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Static structure of liquid K – Sb alloys using the MAEAM potentials

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The structure of K-Sb liquid alloys at different compositions of Sb have been obtained using the modified analytic EAM (MAEAM) based effective pair potentials in conjunction with the Variational Hypernetted Chain (VMHNC) liquid state theory. The effective pair potentials are constructed from the MAEAM potential functions which are parameterized with fitting to both solid and liquid state properties of pure metals. The partial pair correlation functions and total static structure factor in liquid KSb alloys are computed and than compared with experiments and the results of MD studies. The overall agreement has been found in reported works.

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1. Introduction

In the last decade, alloys of alkali metals with elements from the post-transition-metal groups III to VI have been great interest because of the deviation from ideal behavior in their physicochemical properties [1, 2]. It has been noted that the structural, electronic and thermodynamic properties of these groups are at the borderline between metals, semiconductors and salts. The large difference in electro negativities between the constituents causes a charge transfer associated with the formation of alloys with ionic bonding. A single-valence electron of the alkali atoms is transferred to the more electronegative polyvalent element. These alloys belong to the category of liquid semiconductors although both components in the liquid state are metallic.

Concerning the mixing of potassium with antimony, measurements of thermodynamic properties [2], electrical conductivity [2], molar magnetic susceptibility [1] show evidence of a change in the chemical bonding with a sharp effect at the octet composition x_{Sb}=0.25 and a broader x_{Sb}=0.50. Bergman et al. have also studied on the structural and chemical bonding properties of liquid K-Sb alloys by neutron scattering and ab initio molecular dynamics [3, 4]. They have obtained the structural information in K-Sb alloys in a concentration range from pure potassium to x_{Sb}=0.50 from neutron scattering experiments and at compositions corresponding to the solid compounds (K_3 Sb and KSb) with the help of ab initio density functional molecular dynamics (MD) simulations. The local order and electronic properties in molten Zintl-alloys have been also investigated by ab initio local density functional calculations for the crystalline and liquid phases [5].

In the present work, structural properties of K-Sb alloys have investigated with a version of the embedded atom method (EAM), namely the modified analytic embedded atom method (MAEAM). The original EAM which was proposed by Daw and Baskes (DB) [6] has been widely used in a wide range of metallic systems in many aspects of computer simulations, such as point defects alloying, segregation, surface, grain boundary structure and so on [7]. Based on Daw and Baskes' EAM model, Johnson had presented analytic EAM (AEAM) nearest-neighbor models for b.c.c , f.c.c , and h.c.p. metals and alloys [7]. Zhang et al. [8] developed a modified analytic EAM (MAEAM) model based on Johnson's (AEAM) model. Recently Fang et al. [9] have been constructed interatomic potentials for binary immiscible alloy systems with MAEAM, and then calculated the formation enthalpies for those systems. They have demonstrated that the MAEAM may be a reasonable method for immiscible alloys by comparing with other potential models [10]. In our last study, we have proved the MAEAM model can be explain successfully the structural properties of liquid K-Te alloys [11]. It is motivated us to study for the liquid structure of K-Sb alloys.

According to our knowledge, up to now no MAEAM potential model has been applied to the alkali – antimony alloy systems. In the present work the recently proposed MAEAM based potential model [11] has been used to produce an effective pair potential which is capable of predicting the structural properties of liquid K and Sb metals. The parameters of the MAEAM potential functions are parameterized which give a good description of the liquid and still describe the solid accurately.

One of the purpose of the present paper is that to obtain the suitable effective interatomic pair potentials for binary liquid K-Sb alloys based on the MAEAM. For this purpose, Finnis-Sinclair (FS) [12] type effective pair potential form of alloys based on the MAEAM which was proposed by Dalgic and co-workers have been used here [11]. The $K_{0.50}Sb_{0.50}$ and $K_{0.75}Sb_{0.25}$ alloy compositions in order to obtain the static structure properties of liquid binary K-Sb alloys at three specific thermodynamic states have chosen. The choice of the compositions for the studied alloys is related to the phase diagram [13] and experimental results [3, 4].

The presently obtained effective potentials for $K_{0.50}Sb_{0.50}$ and $K_{0.75}Sb_{0.25}$ alloys are used as input data in the structural calculations. The partial static structure factors and pair distribution functions of these alloys have been performed with the variational modified hypernetted chain (VMHNC) liquid state theory [14] which was successfully applied to metallic systems in the EAM calculations [11,15-18]. It is for this reason that we choose the VMHNC theory for our liquid structure calculations using the MAEAM derived effective pair potentials. We have found that the FS type MAEAM of alloy effective potentials reproduce well the observed total structure data for the presented compositions of K-Sb alloys.

2. Theory

In the MAEAM model, the total internal energy of a system can be written as [8]:

$$E_{tot} = \sum F(\rho_i) + \frac{1}{2}\sum \phi(r_{ij}) + \sum M(P_i), \qquad (1)$$

where $F(\rho_i)$ is the embedding function, $\phi(r_{ij})$ is the pair potential between atoms i and j with r_{ij} distance, M(P) is the modification term and ρ_i is the electron density function induced at site i by all other atoms in the system given in the original form as

$$\rho_i = \sum f(r_{ij}) . \qquad (2)$$

The $M(P_i)$, $F(\rho)$ and atomic density function f(r) in Eqs. (1, 2) are taken the forms as those used by Fang et al. [9]. The pair potentials in Eq.(1) can be given for h.c.p metals [9], as

$$\begin{aligned}\phi(r) = k_0 + k_{-1}\left(\frac{r}{r_{1e}}\right)^{-1} + k_1\left(\frac{r}{r_{1e}}\right) + k_2\left(\frac{r}{r_{1e}}\right)^2 + \\ + k_3\left(\frac{r}{r_{1e}}\right)^3 + k_4\left(\frac{r}{r_{1e}}\right)^4 + k_5\left(\frac{r}{r_{1e}}\right)^5 + k_6\left(\frac{r}{r_{1e}}\right)^6\end{aligned} \qquad (3)$$

and for bcc metals as

$$\begin{aligned}\phi(r) = k_0 + k_{-1}\left(\frac{r}{r_{1e}}\right)^{-1} + k_1\left(\frac{r}{r_{1e}}\right) + \\ + k_2\left(\frac{r}{r_{1e}}\right)^2 + k_3\left(\frac{r}{r_{1e}}\right)^3 + k_4\left(\frac{r}{r_{1e}}\right)^4 .\end{aligned} \qquad (4)$$

In the above equations, the fitting parameters for h.c.p. are 10 and for b.c.c. metals are 8. In this work, we concentrate on the liquid state calculations. The potential functions have been parameterized with the method given in Ref. [11, 15, 18].

In order to obtain the effective pair interactions from the MAEAM, the recently proposed alloy effective potential form taken in Ref. [11] is used as:

$$\phi_{eff}^{AB}(r) = \phi_{AB}(r) - 2F'_{AB}(\rho) f_{AB}(r) M_{AB}(P_{AB}) \qquad (5)$$

where the alloy pair potential $\phi^{AB}(r)$ between different atomic species is taken as:

$$\phi^{AB}(r) = \frac{1}{2}\left[\frac{f^B(r)}{f^A(r)}\phi^{AA}(r) + \frac{f^A(r)}{f^B(r)}\phi^{BB}(r)\right] \qquad (6)$$

Here AA and BB indicate A and B, type atoms in a binary alloy respectively. $\phi^{AA}(r)$ and $\phi^{BB}(r)$ are the monatomic potentials given by Eqs. (3-4). In the above equations:

$$f_{AB}(r) = f_{eAB}\left(\frac{r_{1eAB}}{r}\right)^6 \qquad (7)$$

where $r_{1eAB} = (r_{1eAA} + r_{1eBB})/2$, $f_{eAB} = (f_{eAA} + f_{eBB})/2$, The modification term of alloys can be given as

$$M_{AB}(P_{AB}) = \alpha_{AB}\left\{1 - \exp\left[-\left(\ln\left|\frac{P_{AB}}{P_{eAB}}\right|\right)^2\right]\right\} \qquad (8)$$

where $\alpha_{AB} = (\alpha_{AA} + \alpha_{BB})/2$, $P_{eAB} = (P_{eAA} + P_{eBB})/2$, $P_{AB} = \sum_j f_{AB}^2(r_{ij})$.

3. Liquid state theory

With the effective pair potential known, integral equations are able to provide us the liquid structure for metals. In our structural calculations, one of the integral equation theory which has shown to be very reliable theory of liquids is VMHNC has been carried out [18-20]. The well known Ornstein-Zernike (OZ) equation, which for a homogeneous, isotropic, binary system reads (i, j =1, 2) can be written as

$$h_{ij}(r) = c_{ij}(r) + \sum_{l=1}^{2}\rho_l h_{il}(r) * c_{lj}(r) \qquad (9)$$

which defines the partial direct correlation functions, $c_{ij}(r)$, in terms of the total correlation functions $h_{ij}(r) = g_{ij}(r) - 1$, where $g_{ij}(r)$ denote the partial pair distribution functions and ρ_l denote the partial ionic number densities. Eq.(9) is supplemented by the exact closure relation of MHNC in terms of $\phi_{\mathrm{eff}}^{AB}(r)$ are the interatomic pair potentials and the $B_{ij}(r)$ PY bridge functions for binary system. In the present work, we have carried out the VMHNC integral equation theory which was extended by Gonzalez *et al*. [20] so as to minimize the configurational Helmholtz free energy functional $f^{\mathrm{VMHNC}}(\beta, \rho, x_1, \eta_\alpha)$ by the variational condition. The total structure factors for liquid alloys are determined as a linear combination of partial structure factors [11] with the neutron scattering amplitudes which are taken from [3].

4. Results and discussion

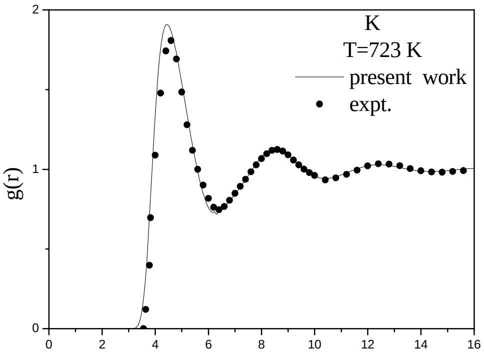
4.1 Pure metals

The MAEAM calculations have been performed for pure K at the thermodynamic states ρ =0.0114 atoms/A^3 (723 K); for liquid Sb ρ =0.0316 atoms/A^3 at 1073 K; which are chosen near melting temperatures. These values are taken from Waseda [21]. Input data for the liquid state calculations are calculated from solid state values of cohesive energy and lattice parameters for K and Sb [22]. The presently obtained liquid state values of cohesive energy are estimated 0.926 eV and 2.747 eV; and liquid lattice parameters are evaluated 5.598A and 3.801A for liquid K and Sb, respectively. We have determined the parameters of the potential functions by combining the two equations for the cut off procedure and the equation of the equilibrium condition, the equation for the cohesive energy; the equation for minimizing the configurational free energy (details are given in Ref. [11]). The model parameters for K and Sb obtained from the presented procedure in Ref. [11] are listed in Table 1.

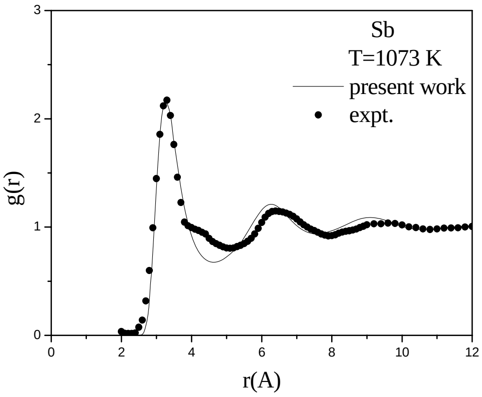
Table 1. The MAEAM potential parameters for K and Sb.

Sb		K	
Parameters	Values	Parameters	Values
n	0.820000	n	0.451600
$F_0(ev)$	1.831658	$F_0(ev)$	0.617492
α (ev)	0.354021	α (ev)	0.317464
$k_{-1}(ev)$	93.71472	$k_{-1}(ev)$	37.22396
$k_0(ev)$	-412.2099	$k_0(ev)$	-159.5869
$k_1(ev)$	767.8241	$k_1(ev)$	275.7329
$k_2(ev)$	-789.9663	$k_2(ev)$	-240.0685
$k_3(ev)$	486.4289	$k_3(ev)$	105.1018
$k_4(ev)$	-179.5267	$k_4(ev)$	-18.45449
$k_5(ev)$	36.78221	$r_c(a)$	6.455200
$k_6(ev)$	-3.226063		
$r_c(a)$	5.425000		

We have noted that the Helmholtz free energy is not fitted in our calculations. The constructed MAEAM effective pair potentials for K and Sb are used as input data in our VMHNC calculations. In Fig. 1 we compare the static structure factors for liquids K and Sb computed from the VMHNC theory using the MAEAM pair potentials, with Waseda's X-ray data [21].



a



b

Fig. 1. Pair distribution functions for liquids (a) K and (b) Sb along with the experimental data [21].

It is seen in Fig. 1 that the agreement between the calculated VMHNC results and experimental data is good for liquid K but for Sb, a major difference exist on the depth of the first minima of g(r).

4.1 The K-Sb alloys

As described in the preceding section, the effective potentials are input data in our structural calculations. We have obtained the static structure properties of liquid binary K-Sb alloys at three specific thermodynamic states namely, for $K_{0.50}Sb_{0.50}$, $\rho = 0.0250$ atoms/A^3 at 980 K and $\rho = 0.0206$ atoms/A^3 at 1100 K; for $K_{0.75}Sb_{0.25}$ $\rho = 0.0152$ at 1100 K. Firstly, we have calculated the MAEAM based effective potentials for these alloys. The FS type MAEAM effective potentials for $K_{0.5}Sb_{0.5}$ are shown in Fig. 2.

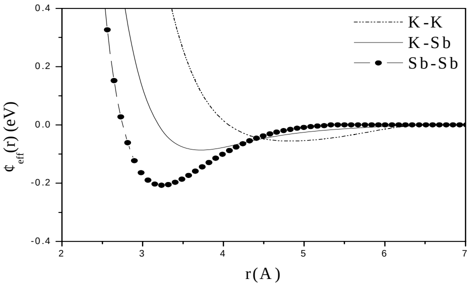


Fig. 2. Effective pair potentials for $K_{0.5}Sb_{0.5}$ liquid alloy

As seen Fig. 2, these partial pair potentials give the correct trends as far as the position of the concerned. As we go from K to Sb in periodic table, the calculated potentials become flatter and the width increases. The partial structure factors for $K_{0.50}Sb_{0.50}$ at 980 K and 1100 K and $K_{0.75}Sb_{0.25}$ at 1100 K liquid alloys have been calculated by using the MAEAM effective pair potentials with the VMHNC liquid state theory. In. Fig 3, we have presented the calculated VMHNC partial distribution functions for K-K, Sb-Sb and K-Sb in $K_{0.50}Sb_{0.50}$ alloy composition by comparing with MD results those obtained by Bergman et al. [3].

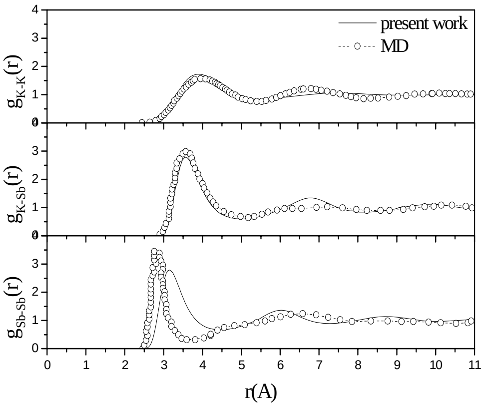
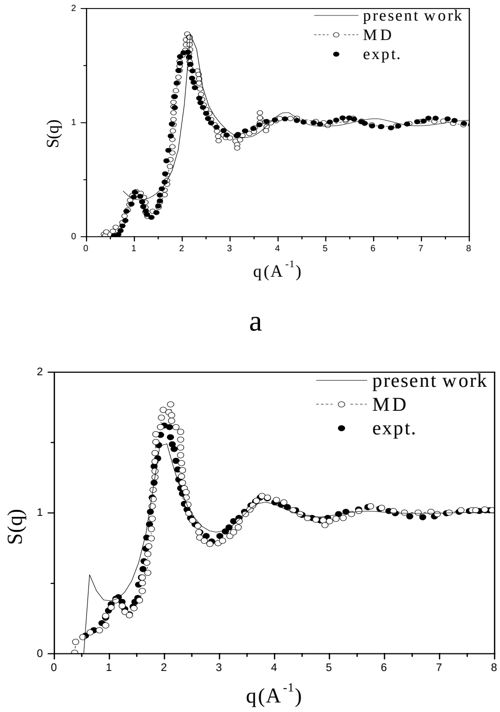


Fig. 3. Partial pair distribution functions for $K_{0.50}Sb_{0.50}$ at 980 K along with the MD data in Ref. [3]

It is seen in Fig. 3 that the present results are well predicted the position and height of the first peak of MD results for $g_{K-K}(r)$ and $g_{K-Sb}(r)$, except $g_{Sb-Sb}(r)$. However a reasonable agreement has been found for $g_{Sb-Sb}(r)$ after the second minima. We note that the main peak of g(r) are shifted towards greater r values as compared with MD results. It would also be noted that a particular feature seen in depth of the first minima of g(r) obtained by MD can not occur for VMHNC. The $g_{Sb-Sb}(r)$ exhibits sharp nearest neighbour peak and have oscillatory tail which is died out more rapidly than in the VMHNC data. Our results for $g_{Sb-Sb}(r)$ show that Sb has a liquid character in this alloy composition. Fig. 4 shows the total structure factors S(q) obtained by the VMHNC calculations for studied alloy compositions. We can compare our results of S(q) with those obtained by MD and experimental data given by Bergman et al. [4]. It appears in Fig.4a that height of the calculated total structure factor is overestimated experiment but agree well with MD results for $K_{0.50}$ $Sb_{0.50}$ composition. Also there are small differences in the phase of oscillations. Both data have damped oscillations than VMHNC ones in the studied alloys compositions.



a

b

Fig. 4. Total Static structure factors for : (a) $K_{0.50}Sb_{0.50}$ at 1100 K; (b) $K_{0.75}$ $Sb_{0.25}$ at 1100 K.

We can conclude from the partial $g_{ij}(r)$ of $K_{0.50}Sb_{0.50}$ alloy at 980K, the first peak in the $g_{K-Sb}(r)$ curve lies midway between the first peaks in the $g_{K-K}(r)$ and $g_{Sb-Sb}(r)$ curves. In Fig. 4b for $K_{0.75}$ $Sb_{0.25}$ composition of alloy, we note the good agreement for the position, amplitude and shape of the S(q), except the position of the pre-peak, with experimental data [4]. For $K_{0.75}$ $Sb_{0.25}$, we find a sharp peak at q=0.64A^{-1} while the experimental result is 1.06A and a main peak at q=2.05A^{-1} [23] compares well with the experimental result which is 2.1A. It is well known that the first sharp diffraction peak is indicative of chemical short-range order.

5. Conclusions

The presented MAEAM provides a realistic description of the pair interaction in liquid K-Sb alloys. We have used the recently improved the functional forms of the effective pair potentials for MAEAM to obtain a good description of the liquid and still describe the solid accurately. We note that our effective pair potentials show long-range character different from other MAEAM derived potentials for solids. The structural calculations were carried out using MAEAM derived effective pair potentials with the VMHNC theory of liquids. Comparison between the results of the VMHNC theory and available experimental data show that the proposed MAEAM formalism for, K-Sb alloy systems is capable of providing a good description in their liquid state. However we can find the chemical short range order in $K_{0.75}$ $Sb_{0.25}$ alloy composition but not in the results of $K_{0.50}Sb_{0.50}$. This discrepancy with experiment make further investigations necessary. The constructed MAEAM potentials can be used in further modelling of thermodynamic and other properties of K-Sb alloys with molecular dynamic and Monte Carlo simulations.

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