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Multi-site order-disorder kinetics in crystalline solids: A generalized formulation

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ABSTRACT

Many crystalline solids have multiple nonequivalent sites among which different atoms show substitutional long-range order-disorder phenomena. The order-disorder kinetics of an atom among any n nonequivalent sites in a crystal can be described by the equation

$$x_i = c_{i1} + \sum_{j=2}^{n} c_{ij}(t)e^{\lambda_j t}$$

where x_i is the site occupancy of the atom at site s_i, n is the number of nonequivalent sites, λ_j ($\lambda_1 = 0$) is constant at a given temperature, pressure, and total composition of the crystal, and $c_{ij}(t)$ is constant or polynomial in t. Four theorems governing a multi-site order-disorder process have been proved, requiring that λ_j must be either zero (only $\lambda_1 = 0$), a negative real number, or a complex-valued quantity with the real part being a nonpositive number. The kinetic model becomes constrained and naturally complies with crystal-chemical conditions when the mole number per formula unit is chosen as the unit of all site-occupancy variables, or site multiplicities are explicitly incorporated into the model. When the mole fraction is directly used as the unit, the model becomes unconstrained, but it is a valid treatment that is as equally applicable to the multi-site order-disorder kinetics as the constrained model.