s3.m1.p3 **Bond-valence models for correlations between structure and conductivity of solid electrolytes.**

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Keywords: fast ion conductors, bond-lehgth bond-valence parameters, reverse Monte Carlo.

A systematic development of materials with tailored properties depends on the availability of reliable structure-property correlations. As an example, a technique to predict the ionic conductivity of solid electrolytes (including the technically important strongly disordered and unordered materials) from their structure was developed. The utilisation of tabulated empirical relations of the type $s = \exp[(R_0{-}R)/b]$ between bond-length R and bond-valence s limits the computational effort to a level that permits systematic studies. Conduction pathways for are modelled by determining the bond-valence mismatch for mobile ions throughout the local structure model of the solid electrolyte presuming that paths of minimum valence mismatch may be identified with potential pathways for the ion transport[1,2].

Contrasting to applications in structure analysis, where bond-valence parameter sets with a universally fixed value of $b{=}0.37\text{Å}$ proved to be suitable[3], this approach requires that bond-valence pseuopotentials should not only reproduce equilibrium distances but also account for differences in the polarizabilities or hardness[4]. This may be achieved by bond-valence parameter sets with variable b. We found that high values of b refer to bonds between particles that differ in their softnesses. Either the "absolute softness" as evaluated from ionisation enthalpies and electron affinities[4] or ionic radii may be employed as independent measures of the softness.

Utilising bond-valence parameters that consider the differences in the softness of Ag-O and Ag-I bonds, both the ionic conductivity and its activation energies in AgI-AgM$_x$O$_y$ glasses (M= Mo, W, B) and crystalline superionic conductors can be predicted from structure models generated by a slightly modified Reverse-Monte-Carlo technique[5]. In these correlations the structures are characterised by the volume fraction of continuous bond-valence pathways, *i.e.* the coherent region through which a mobile ion i may move, without changing its bond-valence sum $V_i = \Sigma s_{ij}$ by more than a fixed threshold value ΔV from its formal valence.

Random walk simulations suggest, that despite their reduced local mobility mainly oxide-coordinated Ag$^+$ significantly contribute to the *d.c.* ionic conductivity.

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s3.m1.p4 **General formalism for phase combination and phase refinement: Mean-Field optimization and Simulated Annealing in reciprocal space.**

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Keywords: computing, hot topics.

Mean Field optimization methodology has been used to recast in a single formalism the problem of phase optimization using an arbitrary energy function, in the presence of an experimentally determined phase probability distribution function (Delarue & Orland, submitted to Acta Cryst A). It results naturally in the generalization of the notion of figure-of-merit and centroïd phase where the weight of Energy refinement is controlled by an effective temperature, in a self-consistent manner. In this way Sim's weighting schemes appear as just the first step of a refinement to be conducted until self-consistency is achieved. In the limit of high temperature, the formalism reduces of course to Blow and Crick classical treatment. The formalism readily allows to use Sayre equation to refine phases and assigns a figure of merit to each reflection. Numerical tests of the method are presented in an attempt to resolve the phase ambiguity problem of protein crystallography in the centrosymmetric P-1 space group using an energy criterion based on Sayre equation. The Mean Field method is very general and should also be useful in other phase refinement problems. For instance, we found that the evaluation of the free energy of the system gives new insight into the Maximum likelihood method.

In addition, a detailed numerical study using the Simulated Annealing technique devoted to solve to phase ambiguity problem in the centrosymmetric P-1 space group using Sayre equation has proved successful using a multistart strategy. The key ingredient to success was i) a detailed characterization of the energy landscape and ii) constant monitoring of the so-called σ^2 map quality index recently defined by Terwilliger (Delarue, submitted to Acta Cryst. A).