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COMPARISON OF SURFACE ENERGY OF BCC ALKALI METALS AND TRANSITION METALS USING MAEAM

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ABSTRACT

The surface energies of the low index (100), (110) and (111) planes of some bcc alkali metals (Li,Na,K,Rb,Cs) and for the bcc transition metals (Fe,W,Mo,Cr,Ta,Nb and V) have been calculated using the Modified Analytical Embedded Atom Method (MAEAM).The surface energy of each (hkl) plane in alkali metals was found to be much more lower than those of the transition metals. The experimental values of surface energies are not tied to specific surfaces and are obtained for polycrystalline materials. They do not correlate with computed values published for any of these surfaces. This is expected since experiments give direct results. For all bcc metals the order of the surface energy is such that $E^s_{(110)} < E^s_{(100)} < E^s_{(111)}$ *which is in agreement with the results obtained except for (111) surface. Our calculated result shows that* $E^s_{(111)} < E^s_{(110)} < E^s_{(100)}$. *This is not in agreement with the result of MAEAM.[1]*

Keywords: Alkali metals, Body centered cubic, Embedded atom method, Modified analytical embedded atom method, Surface energy, (hkl) plane.

Contribution/ Originality

The paper contributes the first logical analysis of the surface energy of transition metals and alkali metals at low index level.

1. INTRODUCTION

A detailed knowledge of the structure and energy of surfaces is important for understanding many surface phenomena such as adsorption, oxidation, corrosion, catalysis, crystal growth etc [2, 3] Surface energies for materials with Face-Centered Cubic (fcc), Body-Centered Cubic (bcc) and diamond structures have been calculated by the original Embedded Atom Method (EAM) developed by Daw and Baskes [3] and Modified Embedded Atom Method (MEAM) extended by Baskes [4]

In this paper, the surface energies of low index (100), (110), (111) bcc alkali metals (Li,Na,K,Rb,Cs) and transition metals (Fe,W,Mo,Cr,Ta,Nb) will be calculated and compared by

using the Modified Analytical Embedded Atom Method (MAEAM) developed by Zhang, et al. [5]. The Modified Analytical Embedded Atom Method (MAEAM) is an extension of the initial Embedded Atom Method (EAM) and the Analytical Embedded Atom Method (AEAM) [6, 7] by adding a modified term to describe the energy change due to the non-spherical distribution of electrons and deviation from the linear superposition of atomic electron density.

We decided to use MAEAM because So far, the MAEAM have shown a remarkable improvement over the AEAM since their results is closer to experimental result than the AEAM. This paper is outlined as follows. Section 1, illustrates the basic concept of the work under study. The mathematical theory is presented in section 2. The results obtained are shown in section 3. While in section 4, we present the analytical discussion of the results obtained. The conclusion of this work is shown in section 5. This is immediately followed a list of references

1.1. Methodology

In this work, the internal energy of the chosen metals were analytically obtained using the Modified Analytical Embedded Atom Method. Their values obtained were used together with cohesive energy and the area of a periodic cell to finally obtain the surface energy.

For efficiency, and to avoid the tedium in computation, all equations in this paper were coded into Microsoft Electronic Spread Sheet (Microsoft Excel).

2. THEORETICAL CONSIDERATION AND CALCULATIONS

Zhang, et al. [8] modified Johnson's Analytical EAM, in a similar way to Pasianot, et al. [9]. They added a modified analytical energy term M(P) to the total energy expression for the EAM to express the difference between the actual total of a system of atoms and that calculated from the original EAM using a linear superposition of spherical atom electron densities. While the analytical EAM energy modified term M(P) take into account the angularity term

$$P = \sum_{m} f^{2}(r_{m}) \frac{r_{mx}^{2} + r_{my}^{2} + r_{mz}^{2}}{r_{m}^{2}}, \quad (1)$$

The modified analytical EAM energy modified term does not include angularity term

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

where $f(r_{ij})$ is the separation distance of atom j from atom i. Again while the modified term M(P) in the analytical EAM of Wangyu, et al. [10] contain both exponential form and natural logarithm,

$$M(P_i) = \alpha \left[1 - \exp\left[-\left(In \frac{P}{P_e} \right)^{2} \right] \right] \quad (3)$$

the modified term in Zhang *et al* only have exponential form

$$M(P_i) = \alpha\left(\rho_i / \rho_e\right)^2 e^{\left[-\left(\frac{P}{P_e}-1\right)^2\right]} \quad (4)$$

The results obtained by the Modified Analytical Embedded Atom Method (MAEAM) have so far shown an improvement over the Analytical Modified Embedded Atom Method (AMEAM).

In the MAEAM the surface energy E^s of a system is calculated using equation (5) below

$$E^s = \sum_N \frac{(E_i + E_c)}{A_s} \quad (5)$$

where E_i is the total energy of the system, E_c is the cohesive energy and A_s is the area of a periodic cell containing one atom. In calculating the total energy of the system, the following input parameters were taken as constants. Zhang, et al. [11]

$$F_0 = E_C - E_{1f} \quad (6)$$

where E_{1f} is mono-vacancy formation energy.

$$n = \sqrt{\frac{\Omega(C_{11} + 2C_{12})(C_{11} - C_{12})}{(216E_{1f}C_{44})}} \quad (7)$$

$$\alpha = \frac{\Omega(C_{12} - C_{44})}{5126.4} - \frac{n^2 F_0}{8} \quad (8)$$

$$f_e = \left[\frac{E_C - E_{1f}}{\Omega}\right]^{3/5} \quad (9)$$

where C_{11}, C_{12} and C_{44} are elastic constants of the bcc metal considered and $\Omega = a^3/2$ is the atomic volume for bcc metals and a is the lattice constant.

$$k_0 = \frac{-E1f}{7} - \frac{\Omega(51519C_{44} + 57111C_{12} - 57111C_{11})}{75582360} \quad (10)$$

$$k_1 = \frac{\Omega(33327C_{44} + 52563C_{12} - 52563C_{11})}{431189920} \quad (11)$$

$$k_2 = \frac{\Omega(147456C_{11} - 147456C_{12} - 59049C_{44})}{302329440} \quad (12)$$

$$k_3 = \frac{1536\Omega(4C_{44} - C_{11} + C_{12})}{66134565} \quad (13)$$

According to the Modified Analytical Embedded Atom Method, the total energy of a system E_i is given as [5, 12]

$$E_i = \sum_i \left[F(\rho_i) + \frac{1}{2}\sum_{i \neq j}\varphi(r_{ij}) + M(P_i)\right] \quad (14)$$

where $F(\rho_i)$ is the energy to embed an atom in site i with electron density ρ_i . r_{ij} is the separation

distance between atoms i and j, $\varphi(r_{ij})$ is the interaction potential between atoms i and j and $M(P_i)$ is

the modified term. It describes the energy change due to the non-spherical distribution of electron P_i .

$$\rho_i = \sum_{i \neq j} f(r_{ij}) \tag{15}$$

$$P_i = \sum_{i \neq j} f^2(r_{ij}) \tag{16}$$

$$F(\rho_i) = -F_0 \left[1 - n \ln\left(\rho_i / \rho_e\right)\right]\left(\rho_i / \rho_e\right)^n \tag{17}$$

$$\varphi(r_{ij}) = k_0 + k_1\left(r_{ij} / r_{ie}\right)^2 + k_2\left(r_{ij} / r_{ie}\right)^4 + k_3\left(r_{ij} / r_{ie}\right)^{12} \tag{18}$$

where r_{ie} is the first nearest neighbour distance at equilibrium.

$$M(P_i) = \alpha\left(\rho_i / \rho_e\right)^2 e^{\left[-\left(\frac{P}{P_e}-1\right)^2\right]} \tag{19}$$

$$f(r_{ij}) = f_e\left(r_{ij} / r_{ie}\right)^6 \tag{20}$$

3. PRESENTATION OF RESULTS

Table-1. Input parameters for selected bcc metals [1]

Metals	a (nm)	Ω (nm³)	E_c (eV)	E_{1f} (eV)	C_{11} (eVnm⁻³)	C_{12} (eVnm⁻³)	C_{44} (eVnm⁻³)
Li	0.35093	0.021609	1.63	0.48	84	71	55
Na	0.42096	0.037299	1.113	0.34	46	39	26
K	0.5321	0.075327	0.934	0.34	28	23	16
Rb	0.5703	0.092743	0.852	0.341	18	15	10
Cs	0.6141	0.115794	0.804	0.322	15	9	13
Fe	0.28664	0.011776	4.28	1.79	1440	840	730
W	0.3165	0.015852	8.9	3.95	3230	1270	980
Mo	0.31468	0.01558	6.82	3.1	2870	1050	690
Cr	0.28846	0.012001	4.1	1.6	2160	410	620
Ta	0.33026	0.018011	8.1	2.95	1640	970	820
Nb	0.33007	0.01798	7.57	2.75	1530	820	180
V	0.30282	0.013884	5.31	2.1	1440	750	270

Ω = atomic volume, E_c = cohesive energy, E_{1f} = mono-vacancy formation energy, C_{11}, C_{12}, C_{44} are elastic constants, a = lattice constant.

Table-2. Calculated Constants for Surface Energy

Metals	F_o	n	α	F_e	K_o	k_1	k_2	k_3
Li	1.1500	0.1055	-0.0015	0.1720	-0.0692	0.0006	-0.0001	0.0001
Na	0.7730	0.1302	-0.0015	0.0977	-0.0490	0.0004	-0.0001	0.0001
K	0.5940	0.1540	-0.0016	0.0547	-0.0491	0.0005	-0.0001	0.0001
Rb	0.5110	0.1347	-0.0010	0.0441	-0.0491	0.0004	0.0000	0.0001
Cs	0.4820	0.1592	-0.0015	0.0373	-0.0465	0.0003	0.0000	0.0001
Fe	2.4900	0.2795	-0.0227	0.3937	-0.2562	-0.0020	0.0018	0.0006
W	4.9500	0.4630	-0.1257	0.4974	-0.5514	-0.0258	0.0121	0.0007
Mo	3.7200	0.5523	-0.1352	0.4234	-0.4288	-0.0262	0.0117	0.0003
Cr	2.5000	0.5405	-0.0877	0.3901	-0.2178	-0.0198	0.0088	0.0002
Ta	5.1500	0.2875	-0.0503	0.4718	-0.4224	-0.0033	0.0030	0.0011
Nb	4.8200	0.6152	-0.2233	0.4539	-0.3854	-0.0130	0.0056	0.0000
V	3.2100	0.4796	-0.0891	0.4153	-0.2953	-0.0088	0.0039	0.0001

Table-3. Computed Surface Energy for (100) Surfaces.

Metals	ρ_e	Pe	ρ_i	Pi	F(ρ)	Mpi	$\frac{1}{2}\sum_{i=j}\varphi(r_{i,j})$	Ei	Es
Li	1.376	0.237	0.979	0.139	-1.149	0.000	-0.273	-1.423	**269.7**
Na	0.782	0.076	0.556	0.054	-0.772	0.000	-0.193	-0.966	**133.1**
K	0.438	0.024	0.311	0.017	-0.593	0.000	-0.193	-0.787	**83.5**
Rb	0.353	0.016	0.251	0.011	-0.510	0.000	-0.194	-0.705	**72.6**
Cs	0.298	0.011	0.212	0.008	-0.481	0.000	-0.183	-0.664	**59.4**
Fe	3.149	1.240	2.239	0.881	-2.479	-0.002	-1.016	-3.497	**1526.2**
W	3.979	1.979	2.829	1.407	-4.894	-0.011	-2.249	-7.155	**2790.9**
Mo	3.387	1.434	2.408	1.020	-3.662	-0.012	-1.768	-5.442	**2230.0**
Cr	3.121	1.218	2.219	0.866	-2.462	-0.008	-0.912	-3.382	**1381.7**
Ta	3.774	1.781	2.683	1.266	-5.127	-0.005	-1.674	-6.805	**1902.1**
Nb	3.631	1.648	2.582	1.172	-4.728	-0.020	-1.571	-6.319	**1839.3**
V	3.323	1.380	2.362	0.981	-3.171	-0.008	-1.199	-4.378	**1628.1**

Table-4. Computed Surface Energy for (110) Surfaces.

Metals	ρe	Pe	ρi	Pi	F(ρ)	Mpi	Σφ(rij)	Ei	Es
Li	0.688176	0.118397	0.833339	0.128933	-1.14976	-1.2E-05	-0.20516	-1.35493	253.0751
Na	0.390798	0.038181	0.473232	0.041578	-0.77276	-1.2E-05	-0.14526	-0.91803	124.6613
K	0.218858	0.011975	0.265023	0.01304	-0.59374	-1.3E-05	-0.14516	-0.73891	78.07222
Rb	0.1765	0.007788	0.21373	0.008481	-0.51083	-8.1E-06	-0.14572	-0.65655	68.08885
Cs	0.149168	0.005563	0.180633	0.006058	-0.48177	-1.2E-05	-0.13734	-0.61912	55.54689
Fe	1.574677	0.619902	1.906835	0.675066	-2.48631	-0.00018	-0.76375	-3.25024	1420.087
W	1.989612	0.989639	2.409296	1.077706	-4.92937	-0.001	-1.689	-6.61937	2579.634
Mo	1.693711	0.717164	2.050978	0.780984	-3.69769	-0.00108	-1.32675	-5.02552	2053.292
Cr	1.560587	0.608858	1.889773	0.66304	-2.48567	-0.0007	-0.68463	-3.17099	1265.027
Ta	1.887216	0.890396	2.2853	0.969632	-5.14191	-0.0004	-1.25844	-6.40075	1765.206
Nb	1.81558	0.824082	2.198554	0.897417	-4.78384	-0.00178	-1.17855	-5.96418	1670.079
V	1.661303	0.689982	2.011734	0.751383	-3.19562	-0.00071	-0.89933	-4.09566	1500.452

Table-5. Computed Surface Energy for (111) Surfaces.

Metals	ρe	Pe	ρi	Pi	F(ρ)	Mpi	Σφ(rij)/2	Ei	Es
Li	1.204309	0.207194	0.90592	0.134201	-1.14949	-0.00021	-0.23915	-1.38885	181.1221
Na	0.683896	0.066816	0.514449	0.043277	-0.77248	-0.00021	-0.16931	-0.94201	89.25393
K	0.383001	0.020956	0.288106	0.013573	-0.59345	-0.00022	-0.16916	-0.76283	55.9216
Rb	0.308875	0.013629	0.232346	0.008828	-0.51063	-0.00014	-0.16985	-0.68063	48.73779
Cs	0.261044	0.009735	0.196366	0.006305	-0.48152	-0.00021	-0.15999	-0.64172	39.80333
Fe	2.755684	1.084828	2.072914	0.702648	-2.48252	-0.00319	-0.88982	-3.37553	1018.233
W	3.481821	1.731868	2.619138	1.12174	-4.91058	-0.01766	-1.96911	-6.89736	1849.197
Mo	2.963994	1.255037	2.229612	0.812894	-3.67856	-0.019	-1.54722	-5.24478	1471.397
Cr	2.731027	1.065501	2.054366	0.69013	-2.47327	-0.01232	-0.79834	-3.28393	907.1592
Ta	3.302628	1.558193	2.484343	1.009249	-5.13366	-0.00707	-1.46609	-6.60682	1266.274
Nb	3.177264	1.442144	2.39004	0.934084	-4.75415	-0.03138	-1.37497	-6.1605	1196.69
V	2.90728	1.207468	2.186949	0.782083	-3.18267	-0.01252	-1.04897	-4.24416	1075.1

Table-6. Comparison of Our Calculated Results with Results of Other Methods [1].

(hkl)		Li	Na	K	Rb	Cs	Fe	W	Mo	Cr	Ta	Nb	V
100	Our result	269.7	133.1	85.5	72.6	59.4	1526	2791	2230	1382	1902	1830	1628
	Yan-Ni and Zhang.	269.3	133	83.3	72.5	59.2	1537	2882	2332	1461	1963	1995	1705
	AEAM						1572	2858	2355	1677	2095	1930	1738
	F- S							2924	2100		2326	1956	1733
	FCD	522	264	142	112	93	2222	4635	3837	3979	3097	2858	3028
	T Binding	430	190	110	81	66	1720	2920	2230	1960	2140	1460	1500
110	Our result	253.1	124.7	78.1	68.1	55.5	1420	2580	2053	1265	1765	1670	1500
	Yan-Ni and Zhang.	252.9	124.7	78.1	68	55.5	1429	2638	2118	1315	1802	1767	1548
	AEAM						1430	2614	2125	1554	1852	1726	1554
	F- S							2575	1829		1980	1669	1473
	FCD	556	253	135	104	82	2430	4005	3454	3505	3084	2685	32.58
	T Binding	400	180	100	73	60	1540	2630	1990	1900	1880	1250	1310
111	Our result	181.1	89.3	55.9	48.7	39.8	1018	1849	1471	907	1266	1197	1075
	Yan-Ni and Zhang.	310.8	153.5	96.1	83.6	68.3	1772	3315	2679	1677	2259	2283	1959
	AEAM	590	287	152	118	92	2733	4452	3740	4123	3455	3045	3541
	F- S												
	FCD												
	T- Binding												
	Experimental Values	530	260	130	110	66	2480	3680	3000	2300	3150	2700	2550

4. DISCURSION

The results of our calculation of surface energies for the five alkali metals Li, Na, K, Rb, Cs and seven transition metals Fe, W, Mo, Cr, Ta, Nb and V are presented in this session. The calculations have been done in Microsoft Excel – an electronic spread sheet and are limited to low index surfaces. By default the calculations in Microsoft Excel are correct to the eighth decimal place and as much as possible accumulation of floating point errors has been avoided.

The input parameters for our calculation include lattice constant (a(nm) and a($\overset{o}{A}$)), cohesive energy (Ec(eV)), mono-vacancy formation energy (E_{1f}(ev)), and elastic constants C_{11}(eVnm^{-3}), C_{12}(eVnm^{-3}) and C_{44}(eVnm^{-3}) Their values for bcc metals considered in his work are presented in table 1. Model parameters that are required for the surface energy calculation are presented also in table 2. These parameters are calculated using equations 6 to 13 above. Compiled values in the

table are in good agreement with published results [1, 13] except for the values of α which differs by about 1%.

As detailed out earlier, the calculation for (100) surface is tabulated in table 3. For this case As = a^2. In the first plane, there are four nearest neighbour with $r = \frac{a\sqrt{3}}{2}$ [14] and four next nearest neighbours in the second plane with r = a.

The result for (110) surface is presented in table 4. For this case, $As = a^2\sqrt{2}$. Only one plane was considered with four nearest neighbours and two next nearest neighbours.

Similarly, the result for (111) surface is shown in table 5. Also, the comparison between this present result and results from other methods are presented in table 6.

5. CONCLUSION

The surface energies of the low index for both the bcc alkali metals Li, Na, K, Rb, Cs and the transition metals Fe, W, Mo, Cr, Ta, Nb and V have been calculated by using the Modified Analytical Embedded Atom Method (MAEAM). The result shows that the surface energy of each (hkl) plane in alkali metals is much lower than that in the transition metals, this is in agreement with the results of other methods [1] For all bcc metals, the order among the three low-index surface energies is such that $E^s_{(110)} < E^s_{(100)} < E^s_{(111)}$ is in agreement with our calculated result except for (111) surface. However, the results of other methods such as MAEAM, Analytical Embedded Atom Method (AEAM), Tight binding (T-B), Finnis Sinclair (F-S)[1] and experiment tends to follow the order $E^s_{(110)} < E^s_{(100)} < E^s_{(111)}$ [13].

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