

Evaluation of Solution Energies of Cr, Fe and Ni Impurity Atoms in Liquid Na by First-principles Calculation

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1. Introduction

The liquid Na is a promising coolant in generation IV reactors due to many attractive characteristics, such as large temperature margins from the operation temperatures (from 663 K to 818 K) to the melting point (371 K) and boiling point (1,156 K), a high thermal conductivity, and a low thermal neutron capture cross section which is needed for fast neutron production [1]. Above all, liquid Na has a good compatibility with structural materials and cladding materials in contrast to the other liquid metal coolants such as liquid lead-bismuth eutectic (LBE) and liquid lead [1].

In order to meet the safety regulations and protect the public and environment from the radiation exposure, the transport of impurity atoms in liquid Na, which is characterized by diffusivity and solubility, is needed to be understood. For instance, it is vital to know the transportation properties of fission products and nuclear fuels for an accident situation and of H, C and O for purity control in a normal operation and of Cr, Fe and Ni for the prevention of corrosion in a long-term operation. However, it is rather difficult to estimate the transportation properties of the impurity elements by experiment due to the following reasons: (i) It is hard to detect the diffusivity and solubility of impurities, if the solubility is not sufficiently high; (ii) The high chemical reactivity of liquid Na with water or air makes the experiment difficult; (iii) There is a large solubility dependency on concentrations of other impurity elements, such as O, C and H *etc.*, due to the chemical interactions.

As another research tool for exploring thermodynamic properties, quantum mechanical calculations based on the density functional theory (DFT) have been widely utilized. In the present study, we aim to establish a method to calculate the solution energy of an impurity atom in liquid Na by using the quantum mechanical calculation. As test cases, the solution energies of Cr, Fe and Ni impurity atoms are estimated at 1000 K and 0 Pa, and are compared with reported experimental values.

2. Computational details

To evaluate the solution energy of an impurity atom in liquid Na, the energies of following systems should be determined,

$$E_{sol} = E_{mixture} - (E_{pure-liquid-Na} + E_{impurity}), \quad (1)$$

where E_{sol} , $E_{mixture}$, $E_{pure-liquid-Na}$ and $E_{impurity}$ are the solution energy, the internal energy of a liquid Na system containing an impurity atom, the internal energy

of a pure liquid Na system, and the internal energy per atom of a crystal of the standard state, respectively. Each energy is determined at 1000 K. Fig. 1 schematically shows energy diagrams for the evaluation.

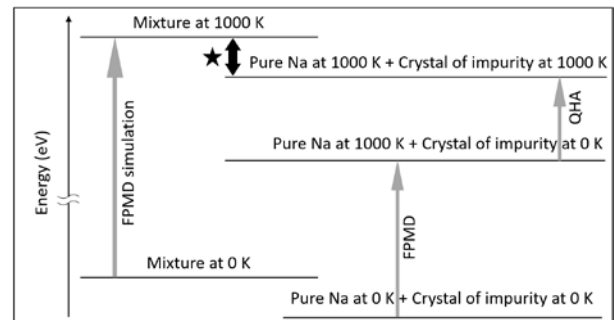


Fig. 1. The schematic of a method to calculate the solution energy of an impurity atom in liquid Na at 1000 K.

The FPMD simulations were performed for liquid states by using the Vienna *ab initio* simulation package (VASP) [2]. The projected augmented wave (PAW) potential was employed to represent the effect of core electrons. Based on the results of our previous research presented in KNS 2017-spring, the exchange-correlation energy was described by the generalized gradient approximation (GGA) of PBE functional. The electron wave functions were expanded with the plane wave basis set by 300 eV energy cutoff and the energy convergence of 10^{-6} eV was set. The $2 \times 2 \times 2$ Monkhorst-Pack grid was used to sample the band energy in the Brillouin zone with the 1st order Methfessel-Paxton smearing method with a smearing width of 0.2 eV.

In the pure liquid Na system, 102 Na atoms having one valence electron ($3s^1$) were prepared with the periodic boundary condition. The temperature was controlled to be 1000 K by Nosé thermostat in the canonical ensemble (NVT). Non spin-polarized calculations were performed as the spin polarization did not occur in some test calculations. The simulations were conducted for 20 ps with a time step of 1.2 fs. Subsequently, a Na atom was replaced with an impurity atom, namely Fe ($3d^54s^1$), Cr ($3d^64s^2$) and Ni ($3d^84s^2$) atom, one by one. For three liquid mixture systems containing a Fe, Cr and Ni atom, respectively, 15 ps simulations were conducted with a time step of 1.2 fs. In all liquid simulations, the first 5 ps data were discarded as an equilibration step. We confirmed that the equilibration was achieved from the convergences of energy, pressure and geometry.

In the evaluation of $E_{impurity}$ at 1000 K, QHA-combined with DFT-PBE calculations were performed in bcc for Cr, Fe and in fcc for Ni. In each crystal system,

the DFT-PBE static calculations were firstly performed to optimize the geometry by allowing volume relaxation. Subsequently, several supercells ($4 \times 4 \times 4$ for bcc, $3 \times 3 \times 3$ for fcc) having a larger/smaller lattice constant from 97% to 103% with the 0.5% interval were prepared. In each system, the atomic forces, which are needed for constructing a dynamic matrix in the vibration analysis, were evaluated by using static DFT-PBE calculation in a system where an atom is displaced by *ca.* 0.01 Å. After that, the *phonopy* code, developed by Atsushi Togo research group [3], was used to evaluate several thermodynamic quantities by QHA.

3. Results and discussion

3.1. First-principles molecular dynamics

To properly evaluate $E_{mixture}$ and $E_{pure-liquid-Na}$ at 1000 K in Eq. (1), the internal energy in each liquid FPMD simulation was obtained by averaging a sufficient number of data, because such thermodynamic quantities fluctuate in the FPMD simulation.

In the error assessment of such time-correlated data, the concept of statistical inefficiency [4] was utilized to appropriately estimate the statistical accuracy in their averages. The statistical inefficiency help us to determine the most efficient minimum block size, in which blocks are no longer time-correlated with each other from the viewpoint of statistics.

Thus, the internal energy data consisted of τ_{total} data points are firstly divided into n_b blocks, each of which has τ_b data points, to achieve $\tau_{total} = n_b \tau_b$. Then, the variance of the internal energy, E , can be written as follows,

$$\sigma^2(\langle E \rangle_b) = \frac{1}{n_b} \sum_{b=1}^{n_b} (\langle E \rangle_b - \langle E \rangle_{total})^2, \quad (2)$$

where $\langle E \rangle_b$ is the average of b -th block and $\langle E \rangle_{total}$ is the average of all the data. The variance becomes inversely proportional to n_b as τ_b increases, meaning that $\langle E \rangle_b$ values of neighboring blocks become statistically time-uncorrelated with each other due to a large enough block size. Then, the statistical inefficiency can be defined as,

$$s = \lim_{\tau_b \rightarrow \infty} \frac{\tau_b \sigma^2(\langle E \rangle_b)}{\sigma^2(E)}. \quad (3)$$

In practice, the statistical inefficiency is estimated as a plateau value in the plot of $\tau_b \sigma^2(\langle E \rangle_b) / \sigma^2(E)$ as a function of $\sqrt{\tau_b}$. For example, Fig. 2 shows such a plot at 1000 K, where the statistical inefficiencies is determined to be approximately 70. Likewise, in all the liquid simulations, the statistical inefficiencies were estimated to be *ca.* 70. It means that it takes approximately 70 time steps to forget the memory of the former data in statistics. Consequently, the time-correlation corrected standard deviation can be expressed as follows,

$$\sigma(\langle E \rangle_{total}) = \sqrt{\frac{s}{\tau_{total}}} \sigma(E). \quad (4)$$

The average internal energy and standard deviation of it in each liquid system at 1000 K are summarized in Table I.

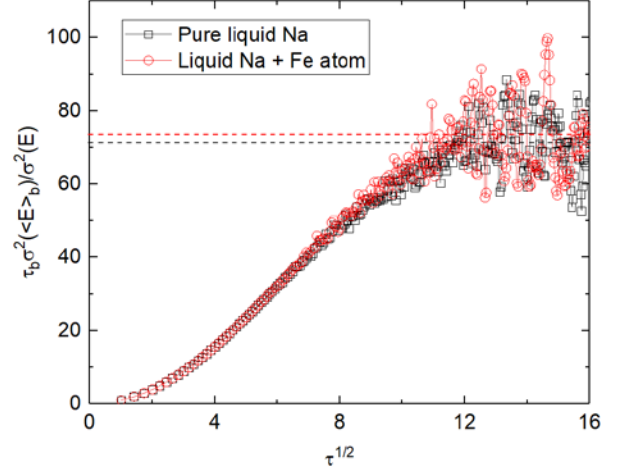


Fig. 2. The statistical inefficiency of the internal energy as a function of square root of τ at 1000 K. The horizontal lines indicate the plateau value.

Table I: The average internal energies and standard deviations of these in liquid systems at 1000 K.

Energy format	$E_{pure-liquid-Na}$	$E_{mixture}$		
System	Pure Na	Na with Cr	Na with Fe	Na with Ni
Total energy (eV)	-112.89	-119.70	-117.96	-116.13
Standard deviation (eV)	0.048	0.068	0.107	0.075

3.2. QHA combined with DFT-PBE

To estimate the internal energy per atom of a crystal in the standard state at 1000 K, $E_{impurity}$, QHA combined with DFT-PBE static calculation was used. The QHA calculation is a powerful tool in the evaluation of thermodynamic quantities, such as the Helmholtz/Gibbs free energy, bulk modulus, heat capacity *etc.* of a crystalline solid material at finite temperatures. It utilizes the phonon dispersion relation determined under the harmonic approximation, and the harmonic approximation is partly corrected by considering volume dependence of phonon frequencies as a part of anharmonic effect.

$E_{impurity}$ in a condensed matter at a finite temperature consists of the Helmholtz free energy and the product of temperature and entropy as follows,

$$E_{impurity} = U_{el} + U_{vib} = F + TS, \quad (5)$$

where U_{el} and U_{vib} are the internal energies induced by interactions of electrons and nucleuses and the vibration energy of atoms, respectively. Thus, to estimate it, the

Helmholtz free energy and entropy should be calculated. In the statistical thermodynamics, the Helmholtz free energy is defined as follows [3],

$$F = \frac{1}{2} \sum_{qv} \hbar w(qv) + k_B T \sum_{qv} \ln \left[1 - \exp \left(\frac{-\hbar \omega(qv)}{k_B T} \right) \right], \quad (6)$$

where $w(qv)$ is the phonon frequency of the mode qv . Meanwhile, the entropy of the system can be obtained to be the negative value of the first derivative of the Helmholtz free energy with respect to the temperature [3],

$$S = -\frac{\partial F}{\partial T} = \frac{1}{2T} \sum_{qv} \hbar w(qv) \coth \left(\frac{\hbar w(qv)}{2k_B T} \right) - k_B \sum_{qv} \ln \left[2 \sinh \left(\frac{\hbar w(qv)}{2k_B T} \right) \right]. \quad (7)$$

Attentively, the above thermodynamic quantities (F and S) are needed to be calculated at the equilibrium volume. Therefore, the equilibrium volumes are estimated by choosing the volume that produces the minimum Gibbs free energy at a given set of constant pressure and temperature. The Gibbs free energy is defined as follows,

$$G(T; P) = \min_v (F(T; V) + PV), \quad (8)$$

In the present study, because the pressure is set to be 0 Pa, the PV term in the right hand side is neglected. Subsequently, the equilibrium volume yielding the minimum value of the right hand side in Eq. (8) is estimated as portrayed in Fig. 3. With the determined equilibrium volume, the internal energy per atom of Cr-bcc, Fe-bcc and Ni-fcc at 1000 K are evaluated by using Eq. (5), Eq. (6) and Eq. (7). The results are summarized in Table II.

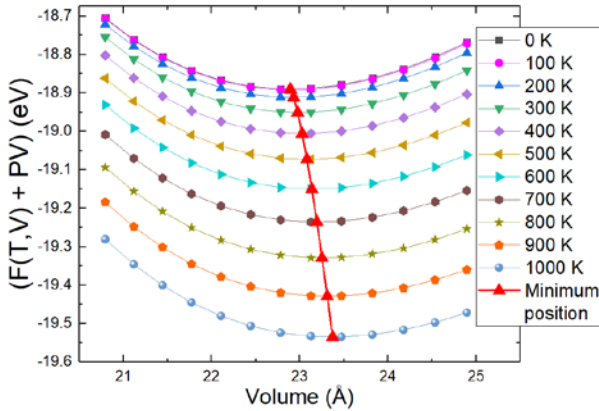


Fig. 3. The summation of the Helmholtz free energy and PV term as a function of volume at a given temperature (Cr-bcc). The Red line indicates the equilibrium volumes, which produce the Gibbs free energy.

Table II: The internal energies per atom, $E_{impurity}$, and expected errors of Cr-bcc, Fe-bcc and Ni-fcc at 1000 K.

System	Cr bcc	Fe bcc	Ni fcc
Internal Atomic energy (eV)	-9.22	-7.96	-5.19
Expected error (eV)	0.088	0.064	0.112

Further, the expected error, $\sigma_{impurity}$, of $E_{impurity}$ in reference to the experimental data were assessed by enthalpy differences as follows,

$$\sigma_{impurity} = [H - H^0]_{calculation} - [H - H^0]_{exp}. \quad (9)$$

This is because the enthalpy is almost equal to the energy for a condensed phase (liquid or solid) if the pressure is not so high.

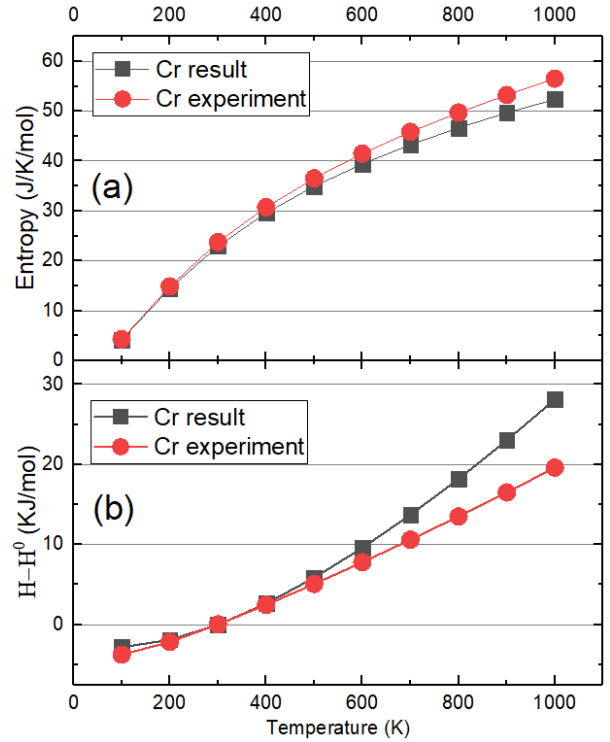


Fig. 4. The results of (a) the entropy and (b) the enthalpy differences of Cr-bcc as a function of temperature with the experimental data [5].

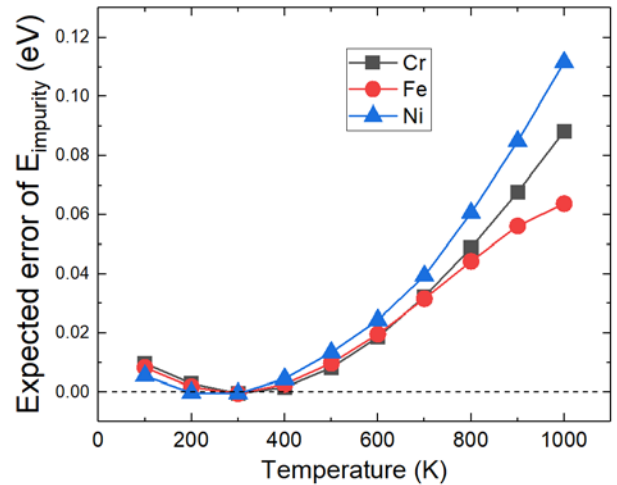


Fig. 5. The expected errors, $\sigma_{impurity}$, of $E_{impurity}$ for Cr-bcc, Fe-bcc and Ni-fcc as a function of temperature in eV unit.

The enthalpy (H) of a system can be calculated as the summation of the Gibbs free energy and the product of temperature and entropy ($H=G+TS$). The Gibbs free energy was already evaluated in Fig. 3. The entropy can

be calculated with Eq. (7), which is compared with the experimental result in Fig. 4(a) as a function of temperature. Regarding the reference point of the enthalpy (H^0), the enthalpy at 298.15 K is set to be 0 kJ/mol in the experiment [5], while that at 300 K is set to be 0 kJ/mol in the present calculation for the simplicity. The results of enthalpy differences ($H-H^0$) are compared to experimental data [5] in Fig. 4(b) and the corresponding errors are presented in Fig. 5 and Table II in eV unit.

3.3. Discussion on the solution energy

As a result, the solution energies of Cr, Fe and Ni atoms in liquid Na are evaluated based on Eq. (1). Furthermore, the calculation errors of solution energies are assessed from the estimated errors in Section 3.1 and 3.2, as follows,

$$\sigma_{sol} = \sqrt{\sigma_{mixture}^2 + \sigma_{pure-liquid-Na}^2 + \sigma_{impurity}^2}. \quad (10)$$

The results are summarized in Table III with experimental data [6].

Table III: The calculated solution energies of Cr, Fe and Ni atoms in liquid Na together with experimental data [6]. The estimated errors of results are presented in parentheses.

Solution energy (eV)	Calculation results	Experiment [6]
Cr	2.41 (0.11)	1.79
Fe	2.97 (0.13)	0.81
Ni	1.94 (0.15)	0.31

However, the calculation results have much larger values than experimental data. The disparity is likely to be induced mainly by a premise in the present study that the impurity element exists as an isolated atom in liquid Na. From this point of view, the following two points need to be discussed: (i) As reported in a number of previous researches, the solubility and the solution energy of Cr, Fe and Ni atoms in liquid Na are largely affected by coexisting oxygen impurity. However, in the present study, we do not deal with oxygen impurity at all; (ii) In reality, these metallic impurity element may tend to form a metal cluster rather than to exist as an isolated atom. Thus, such differences cause a considerable disparity in the solution energy.

To further quantitatively study the effects of oxygen concentration and of metal clustering on the solution energy of the impurity elements, we plan to conduct the following tasks: (i) By inserting oxygen atoms near the Fe atom and making iron oxides, such as Fe-O, Fe-O₂ and Fe-O₃ in liquid Na, we will find which compound is the most favorable energetically, and how much energy will be gained; (ii) By inserting Fe atoms near the original Fe atom in liquid Na, the effect of metal clustering will be checked through the energy gain. These new studies will improve our method to reflect the real condition.

4. Conclusion

In the present study, we have suggested a method to calculate the solution energy of Cr, Fe and Ni atom in liquid Na from the energies of several systems evaluated by first-principles calculations. For liquid systems, the FPMD simulations have been conducted to evaluate the internal energy of the system. The concept of statistical inefficiency has been used to estimate the error of averaged internal energy in each liquid system. Regarding the estimation of the internal energy per atom of a crystalline system, the QHA combined with DFT-PBE calculations have been utilized. As a result, the solution energies of Cr, Fe and Ni atoms in liquid Na were estimated to be 2.41 (± 0.11), 2.97 (± 0.13) and 1.94 (± 0.15) eV, respectively. However, there are considerable disparities in solution energies between the calculation results and experiments. It may be induced by our premise that the impurity is dissolved in liquid Na as an isolated atom. We consider that the coexistence of oxygen impurity or/and clustering of impurity atoms are possible causes of the disparity. To further understand these effects, additional studies will be conducted in near future.

5. Acknowledgement

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