

First Principles Computational Studies of Spontaneous Reduction Reaction of Eu(III) in Eutectic LiCl-KCl Molten Salt

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1. Introduction

Using first principles calculations, we study fundamental mechanism of spontaneous reduction reaction of Eu^{3+} to Eu^{2+} in eutectic LiCl-KCl molten salt. We decouple the reaction Gibbs free energy into enthalpy and entropy contributions using rigorous thermodynamic formalism. Key structural features of the solvation shell are characterized by the radial distribution function (RDF) and the coordination number. Compared to Eu^{2+} the Eu^{3+} ion has a more rigid framework of the solvation shells, corroborating its stronger electrostatic interaction with neighboring ligands of Cl⁻ ions and a more favorable state on the aspect of enthalpy. Computations on vibrational frequency, however, pose significant contribution of vibrational entropy to the reaction Gibbs free energy for the reduction. Vibration frequency of Eu^{2+} is smaller than that of Eu^{3+} , driving a more positive change of the entropy in the reduction reaction. Furthermore, an Eu^{2+} diffuses more quickly than an Eu^{3+} in the LiCl-KCl molten salt with switching mechanism of ligand Cl⁻ ions in the solvation shell. Our results propose that the spontaneity of the reduction reaction is driven by the entropic contribution by overcoming the penalty of the reaction enthalpy.

2. Computation Methods

All the simulations were calculated using Vienna Ab-initio Simulation Package (VASP) based on the plane wave basis sets with 500 eV cut-off energy. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)¹ was used

as exchange correlation functional and the projected augmented wave (PAW) potential² was utilized to substitute core electrons of Li, K, Cl and Eu. Ab-initio molecular dynamics (AIMD) simulations were performed in the canonical ensemble with a Nosè-Hoover thermostat³ conditions fixing total number of atoms (N), volume (V) and temperature (T). To distinguish the Eu^{2+} and Eu^{3+} , GGA+U parameters were obtained, which are -12 and 2 eV. The model systems were constructed as shown Fig. 1.

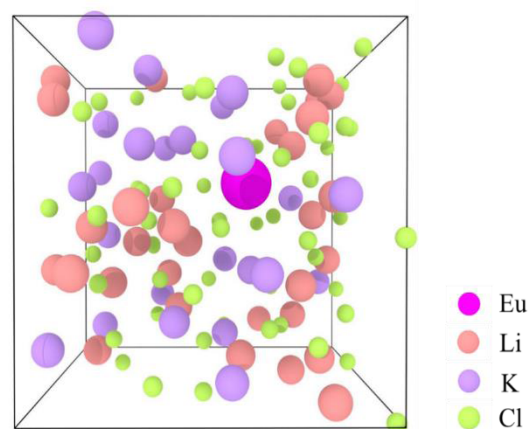
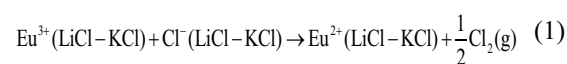


Fig. 1. Model system.

LiCl-KCl molten salt were packed in a 15^3 \AA^3 cubic cell based on eutectic composition and density. To describe the Eu^{2+} (Eu^{3+}), EuCl_2 (EuCl_3) were added in the cubic cell, respectively.

3. Results and Discussion



Gibbs free energy of reaction (1) was decoupled

into enthalpic and entropy contributions. Entropic contributions were confirmed by the results of AIMD simulations.

3.1 Structure of solvation shell

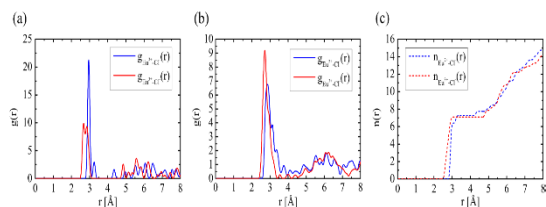


Fig. 2. The figure (a) indicates RDFs at 5 ps and the figure (b) does average RDFs that 10 samples were selected from 4 ps to 5 ps with interval of 0.1 ps. The coordination numbers of $\text{Eu}^{2+/3+}$ at 5 ps are shown in (c).

Blue and red lines denote those of Eu^{2+} and Eu^{3+} , respectively.

Solvation shells of Eu^{2+} and Eu^{3+} in a LiCl-KCl molten salt were calculated. The solvation shell of Eu^{3+} was more rigid than that of Eu^{2+} because of stronger electrostatic interaction between Eu^{3+} and Cl^- .

3.2 Vibrational frequency

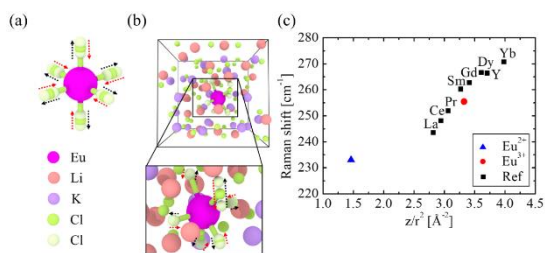


Fig. 3. Vibration mode of MCl_6 ($\text{M}=\text{Eu}^{2+}$ and Eu^{3+}) complex in (a) vacuum and (b) molten salt. (c) Vibration frequencies of various rare-earth elements in a molten salt.

Vibration frequencies of α_{1g} mode for Eu^{2+} and Eu^{3+} were calculated. As the vibration frequency get increase, which means stronger electrostatic interactions with Cl^- ions, the entropy becomes smaller. Based on the results, the entropy of the reaction (1) is positive because Eu^{3+} has stronger electrostatic interaction with molten salt.

3.3 Diffusion coefficients of Eu^{2+} and Eu^{3+}

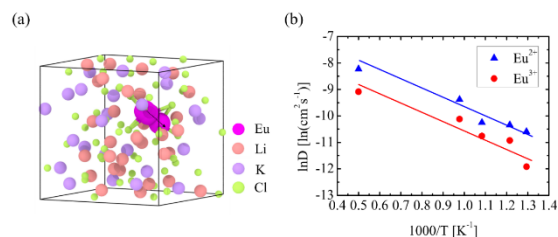


Fig. 4. (a) Diffusion mechanism of Eu ions in LiCl-KCl molten salt. (b) Diffusion coefficients of Eu^{2+} and Eu^{3+} in LiCl-KCl molten salt at various temperatures.

Diffusion coefficients of Eu^{3+} are smaller than that of Eu^{2+} because Eu^{3+} has rigid solvation shell structure comparing to Eu^{2+} .

4. Conclusion

We utilized first principles DFT calculations and AIMD simulations to understand fundamental mechanism of spontaneous reduction of Eu^{3+} to Eu^{2+} in LiCl-KCl eutectic molten salt. We decoupled reaction Gibbs free energy into enthalpic and entropic contributions. The rigidity of the solvation shells was estimated by RDF, oxidation and coordination numbers, which largely described the enthalpic change.

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