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THERMODYNAMIC PROPERTIES OF ALKALI METALS UNDER INFLUENCE OF IMPURITY

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Abstract. An analytical method for calculation and evaluation of thermodynamic properties of alkali metals under the influence of impurity atom has been developed based on quantum statistical theory with correlated Einstein model. Mean square relative displacement (MSRD), effective local force constants, correlated Einstein frequency and temperature of pure alkali metals and of those with impurity have been calculated and compared each to other. The ratio of calculated local force constants of alkali metals with impurity to those of pure metals specifies the rate of influence of the impurity.The proportionality of MSRD to Einstein frequency and temperature and its inversal proportionality to the effective local force constants have been proved. Numerical results for K, Na, Cs and Rb illustrate the detailes of theoretical conclusions.

1. Introduction

Alkali metals play very important role in the chemistry and in the material science using these substances, that is why understanding physical properties of alkali metals is always required. To study thermodynamic properties of a substance it is necessary to investigate its MSRD and the effective local force constants [1-8] which are contained in the X-ray absorption fine structure (XAFS). Moreover, the impurity or dopant atom can infuence on the physical parameters taken from the XAFS spectra [9] and on the efficiency of using these substances.

The purpose of this work is to develop a method for calculation and evaluation of the effective local force constants and MSRD of alkali metals containing a dopant or impurity (I) atom as absorber in the XAFS process. The neighboring scattering atoms as the hosts (H) are the alkali metal atoms. The derivation is based on the quantum statistical theory with the correlated Einstein model [6] which is considered at present as "the best theoretical framework with which the experimentalist can relate force constants to temperature dependent XAFS" [8]. The MSRD for the bond of impurity-impurity (I-I), host-host (H-H) and impurity-host (I-H) atoms are computed and compared each to other, through that the thermodynamic properties of pure alkali metals and of the ones with an impurity atom are evaluated. It is shown that the ratio of the calculated effective local force constants of alkali metals with impurity to the ones of pure alkali metals specifies the rate of influence of impurity on the thermodynamic properties of alkali metals. Proportionality of MSRD to Einstein frequency and temperature and its inversal proportionality to the effective local force constants have been proved. Numerical calculations for alkali metals K, Na, Cs, Rb have been done, in which Ni, Ca and Na atoms have been chosen as impurity atoms.

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2. Formalism

The expression for the MSRD in XAFS theory is derived based on the anharmonic correlated Einstein model [6] according to which the effective interaction Einstein potential of the system is given by

$$V_{eff} = \frac{1}{2}k_{eff}x^2 + k_3x^3 + ... = V(x) + \sum_{j\neq i} V\left(\frac{\mu}{M_i}x\hat{\mathbf{R}}_{12}.\hat{\mathbf{R}}_{ij}\right); \mu = \frac{M_1.M_2}{M_1+M_2}. \qquad (1)$$

Here k_{eff} is effective local force constant, k_3 the cubic parameter giving an asymmetry in the pair distribution function, and $\hat{\mathbf{R}}$ is the bond unit vector. The correlated Einstein model may be defined as a oscillation of a pair of atoms with masses M_1 and M_2 (e.g., absorber and backscatterer) in a given system. Their oscillation is influenced by their neighbors given by the last term in the left-hand side of Eq. (1), where the sum i is over absorber ($i = 1$) and backscatterer ($i = 2$), and the sum j is over all their near neighbors, excluding the absorber and backsctterer themselves. The latter contributions are described by the term $V(x)$.

Applying the Morse potential for weak anharmonicity in the expansion

$$V(x) = D\left\{ e^{-2\alpha.x} - 2e^{-\alpha.x}\right\} \cong D(-1 + \alpha^2x^2 - \alpha^3x^3 + ...) \qquad (2)$$

to the effective potential of the system of Eq. (1) (ignoring the overall constant for convenience) we obtain

$$k_{eff} = D\alpha^2\left(S - \frac{15}{2}\alpha a\right) = \mu\omega_E^2; k_3 = -\frac{5}{4}D\alpha^3; \theta_E = \frac{\hbar\omega_E}{k_B}, \qquad (3)$$

where x is the deviation of instantaneous bond length between the two atoms from equilibrium, D is the dissociation energy and $1/\alpha$ corresponds to the width of the potential; k_B is the Boltzmann constant; ω_E, θ_E are the Einstein frequency and Einstein temperature; a describes the assymmetry of the potential due to anharmonicity.

Using the definition [2 - 7] $y = x - a$ as the deviation from the equilibrium value of x at temperature T and quantum statistical theory [16] the MSRD is described by

$$\sigma^2 = \frac{1}{Z}Tr(\rho.y^2) = \frac{1}{Z}\sum_n e^{n\hbar\omega_E} < n|y^2|n > = \frac{\hbar\omega_E}{2k_{eff}}\frac{1+z}{1-z}, z = e^{-\theta_E/T}, \qquad (4)$$

where we express y in terms of anihilation and creation operators, $\hat{a}$ and $\hat{a}^+$, i. e.,

$$y = \kappa(\hat{a} + \hat{a}^+); \kappa^2 = \frac{\hbar}{2\mu\omega_E} \qquad (5)$$

and use harmonic oscillator state $|n>$ with eigenvalue $E_n = n\hbar\omega_E$ (ignoring the zero-point energy for convenience).

Therefore the expression for the MSRD is resulted as

$$\sigma^2(T) = \sigma_o^2\frac{1+z}{1-z}; \sigma_o^2 = \frac{\hbar\omega_E}{2SD\alpha^2}, \qquad (6)$$

where σ_o^2 is the zero-point contribution to σ^2. In the derivation of the above expressions we have developed astructural parameter

$$S = 2 + \sum_{j=2}^{N} (\hat{\mathbf{R}}_{01}\hat{\mathbf{R}}_{0j})^2; \hat{\mathbf{R}} = \mathbf{R}/|\mathbf{R},| \tag{7}$$

where N is atomic number of the first shell, $\mathbf{R}_{01}$ is directed from absorber located at point 0 to the location of the first scatterer at $j = 1$, and $\mathbf{R}_{0j}$ are from absorber to the other scatterers.

In the case of impurity using the method described in [13] the Morse potential parameters D_{IH} and α_{IH} for the bond (IH) is given by a plus average of the ones of the constituent impurity (I) atom as absorber and of the host (H) atom as scatterer

$$D_{IH} = \frac{D_I + D_H}{2}; \alpha_{IH} = \left(\frac{D_I \alpha_I^2 + D_H \alpha_H^2}{D_I + D_H} \right)^{1/2}. \tag{8}$$

From Eq. (4) it is also shown that the MSRD is proportional to the correlated Einstein frequency and temperature and inversaly proportional to the effective local force constant. The XAFS function is proportional to the Debye-Waller factor [9]

$$\chi(k) \sim e^{-2k^2\sigma^2}, \tag{9}$$

where k is wave vector of the photoelectron; that is why the changes of the MSRD σ^2 influence on the XAFS, thus influencing on the information taken from these spectra.

3. Numerical results and discussions

Now we apply the above expressions to numerical calculations for alkali metals K, Na, Cs and Rb, in which Ni, Ca, Na have been chosen as impurity atoms. Structural parameter S has been calculated and it is equal to 5 for *fcc*, *hcp* and 11/3 for *bcc*. Morse potential parameters for the pure metals have been calculated using the procedure presented in [12, 14] for the pure metals and the plus averaging procedure for the ones with impurity. The ratio of the effective local force constant of alkali metals with impurity (f_{eff}^{IH}) to the one of pure metals (f_{eff}^{HH}) is denoted by

$$r = f_{eff}^{IH}/f_{eff}^{HH}. \tag{10}$$

The calculated values of Morse potential parameters; correlated Einstein frequency and temperature; effective local force constant for the pure alkali metals Na, K, Cs, Rb and dopant metals Ni, Ca are written in Table I. These values for the case with the impurity atoms Ni, Ca, Na are presented in Table II. All these values change very strongly when the alkali metals contain an impurity atom, especially at short distances and near to the equilibrium. From the ratio r we can see very strong change of the effective local force constants of the alkali metals containing an impurity atom compared to the ones of the pure metals, for example the effective local force constant of Cs containing a Ni atom is increased by 35 times compared to the one of pure Cs, but the effective local force constant of Cs containing a Na atom is only 62 percent of the one of the pure Cs. All these changes will influence on the MSRD contained in XAFS spectra. Figure 1 shows significant difference of the Morse potential of alkali metal Na from the one containing an impurity atom K or an impurity atom Ca. Figure 2 shows the temperature dependence of MSRD σ^2 of alkali metal Na compared to those containing an impurity atom Ca or Cs. The values of σ^2 , correlated Einstein temperature and the ratio r of alkali metal Na change significantly when Na is doped by an impurity atom K or an impurity atom Ca. All these changes show the proportionality of the MSRD to the Einstein frequency and temperature and its inversal proportionality to the effective local force constant. The calculated MSRD of pure and doping alkali metals contain zero point energy contribution and are linearly proportional to the temperature T at high temperature, thus satisfying all fundamental properties of this quantity proved by theory and experiment [1, 3, 8, 9, 15].

Table I. Calculated values of Morse potential parameters D, α ; correlated Einstein frequency ω_E and temperature θ_E ; effective local force constant k_{eff} for alkali metals *Na, K, Cs, Rb* and for dopant metals *Ni, Ca*.

Bond	D(eV)	α (Å^{-1})	$\omega_E(\times 10^{13}\ Hz)$	$\theta_E(K)$	$k_{eff}(N/m)$
Ni-Ni	0.421	1.420	3.722	284.31	4.239
Ca-Ca	0.162	0.805	1.587	121.25	0.526
Na-Na	0.063	0.590	0.838	63.97	0.081
K-K	0.054	0.498	0.491	37.54	0.049
Rb-Rb	0.046	0.430	0.266	20.29	0.031
Cs-Cs	0.045	0.416	0.203	15.48	0.028

Table II. Calculated values of Morse potential parameters D, α ; correlated Einstein frequency ω_E and temperature θ_E ; effective local force constant k_{eff} and the ratio r for alkali metals *K, Cs, Rb* with *Ni, Ca, Na* atoms as impurity atoms..

Bond	D(eV)	α (Å-1)	$\omega_E(\times 10^{13}\ Hz)$	$\theta_E(K)$	$k_{eff}(N/m)$	r
K-Ni	0.237	0.959	2.069	158.03	1.091	22.26
K-Ca	0.108	0.652	1.055	80.60	0.230	4.69
K-Na	0.059	0.544	0.632	48.28	0.64	0.79
Cs-Ni	0.233	0.918	1.401	107.01	0.980	35.00
Cs-Ca	0.104	0.611	0.654	50.00	0.193	6.97
Cs-Na	0.054	0.503	0.352	26.91	0.050	0.62
Rb-Ni	0.233	0.925	1.630	124.51	0.998	32.19
Rb-Ca	0.104	0.618	0.780	59.57	0.199	6.33
Rb-Na	0.055	0.510	0.461	35.18	0.60	0.74

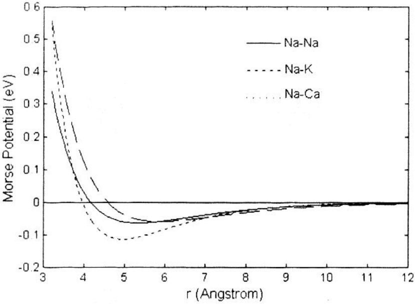

Figure 1: Morse potential of alkali metal *Na* (solid) compared to the one of *Na* containing an impurity atom *K* (dash) or an impurity atom *Ca* (dot).

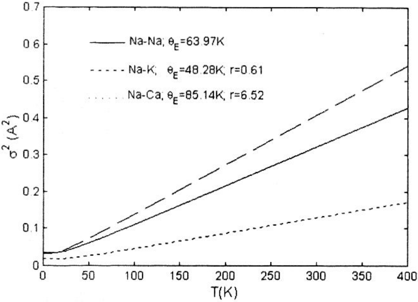

Figure 2: Temperature dependence of MSRD $\sigma^2(T)$ of alkali metal *Na* (solid) compared to the one containing an impurity atom *K* (dash) or an impurity atom *Ca* (dot).

All the above calculations have been also carried out using the Morse potential parameters of another sourse [12]. They provide very good agreement with our results which can be seen in Table III.

Table III. Morse potential parameters for *Ni, Ca, Na, K, Rb* and *Cs* calculated in present work compared to those of another method.

Bond	*D(eV)*		$\alpha(\AA^{-1})$	
	Present	*Ref. 12*	*Present*	*Ref. 12*
Ni-Ni	0.421	0.4205	1.420	1.4199
Ca-Ca	0.162	0.1623	0.805	0.8054
Na-Na	0.063	0.0633	0.590	0.8599
K-K	0.054	0.0542	0.498	0.4977
Rb-Rb	0.046	0.0464	0.430	0.4298
Cs-Cs	0.045	0.0449	0.416	0.4157

4. Conclusions

A new analytical method for calculation and evaluation of thermodynamic properties of alkali metals under the influence of impurity atom has been developed based on the quantum statistical theory with correlated Einstein model.

The calculated Morse potential parameters, MSRD, local effective force constants, correlated Einstein frequency and temperature of alkali metals are significantly different from those when the alkali metals are doped by an impurity atom.

The ratio of the calculated effective local force constant of alkali metals with an impurity atom to the ones of pure metals specifies the rate of influence of impurity on thermodynamic parameters of alkali metals.

The proportionality of the MSRD to the Einstein frequency and temperature and its inversal proportionality to the effective local force constants has been proved.

Numerical results for K, Na, Cs and Rb illustrate the detailes of theoretical conclusions. They may be also useful for analysis of experimental data related to these quantities.

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