Ionic model with interaction of defects to description of the order-disorder transition in non-stoichiometric solid uranium dioxide

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Ionic representation was proved to be successful in thermodynamic description of liquid phase and non-congruent gas-liquid coexistence in systems like non-stoichiometric uranium oxides [1, 2]. A new model approach to thermodynamic description of imperfect and non-stoichiometric ionic solids near the pre-melting transition into superionic state is discussed. Along with short- and long-ranged inter-ionic interactions, the model takes into account the formation of Frenkel defects as well as Coulomb and short-range interactions between these defects. Contrary to existing approaches [3,4] based on ideal-lattice-gas and Debye-Hueckel approximations, we consider the imperfect solid as a highly non-ideal Coulomb system and treat the short-range interactions of Frenkel defects explicitly as interactions of quasi-dipoles.

A simplified analytical EOS for free energy of a perfect anharmonic solid combined with additional contributions from formation and interaction of defects, after fitting of a few numerical constants reproduces the locations of known phase transitions and predicts the variations of thermodynamic properties with temperature, density and stoichiometry.

Results are compared with experimental and computer simulation data for solid UO_{2+x}. The EOS predicts correctly the behavior of thermodynamic functions, including the pre-melting of the oxygen sub-lattice in UO_{2+x}. When combined with theoretical model for uranium dioxide EOS for fluid state [5] it has been successfully used [6] in prediction of liquid/solid and vapour/solid equilibrium.

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