

EAM APPROACH TO ENTHALPY OF FORMATION OF ALKALI METAL ALLOYS^①

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ABSTRACT A new embedded atom method(EAM) potential is used to calculate the enthalpy of formation of disordered alkali metal alloys as a function of the concentration. In the new EAM model, a new pair potential is proposed and a modified term which makes the EAM model be able to describe the negative Cauchy pressure of alkali metal cesium is introduced. The results agree well with the experiments and with other theoretical calculations.

Key words EAM approach enthalpy of formation alkali metal alloys

1 INTRODUCTION

The theoretical study of the alloy formation process is always an interesting subject, this stimulates the study of enthalpy of formation for alloys. Significant progress has been achieved in the first principle's calculation of the enthalpy of formation of transition metal alloys^[1, 2] and simple metal alloys^[3-5]. A great progress has also been achieved in the empirical and semi-empirical thermodynamic calculations of the enthalpy of formation of transition metal alloys^[6-10] and simple metal alloys^[8, 11]. The calculations performed by the authors for alloys of simple metals used the Miedema empirical thermodynamic theory; the advantage of the Miedema theory is its simplicity of calculations.

Recently, a new semi-empirical theory, embedded atom method, was developed by Daw and Baskes^[12] on the basis of density function theory. The theory has been successfully applied to studying the cohesive energy of pure metals and alloys^[13-20]. These studies suggest the ap-

plication of the EAM to the study of enthalpy of formation for simple alkali metals. In order to treat the negative Cauchy pressure of metal cesium, we use the modified EAM model developed by Ouyang *et al*^[20]. In this model, the negative Cauchy pressure can be fitted exactly.

2 EAM MODEL FOR A METAL

The total energy of an assembly of a metal, according to the formalism of the modified EAM model^[20, 21] is

$$E_{\text{tot}} = \sum_i (F_i(\rho_i)) + \frac{1}{2} \sum_{i,j} \phi(r_{ij}) + \sum_i M_i(p_i) \quad (1)$$

$$\rho_i = \sum_{j \neq i} f(r_{ij}) \quad (2)$$

$$p_i = \sum_{j \neq i} f^2(r_{ij}) \quad (3)$$

where $\phi(r)$ is the effective two-body potential, $F(\rho)$ is the embedding energy, $M(p)$ is the modified term, ρ is the electron density of an atom due to all other atoms, p represents the modified part of electron density resulting from

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angular distribution of p , d , f electrons, $f(r)$ is the atomic electron density distribution function, and r_{ij} is the distance between atoms i and j .

The embedding function and the function of electron density distribution of an atom are taken the same forms as those of Johnson and Oh^[22]:

$$F(\rho) = -F_0(1 - n \ln \frac{\rho}{\rho_e})(\frac{\rho}{\rho_e})^n \quad (4)$$

$$f(r) = f_e(\frac{r_1}{r})^\beta \quad (5)$$

where ρ_e is the equilibrium value of ρ , F_0 , n , f_e and β are parameters to be determined.

The two-body potential $\phi(r)$ and modified term $M(p)$ are taken as^[20, 21]

$$\phi(r) = k_0 + k_1(\frac{r}{r_1})^2 + k_2(\frac{r}{r_1})^4 + k_3(\frac{r_1}{r})^{12} \quad (6)$$

$$M(p) = \alpha[(\frac{p}{p_e} - 1)^2] \times \exp[-(\frac{p}{p_e} - 1)^2] \quad (7)$$

where r_1 is the equilibrium value of the nearest-neighbour separation; k_0 , k_1 , k_2 and k_3 are model parameters; and p_e is the equilibrium value of p .

The determination of model parameters is given in detail previously^[20]. The physical properties of pure alkali metals are listed in Table 1. All the EAM model parameters calculated are listed in Table 2. The two-body potential function $\phi(r)$ and electron density distribution function $f(r)$ are cut off with a cubic spline function as we used before^[18].

This model has been successfully applied to studying enthalpy of formation of *bcc* transition metal alloys^[20] and the diffusion properties of

Table 2 Model parameters determined from input physical parameters

Par.	Li	Na	K	Rb	Cs
k_0	- 0.144	- 0.122	- 0.137	- 0.113	- 0.122
k_1	0.091	0.068	0.078	0.055	0.045
k_2	- 0.015	- 0.009	- 0.009	- 0.005	0.009
k_3	0.017	0.014	0.017	0.013	0.020
f_e	0.184	0.098	0.055	0.044	0.037
F_0	1.290	0.773	0.594	0.511	0.482
n	0.126	0.132	0.155	0.143	0.164
α	0.008	0.013	0.015	0.014	- 0.015
β	6	6	6	6	6

transition metals^[21]. The obtained results are in good agreement with the results of experiments and of other theoretical calculations.

3 DISORDERED SOLID ALLOYS OF ALKALI METALS

In an alloy, the two-body potential or alloy potential between different type of atoms A and B is taken the same as that of Johnson^[22]:

$$\phi^{AB}(r) = \frac{1}{2}(\frac{f^A(r)}{f^B(r)}\phi^{BB}(r) + \frac{f^B(r)}{f^A(r)}\phi^{AA}(r)) \quad (8)$$

where $\phi^{AB}(r)$ is the alloy potential between atoms A and B . $f^A(r)$, $f^B(r)$, $\phi^{AA}(r)$ and $\phi^{BB}(r)$ indicate the corresponding functions $f(r)$ and $\phi(r)$ for atomic types A and B respectively.

The atomic spacing of alloy is approximated by the value of Vegard's law. Let r_A and r_B represent the atomic spacings of pure metals A and B respectively, then the atomic spacing r_{AB} , in alloy, is

$$r_{AB} = xr_A + (1 - x)r_B \quad (9)$$

where x is the concentration of A in an alloy.

Using the analytic model, the enthalpies of formation ΔH for all alkali metal-alkali metal combinations have been calculated. The present calculations are concerned with room temperature. The results are shown in Fig. 1. One can conclude from the figure that: (1) the enthalpy of formation of these alloys is positive; (2) for

Table 1 Input physical parameters

Par.	Li	Na	K	Rb	Cs	Ref.
$a/\text{\AA}$	3.509	4.210	5.321	5.703	6.141	[23]
E_c/eV	1.630	1.113	0.934	0.852	0.804	[24]
E_f/eV	0.340	0.340	0.340	0.341	0.322	[25]
$\Omega B/\text{eV}$	1.633	1.538	1.891	1.512	1.305	[26]
$\Omega G/\text{eV}$	0.768	0.641	0.818	0.618	1.040	[26]
A	8.382	7.178	6.431	6.061	4.161	[26]

given A and variable B , ΔH increases as the atomic spacing increases; (3) $\Delta H(x)$ is often a non-symmetric function of x , ΔH is smaller at both sides when the solute has a smaller atomic volume than the solvent.

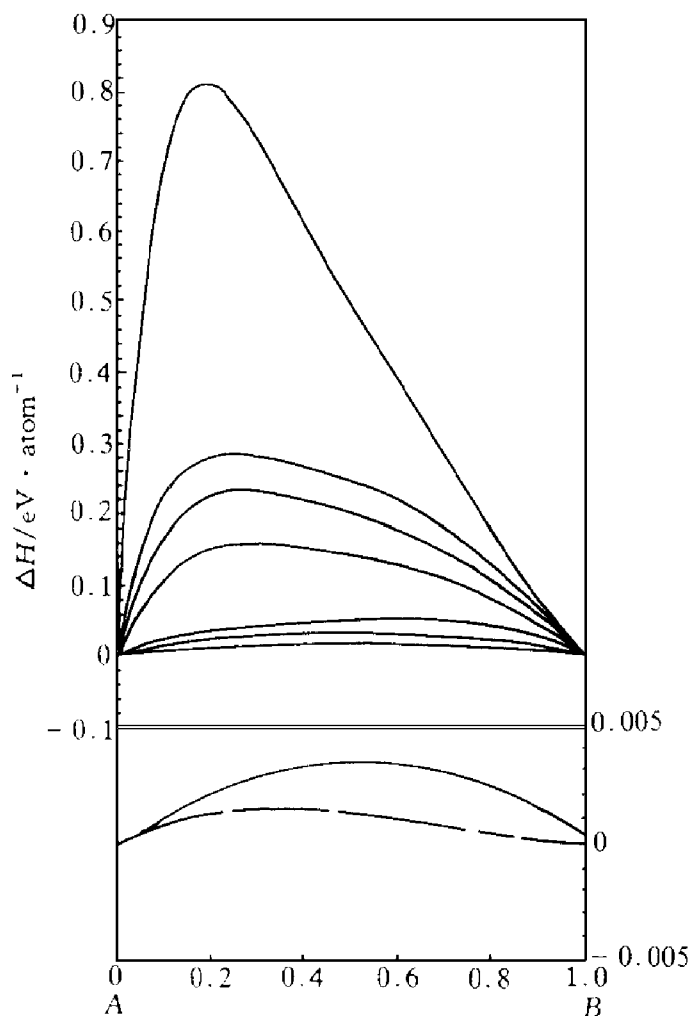


Fig. 1 Heat of formation ΔH as a function of composition in AB alloys
(The curves correspond (in order of increasing ΔH) to the alloys RbCs, KRb, KCs, LiNa, KNa, NaRb, NaCs, LiK, LiRb, LiCs.)

Yokokawa and Kleppa^[27] have measured the enthalpy of mixing of all alkali metal-alkali metal alloys at temperature of 111 °C except for Li-bearing alloys, because the lithium alloys are not stable at this temperature. The present calculations that the lithium alloys have a large positive ΔH are in agreement with the experimental facts. The other alloys are liquid at 111 °C. The measured enthalpies of mixing are positive in all cases, except for RbCs. The order, according to increasing magnitude of ΔH , is RbCs, KRb, KCs, NaK, NaCs and NaRb. This order agrees

with Fig. 1, except for an inversion of the pair NaCs-NaRb, and the present order is the same as that of Iniquez and Alonso^[4], but differs from that of Ouyang *et al.*^[11] calculated with Miedema theory. According to the effects of size factor on the enthalpy of formation of alloy discussed in the last paragraph of the section, the present results are more reasonable. The similar features of the asymmetry are in agreement with the liquid alloy results of Yokokawa *et al.*^[27] and with the solid alloy results given by Iniquez *et al.*^[4].

In Fig. 2, the enthalpies of formation for KRb disordered alloy system calculated by Hafner *et al.*^[5], Iniquez *et al.*^[4], Ouyang *et al.*^[11] and extrapolated from experimental data are compared with the present results. From Fig. 2, it can be seen that the present results are little larger than the results of Ouyang *et al.*^[11] but less than the results of Iniquez *et al.*^[4]. It is noticeable that the agreement of the present results and those of Hafner *et al.*^[5] and of the experimental data^[27] is pretty good. This indicates that the present calculations are more reasonable.

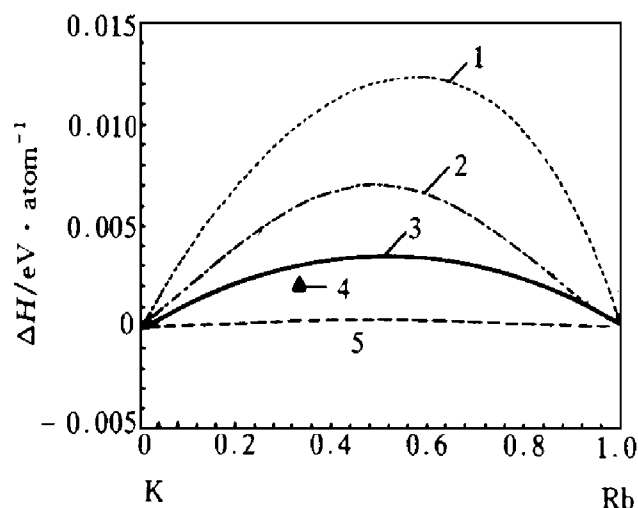


Fig. 2 Heat of formation of K-Rb system
1—Iniquez; 2—Hafner; 3—EAM;
4—Yokokawa; 5—Ouyang

Yokokawa and Kleppa^[27] have made an extrapolation to estimate ΔH for the solid alloys KRb, KCs and RbCs. Their results are compared in Table 3 with our results. It is noticeable that the extrapolated ΔH for solid RbCs is posi-

Table 3 Enthalpies of formation, ΔH (in 10^{-3} eV/atom),
of equiatomic disordered solid alloys

Alloy	This work	Ouyang ^[11]	Iniquez ^[4]	Hafner ^[28]	Tanigawa ^[6]	Yokokawa ^[27]
RbCs	1	0.4	20	5	2.7	0.5
KCs	14	1.4	5.3	29	4.3	1.9
K _{0.3} Rb _{0.7}		3	6.7			
KRb	4	0.4	7.7		3.5	
NaCs	138	37	280	6.3	4	
NaRb	49	29	160	215	123.8	
NaK	33	21	100	13	77.6	
LiCs	491	215	650	48	46.1	7
LiRb	243	190	470			
LiK	197	160	370	274		
LiNa	34	53	94	74		

tive. The present result is in excellent agreement with the experimental data.

In Table 3, the theoretical enthalpies of formation of equiatomic disordered alloy calculated by Iniquez and Alonso^[4], by Hafner and Sommer^[28] and by Ouyang *et al.*^[11] are given. In Hafner's calculation, Vegard's law was not assumed. Instead, the equilibrium volume of the alloy was calculated with the theory. The calculated deviation with respect to Vegard's law was in most cases smaller than 1%. The enthalpies of formation of Hafner *et al.*^[28] and of Iniquez *et al.*^[4] are larger than ours. Finally, we have given in Table 3 the results of Tanigawa and Doyama^[6]. The present results show an excellent agreement with those calculated by Tanigawa and Doyama^[6].

In general speaking, these alloys nearly follow Vegard's law. The relative deviations measured for the liquid alloys by Huijben *et al.*^[29, 30] are smaller than 1% except for NaCs system, and with negative sign. To analyse the effect of these deviations on ΔH , the enthalpy of formation for equiatomic composition NaCs alloy as a function of atomic spacing has been calculated. The results are shown in Fig. 3. It can be seen from Fig. 3 that atomic spacing of minimum energy deviates positively from Vegard's law, which is contrary to the conclusion of Iniquez and Alonso^[4]. The minimum process has little effect on the results of KRb, KCs and RbCs sys-

tems, but it affects the results of NaCs much more, this makes the enthalpy of formation decrease nearly to -22% at the equiatomic composition. The relative deviation is 0.2% with positive sign for K-Rb alloys, which agrees with the results of Hafner and Punz^[5] and with the results of experiments^[31]. This makes our results close to those of Tanigawa and Doyama^[6]. It is

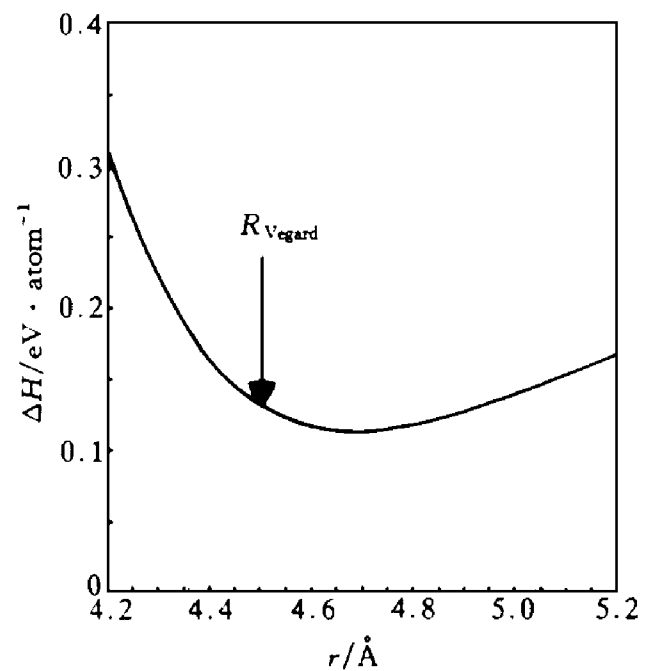


Fig. 3 Heat of formation of equiatomic composition of NaCs as a function of distance of nearest neighbour

(The arrow indicates the position of atomic spacing calculated from Vegard's law.)

also noted that the present EAM model can reproduce the bulk modulus exactly. Then the present results are more reasonable.

The empirical theory of Hume-Rothery^[32] is often used to explain the alloying properties of metals, which theory includes three main factors, namely, the atomic size, the electronegativity and the valence. Alkali metals are from the same group with equal valence and similar electronegativity. The factors affecting the alloying properties are mainly the atomic size. To analyse the influence of atomic size, the present calculated ΔH at equiatomic composition is plotted versus $|r_A - r_B|/r_A$, as shown in Fig. 4. The ΔH increases monotonically as $|r_A - r_B|/r_A$ increases, which indicates that the enthalpy of formation for alkali metal alloys is mainly controlled by the atomic size factor.

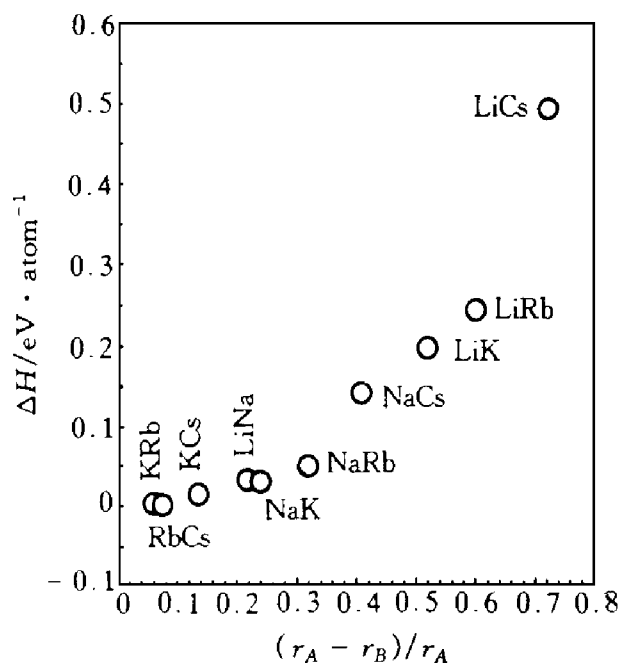


Fig. 4 Heat of formation for equiatomic alloy versus size factor $|r_A - r_B|/r_A$

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