Atomic ordering in M_2X-type MXenes: statistical thermodynamics and kinetics

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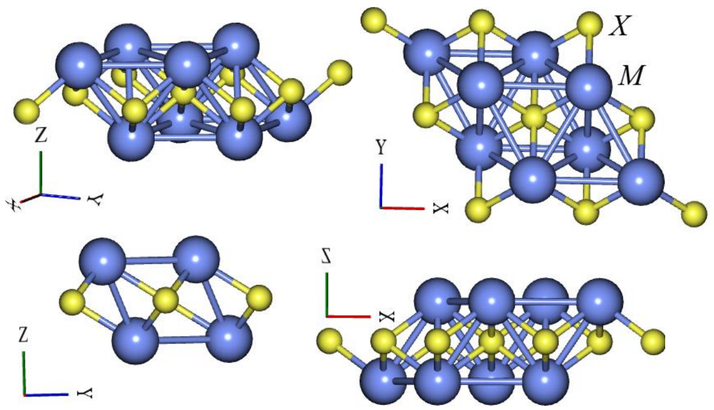
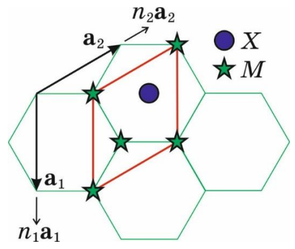
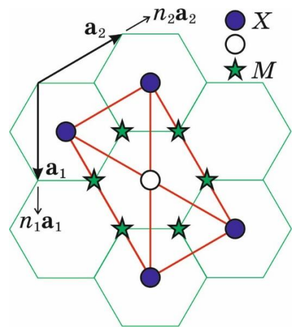
The statistical-thermodynamics and kinetics models of long-range atomic order in the interstitial solid solution M–X, based on a quasi-2D M_2X-type MXene lattice, are proposed. Ordered distributions of interstitial atoms (X) over the interstices of the hexagonal host-metal (M) lattice at the different compositions and temperatures are described theoretically. If interstitial positions in the host-metal lattice are vacant, then we denote them as ∅. In this case, the distribution of the interstitial components (X and ∅) over the interstices of the hexagonal lattice can be described by a single-particle function that defines the probability of finding an interstitial atom in a given interstitial position of the solvent crystal lattice.

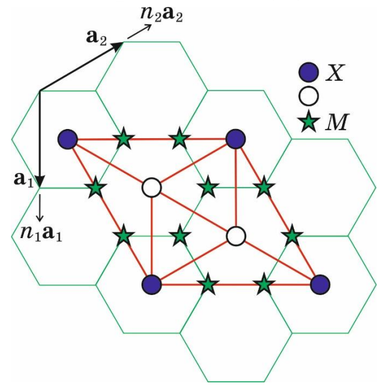
(SUPER)STRUCTURES

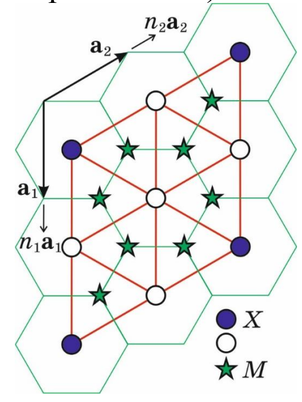


Top view of primitive unit cells of interstitial superstructures in M_2X-type MXene for different relative content κ_{st} = 1, 1/2, 1/3, and 1/4 of the non-metal interstitial X atoms, where stars (★) denote metal M atoms, and open circles (○) — empty (in the superstructure) interstices.









MODEL

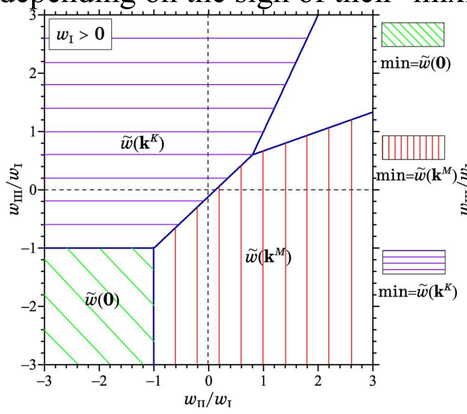
Configurational free energy: $\Delta F = \Delta U - T\Delta S \cong 1/2\sum_{\mathbf{R},\mathbf{R}'} w(\mathbf{R}-\mathbf{R}')P(\mathbf{R})P(\mathbf{R}') + k_BT\sum_{\mathbf{R}}\left[P(\mathbf{R})\ln P(\mathbf{R}) + \left(1-P(\mathbf{R})\right)\ln\left(1-P(\mathbf{R})\right)\right]$

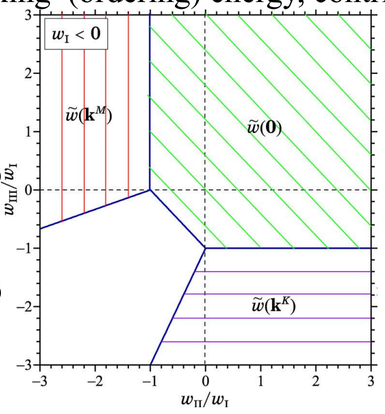
T — absolute temperature of M–X, ΔU and ΔS — configurational internal energy and entropy, k_B — Boltzmann constant, $P(\mathbf{R})$ — probability of finding an interstitial atom X in the interstice of the primitive unit cell with radius-vector $\mathbf{R}$ of the host-metal (M) crystal lattice; $w(\mathbf{R}-\mathbf{R}') \equiv W^{XX}(\mathbf{R}-\mathbf{R}') + W^{\varnothing\varnothing}(\mathbf{R}-\mathbf{R}') - 2W^{X\varnothing}(\mathbf{R}-\mathbf{R}')$ is the mixing energy of X and ∅ components of interstitial subsystem, where $W^{\alpha\beta}(\mathbf{R}-\mathbf{R}')$ — effective pair-wise interaction energy of α, β (α, β = X, ∅) atoms occupying interstices in the primitive unit cells with radius-vectors $\mathbf{R}$ and $\mathbf{R}'$. $\tilde{w}(\mathbf{k}^{\Gamma,K,M}) \equiv \sum_{\mathbf{R}} w(\mathbf{R}-\mathbf{R}')\exp(-i\mathbf{k}^{\Gamma,K,M}(\mathbf{R}-\mathbf{R}'))$ — Fourier-component of mixing energy; $\mathrm{k}^{\Gamma,M,K}$ is a wave vector in the reciprocal space, which generates the superstructure.

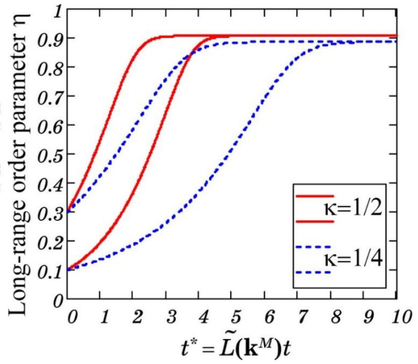
Onsager-type kinetic equation for relaxation kinetics of the long-range order parameter during the exchange (ring) mechanism of diffusion of interstitial X and ∅ components over the interstices of the hexagonal host-metal (M) lattice: $dP^{\alpha}(\mathbf{R},t)/dt \approx -\left(1/k_BT\right)\sum_{\beta=X,\varnothing}\sum_{\mathbf{R}'}\kappa_{\alpha}\kappa_{\beta}L^{\alpha\beta}(\mathbf{R}-\mathbf{R}')\left(\delta\Delta F/\delta P^{\beta}(\mathbf{R}',t)\right)$, where t is annealing time, $L^{\alpha\beta}(\mathbf{R}-\mathbf{R}')$ (α, β = X, ∅) — kinetic coefficient.

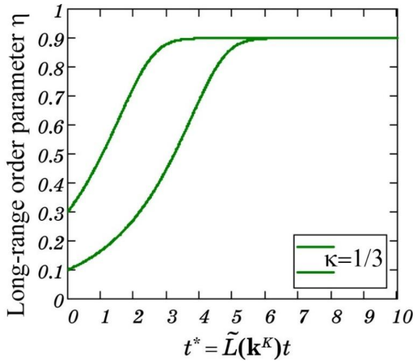
CALCULATED RESULTS

The ranges of interatomic-interaction parameter values corresponding to the generation of ordering in a subsystem of interstitial atoms characterised by a given superstructure type are obtained. All predicted interstitial superstructures could be stable at certain (appropriate) energy-parameter values, even if taking into account the latter only for the first three interstitial coordination shells. However, their account taken only for the first shell renders the impossibility of predicting some superstructures. The contribution of interactions between atoms at different distances, depending on the sign of their ‘mixing’ (ordering) energy, contributes to or impedes the atomic ordering that determines the structure symmetry.









$$\frac{d\eta}{dt} \cong -\kappa(1-\kappa)\tilde{L}(\mathbf{k}^M)\left[\frac{\tilde{w}(\mathbf{k}^M)}{k_BT}\eta + \ln\frac{(\kappa+\eta/2)(1-\kappa+\eta/2)}{(\kappa-\eta/2)(1-\kappa-\eta/2)}\right]$$

$$\frac{d\eta}{dt} \cong -\kappa(1-\kappa)\tilde{L}(\mathbf{k}^K)\left[\frac{\tilde{w}(\mathbf{k}^K)}{k_BT}\eta + \ln\frac{(\kappa+2\eta/3)(1-\kappa+\eta/3)}{(\kappa-\eta/3)(1-\kappa-2\eta/3)}\right]$$

$$\frac{d\eta}{dt} \cong -\kappa(1-\kappa)\tilde{L}(\mathbf{k}^M)\left[\frac{\tilde{w}(\mathbf{k}^M)}{k_BT}\eta + \ln\frac{(\kappa+3\eta/4)(1-\kappa+\eta/4)}{(\kappa-\eta/4)(1-\kappa-3\eta/4)}\right]$$