpolated. Identifying that a monoclinic crystal is a slightly deformed supercell of a cubic lattice is also not trivial.