DEMYSTIFICATION OF MIZUSAKI'S α-FACTOR FOR THE POSITIVELY-DEVIATED DEFECT BEHAVIOR OF HYPERSTOICHIOMETRIC OXIDES

H.-I. Yoo, Daegu-Gyeongbuk Institute of Science and Technology, Daegu, Korea
hiyoo@snu.ac.kr
J. Mizusaki, Tohoku University, Sendai, Japan

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Many hyperstoichiometric (p-type) ternary or higher oxides of present technological interests, e.g., $La_{1-x}Sr_xCrO_{3-\delta}$ exhibit a positive deviation from the ideal defect structure. Mizusaki et al. [1] could beautifully explain the positively-deviated defect structure by introducing an empirical factor α such as

$$\Delta H^{xs} = \alpha \delta \square .$$

Here, ΔH^{xs} stands for the excess enthalpy of oxidation reaction involving oxygen vacancies and holes or

$$1/2\ O_2 + V_O^{\bullet\bullet} = O_O^x + 2h^{\bullet} .$$
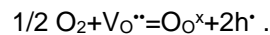
The authors[1] interpreted this α-factor as representing the interactions among lattice ions and defects, but its true physico-chemical face has since remained a mystery notwithstanding so frequent invoking to the defect chemistry stage.
It has recently turned out that this factor corresponds to the first order approximation of the hole-degeneracy effect. We will demystify this α-factor in this line.

[1] J. Mizusaki, S, Yamauchi, K. Fueki, and A. Ishikawa, "Nonstoichiometry of the perovskite-type oxide $La_{1-x}Sr_xCrO_{3-\delta}$," Solid State Ionics 12 (1984) 119.