Investigation of in-reactor cesium chemical behavior in TEPCO's Fukushima Daiichi Nuclear Power Station accident
(4) Quantum modelling of Cs substances in the case of LWR severe accident

*Faoulat Miradji[1,2], Chikashi Suzuki[1], Kunihisa Nakajima[1,2] and Masahiko Osaka[1,2]

[1]JAEA, [2]IRID

Abstract

Theoretical calculations were conducted in order to provide the unknown thermochemical properties of Cs-Si-Fe-O systems for the establishment of Cs chemisorption model based on the mass transfer theory. The computational methodology was validated by calculating the thermal properties of $Cs_2Si_4O_9$ revealing a good agreement with the literature data.

Keywords: Cesium, silicates, DFT, thermodynamic, LWR

1. Introduction

Within the framework of the 1-F severe accident (SA), Cs retention onto reactor surfaces should be characterized as it impacts Cs distribution. To build a Cs chemisorption model based on the mass transfer theory [1], the thermal properties of identified Cs-Fe-Si-O chemisorbed species are needed. In particular, the thermodynamic properties of chemisorbed species $CsFeSiO_4$, a newly identified substance in our experiments are unknown[2]. In order to obtain in a reasonable time a first estimation of the target properties, we performed quantum chemical calculations. This methodology allows obtaining accurate properties of substances from the fundamental laws of quantum mechanics, ensuring the independence of the calculated data, allowing minimizing the range of discrepancies of derived values that can be larger when the data are derived from empirical experimental tests. We present in a first part the construction of the computational methodology, which was validated by computing the properties of $Cs_2Si_4O_9$ and in a second part, the results obtained for $CsFeSiO_4$ investigations.

2. Methodology

Density Functional Theory (DFT) was applied to obtain the geometric, electronic and energetic properties of target species. Phonon calculations in the harmonic approximation were performed to derive the thermodynamic data.

3. Results and discussion

In Figure 1, the calculated heat capacities of two $Cs_2Si_4O_9$ prototypes are compared with their corresponding literature values, obtained by Cordfunke using calorimetric measurements of a $Cs_2Si_4O_9$ solution [4].

The calculated data are in good agreement with the literature values, falling into the accuracy of thermochemical data (0.05 eV/atom)[5], validating the appropriateness of built methodology. To compute the fundamental data of $CsFeSiO_4$, several configurations were investigated with only one available in the literature [3]. Indeed, this compound was identified currently in our experiments as a chemisorbed species from CsOH (g) reaction within stainless steel surfaces SS304 and 316[2].

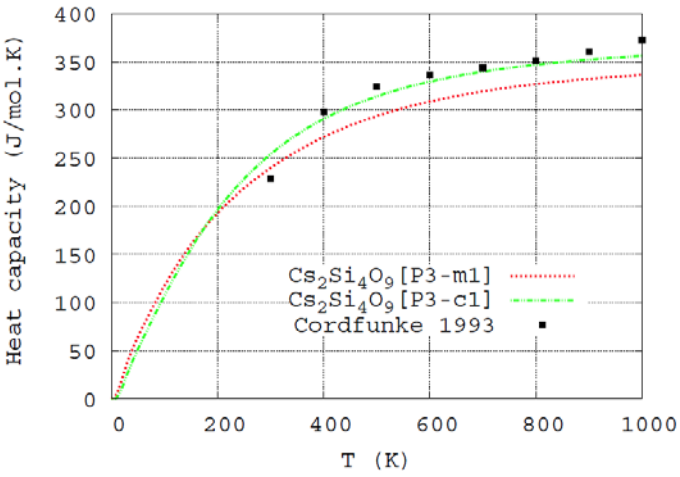

Figure 1 : Calculated heat capacities of $Cs_2Si_4O_9$ compared with literature [4]

4. Conclusion

A computational methodology was established for the first time to calculate the properties of $Cs_2Si_4O_9$ and $CsFeSiO_4$ substances, the later having no existing values in the literature regarding its thermal properties. The results related to $CsFeSiO_4$ substances will be discussed in this presentation as well as the perspectives on the derivation of remaining Cs chemisorbed species unknown properties.

Acknowledgement

The content of this material includes output of the METI subsidy for Project of Decommissioning and Contaminated Water Management (upgrading level of grasping state inside reactor).

References

[1] S. Nishioka et al., AESJ Fall Meeting 2017, 2P09. [2] F.G. Di Lemma et al., J. of Nucl. Mat., 2017. [3] Henry P., Chem. Commun. 1998. [4] E. H. P. Cordfun ke, J. Chem. Therm. 1993. [5] Stevanovic et al., Phys. Review B., 2012.