

Development of a modified embedded atom method for bcc transition metals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 8917

(<http://iopscience.iop.org/0953-8984/15/50/021>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.125

The article was downloaded on 19/05/2010 at 17:54

Please note that [terms and conditions apply](#).

Development of a modified embedded atom method for bcc transition metals

Xiaoying Yuan¹, Kunio Takahashi¹, Yifang Ouyang² and Tadao Onzawa³

¹ Department of International Development Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

² Department of Physics, Guangxi University, Nanning 530004, People's Republic of China

³ Department of Mechanical and Control Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Received 3 July 2003

Published 3 December 2003

Online at stacks.iop.org/JPhysCM/15/8917

Abstract

A new scheme of the modified embedded atom method (MEAM) is developed by modifying the analytic form of the embedding function. The new MEAM parameters for Mo, W, V, Nb, Ta and Fe have been determined by relating them to not only bulk properties but also some non-bulk properties. The new scheme was applied to calculate the elastic stiffness of the crystal, the vacancy formation energy, the lattice stability, the surface energies for low-index crystal faces and the bond length and the binding energy for the dimer. The results give a fairly good agreement with the experimental data.

1. Introduction

The modified embedded atom method (MEAM) potential was proposed by Baskes *et al.*, as a method to calculate the energy of a multi-atom system. The MEAM is a semi-empirical quantum mechanical calculation, which is based on density-functional theory [1, 2].

The MEAM has been widely applied to bulk systems and shows a good ability to accurately describe the properties of many materials [3–8]. Recently, the MEAM has also been tried for some non-bulk systems, such as the (110)-(1 × 2) missing row surface reconstructed of several fcc materials [9], the (100)-(1 × 5) hexagonal surface reconstructions of Ir [10], and some properties of the Si(100) and (111) surfaces [11, 12]. The applicability of the MEAM to non-bulk systems has also been proved by the calculations of the bond length of the dimer for 23 materials [13] and the most stable structure for silicon clusters Si₂–Si₁₀ [14].

All the results above suggest that the MEAM is a useful tool to calculate non-bulk properties. However, it was found that the MEAM has an apparent error: it returns negative values of surface energy for Li(100), Li(110) and Li(111), if the relaxation of surface atom positions is taken into account. In order to correct this problem, we developed a new scheme to obtain the MEAM potential. In this scheme, a new parameter κ is introduced into the embedding function, and a formula is chosen to obtain the background electron density from the

partial electron densities, which will never return a negative or divergent value. Furthermore, in order to increase the applicability of the MEAM to non-bulk systems, the MEAM parameters are determined by not only bulk properties but also some non-bulk properties, such as the bond length of the dimer and the change of surface interlayer distance. In [15], we applied this scheme to determine the potential of lithium and calculated many properties of bulk and non-bulk systems for Li. The results were compared with the experimental data and they have fairly good agreement.

The purpose of this work is to apply this new scheme of the MEAM to bcc transition metals (Mo, W, V, Nb, Ta and Fe) and to prove that the new MEAM potential can be transferred to other bcc metals. The validity of the new potential is examined by calculating several properties of bcc transition metals such as the vacancy formation energy, the low-index surface energies, and the bond length and binding energy for the dimer. The results are compared with available values in the literature.

2. Theory

2.1. The model

In the MEAM theory [1–4, 10, 15], the total energy E of a system of a single type of atom can be written as the following:

$$E = \sum_i \left[F(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(R_{ij}) \right]. \quad (1)$$

Here, F is the embedding function, which depends on the background electron density $\bar{\rho}_i$ at site i , ϕ_{ij} is a pair interaction between atoms i and j and R_{ij} is the distance between atom i and atom j .

The embedding function F is the energy to embed an atom into the electron sea (background electron density) constituted by all other atoms of the system. Here, F is taken as

$$F(\bar{\rho}_i) = A E_0 (\bar{\rho}_i / Z_0) (\ln(\bar{\rho}_i / Z_0) - \kappa) \quad (2)$$

where A and κ are the parameters to be determined in the following section, E_0 is the sublimation energy (the negative of the cohesive energy E_{coh}) and Z_0 is the number of nearest neighbours in the bulk of the perfect crystal (for bcc materials $Z_0 = 8$).

The background electron density $\bar{\rho}_i$ is assumed to be a function of partial electron densities $\rho_i^{(l)}$ $l = 0-3$ [2], which is written as

$$\rho_i^{(0)} = \sum_{j(\neq i)} \rho_j^{a(0)}(R_{ij}) \quad (3a)$$

$$(\rho_i^{(1)})^2 = \sum_{\alpha} \left[\sum_{j(\neq i)} x_{ij}^{\alpha} \rho_j^{a(1)}(R_{ij}) \right]^2 \quad (3b)$$

$$(\rho_i^{(2)})^2 = \sum_{\alpha, \beta} \left[\sum_{j(\neq i)} x_{ij}^{\alpha} x_{ij}^{\beta} \rho_j^{a(2)}(R_{ij}) \right]^2 - \frac{1}{3} \left[\sum_{j(\neq i)} \rho_j^{a(2)}(R_{ij}) \right]^2 \quad (3c)$$

$$(\rho_i^{(3)})^2 = \sum_{\alpha, \beta, \gamma} \left[\sum_{j(\neq i)} x_{ij}^{\alpha} x_{ij}^{\beta} x_{ij}^{\gamma} \rho_j^{a(3)}(R_{ij}) \right]^2 \quad (3d)$$

where $x_{ij}^{\alpha} = R_{ij}^{\alpha} / R_{ij}$, and R_{ij}^{α} is the α component of the distance vector between atoms j and i . The $\rho_j^{a(l)}(R_{ij})$ $l = 0-3$ are the partial atomic electron densities which are contributed

by atom j at a distance R_{ij} from site i . The equations of partial atomic electron density have been assumed to be given by a simple exponential form [2]

$$\rho_j^{a(l)}(R_{ij}) = \exp(-\beta^{(l)}(R_{ij}/R_0 - 1)) \quad (4)$$

where R_0 denotes the equilibrium nearest-neighbour distance in the bulk of the perfect crystal, and the exponential decay factors for the atomic densities, $\beta^{(l)}$, are parameters to be determined.

In general, the background electron density can be obtained from the partial electron densities as

$$\bar{\rho}_i = \rho_i^{(0)} G(\Gamma) \quad (5)$$

with

$$G(\Gamma) = \frac{2}{1 + \exp(-\Gamma)} \quad (6)$$

and

$$\Gamma = \sum_{l=1}^3 w^{(l)} (\rho_i^{(l)} / \rho_i^{(0)})^2 \quad (7)$$

where $w^{(l)}$ are the weighting factors for the atomic densities.

In order to determine the pair interaction ϕ_{ij} , we consider the reference structure as a homogeneous monatomic solid with interactions limited to the first neighbours only [2]. In the reference structure, ϕ_{ij} can be quite easily obtained by using equation (1)

$$\phi_{ij} = \frac{2}{Z_0} [E^u(R_{ij}) - F(\bar{\rho}_i^0)] \quad (8)$$

where $\bar{\rho}_i^0$ is the background electron density for the reference structure and E^u is the energy per atom for the reference structure as a function of the nearest-neighbour distance R_{ij} ; it is given by a universal energy function proposed by Rose *et al* [16],

$$E^u(R_{ij}) = -E^0(1 + a^*)e^{-a^*} \quad (9)$$

with

$$a^* = \alpha(R_{ij}/R_0 - 1). \quad (10)$$

Here α is an exponential decay factor, which is related to the bulk modulus.

Using this pair interaction, ϕ_{ij} and equation (1), the energy per atom, E_i , for any configuration of atoms is given by

$$E_i = \frac{1}{Z_0} \sum_{j(\neq i)} E^u(R_{ij}) + \left[F(\bar{\rho}_i) - \frac{1}{Z_0} \sum_{j(\neq i)} F(\bar{\rho}_i^0) \right]. \quad (11)$$

The key difference of this scheme from the original MEAM is that we introduce a new parameter κ into the embedding function, and it is used as a constant value of zero in the original MEAM. In figure 1 we show the effect of parameter κ on the energy per atom in both an atom in the bulk and at the surface for iron. This effect will disappear in most applications of bulk properties because of symmetry (figure 1(a)), but κ strongly affects the shape of the curve of E_i in non-bulk systems as shown in figure 1(b). This means κ has an influence on the properties of non-bulk systems. So we suppose that we can improve the applicability of the MEAM to non-bulk systems by determining a proper value of κ .

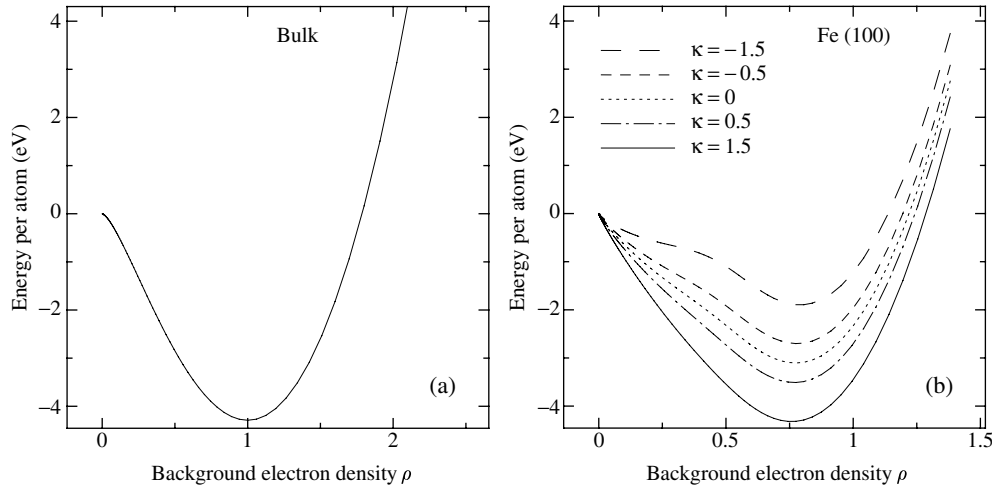


Figure 1. Effect of parameter κ on energy per atom. (a) Atom in bulk; (b) atom at surface.

Table 1. Values of physical quantity and their error estimate ε (%) used to determine the MEAM parameters. The values listed are the bulk modulus B (GPa) [17], two kinds of shear elastic constant, γ and γ' (GPa) [17], the bond length and the binding energy for the dimer, r_{de} (au) and E_{de} (eV/atom), structure energy differences and relative changes in nearest-neighbour distances for both fcc to bcc and simple cubic to bcc, ΔE_{f-b} , ΔE_{s-b} (eV) and Δr_{f-b} , Δr_{s-b} (%) [2, 3, 20], and the relaxation of the interlayer spacing, Δd_{12} and Δd_{23} (%) for the (100) and (110) surfaces [3, 21, 22].

	B	γ	γ'	r_{de}	E_{de}	ΔE_{f-b}	Δr_{f-b}	ΔE_{s-b}	Δr_{s-b}	(100)		(110)	
										Δd_{12}	Δd_{23}	Δd_{12}	Δd_{23}
Mo	265	111	145.5	1.939	4.20	0.28	6	0.12	-4	-3.3	0.3	-3.3	0.6
W	307.7	157	157	2.196	2.82	0.33	5	0.20	-3	-3.2	-0.3	-3.1	0.0
V	156.7	43.2	55	1.754	2.41	0.15	8	0.06	-5	-6.7	1.0	-4.2	0.9
Nb	169.7	28.4	56.5	2.130	3.50	0.14	8	0.05	-5	-12.5	3.0	-7.3	2.2
Ta	191.3	82.6	53	2.158	2.65	0.26	7	0.15	-4	-5.9	0.8	-3.5	0.6
Fe	166.7	117	47.5	2.153	1.63	0.03	5	0.21	-3	-1.5	0.0	-1.5	0.1
ε	± 5	± 5	± 5	± 10	± 10	± 10	± 10	± 30	± 30	± 20	± 20	± 20	± 20

3. Determination of the parameters

The method for determining MEAM parameters has been fully discussed in [15] and we will only give a brief review here.

In this scheme, there are 13 parameters for each pure element. Without losing generality, $w^{(0)}$ can be equal to unity, and E_0 and R_0 can be obtained from experiments directly. Other parameters can be determined by relating them to physical quantities of bulk as well as non-bulk systems, which include the bulk modulus B , two kinds of shear elastic constant, γ and γ' , the bond length and the binding energy for the dimer, r_{de} and E_{de} , structure energy differences and relative changes in nearest-neighbour distances for both fcc to bcc, ΔE_{f-b} and Δr_{f-b} , and simple cubic (sc) to bcc, ΔE_{s-b} and Δr_{s-b} , and the relaxation of the interlayer spacing between i th and j th layers, Δd_{ij} . The overall values of physical quantity used to determine the MEAM parameters are obtained from the literature except r_{de} and E_{de} . These values are listed in table 1.

Table 2. MEAM parameters for Mo, W, V, Nb, Ta and Fe. The values listed are the sublimation energy E_0 (eV), the equilibrium nearest-neighbour distance R_0 (Å), the exponential decay factor for the universal energy function α , the scaling factor for the embedding energy A , the adjustment parameter for the embedding function κ , the exponential decay factors for the atomic densities $\beta^{(l)}$ and the weighting factors for the atomic densities $w^{(l)}$.

	E_0	R_0	α	A	κ	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$\beta^{(3)}$	$w^{(0)}$	$w^{(1)}$	$w^{(2)}$	$w^{(3)}$
Mo	6.81	2.73	5.8483	1.0000	-0.8913	4.4565	1.1414	1.0000	6.2567	1.0	2.1355	4.9456	-0.3851
W	8.66	2.74	5.6189	0.9800	-2.5754	3.9697	1.1711	1.0000	7.2824	1.0	0.4162	2.2983	-0.0088
V	5.30	2.63	4.8198	1.0000	-0.4629	4.1001	2.8546	1.0000	1.0435	1.0	0.1340	2.7904	3.2616
Nb	7.47	2.86	4.7910	1.0000	-1.4712	4.3712	1.3976	1.0170	5.1653	1.0	0.9194	1.5426	0.2287
Ta	8.09	2.86	4.8891	1.0000	-4.4247	3.9271	1.7002	2.2548	1.6840	1.0	0.3068	0.6159	0.2682
Fe	4.29	2.48	5.0596	0.8931	-0.8354	3.0787	1.0058	2.0267	4.5451	1.0	3.0697	2.2889	-0.6446

The dissociation energies and the atomic distances at equilibrium of the dimer have been calculated by density functional theory (DFT). The double zeta valence base set, LANL2DZ, proposed by Hay and Wadt [18, 19] was used in the calculations. This base set was obtained by using the approximation of the effective core potential (ECP) and fitting to the results of calculation with full electrons by energy optimization. It has been successfully applied to calculate compounds including heavy elements. The exchange and correlation interactions used the functions proposed by Bechel3LYP [29–31]. The computations were performed using the Gaussian98W program package [32].

By using the quantities above, ten nonlinear functions can be obtained. The MEAM parameters can be obtained by using a numerical procedure to solve the simultaneous equations. Because the correct value of each property has considerable uncertainty, we have estimated the error of each physical quantity based on their correctness. Those estimated errors are also listed in table 1. In table 2 we propose the MEAM parameters for the bcc transition metals of Mo, W, V, Nb, Ta and Fe.

4. Application

In order to test this model, we calculated the pure metal properties of a wide range of bulks, surfaces and clusters by using the new MEAM potential. When the MEAM is applied to the problems of vacancy and surface, the initial nearest-neighbour distance is set to be the equilibrium nearest-neighbour distance in the bulk, and the stable positions for atoms are determined by the procedure of relaxation described follows:

First, we move one atom in the X direction to a locally stable position, then Y and Z directions. Next, another atom is moved to its locally stable position. Following the same procedure, all the atoms will be moved one by one to their locally stable positions. After the last atom, we go back to the first one and do it again. The whole procedure shall be repeated until the stable positions of all atoms are fixed, namely, they do not move any more under this operation.

Moreover, an assumption is used in this scheme that the interaction is restricted to the nearest neighbour only, so either a cut-off function or screening procedure is necessary. We choose the screening function, which is defined by Baskes [2].

For these bcc transition metals, the three elastic stiffnesses of the crystal, C_{11} , C_{12} and C_{44} , have been calculated, and the results are in fairly good agreement with experimental values as shown in table 3.

Figure 2 shows the lattice stability of bcc, fcc, hcp, dia and sc structures for different atomic distances. From figure 2 we can see the bcc structure is stable at the equilibrium atomic

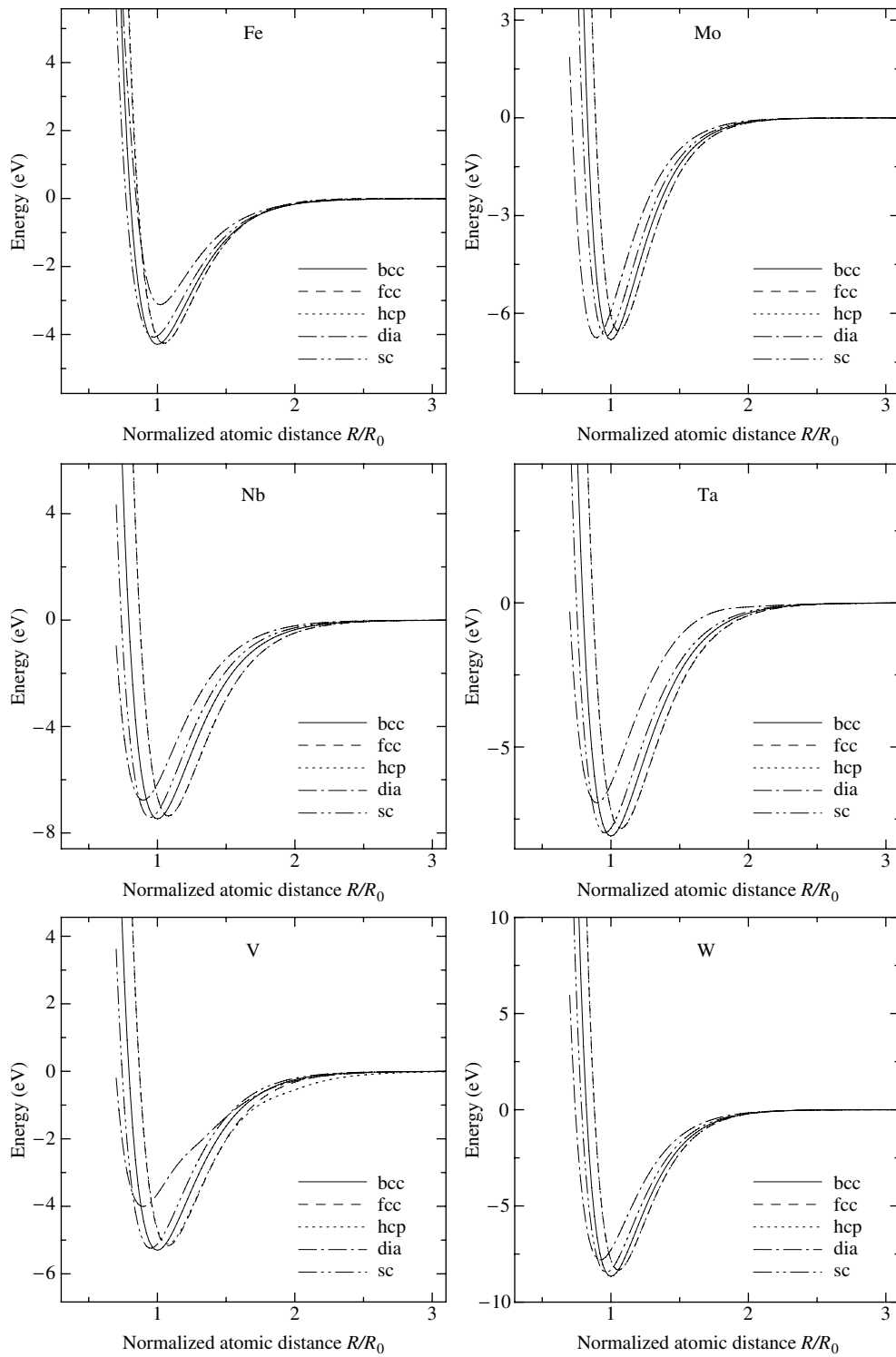


Figure 2. Lattice stability of bcc, fcc, hcp, diamond and sc structures for the bcc transition metals.

Table 3. Calculated values of the elastic stiffness C_{11} , C_{12} and C_{44} (GPa) compared to the experimental values [17].

	C_{11}		C_{12}		C_{44}	
	This work	Expt	This work	Expt	This work	Expt
Mo	458.04	459	168.48	168	111.00	111
W	516.71	517	203.15	203	157.00	157
V	230.00	230	120.00	120	43.25	43.2
Nb	244.73	245	132.14	132	28.40	28.4
Ta	262.57	262	155.72	156	77.16	82.6
Fe	231.74	230	134.14	135	117.15	117

Table 4. Calculated vacancy formation energy, in electronvolts. Experimental values are from [23] and [24], and other calculations are from [25] except for Fe, which is from [26].

	Present	Expt	Other calculations
Mo	3.59	3.2	2.2, 2.54, 3.67, 3.13
W	4.28	3.95	3.8, 3.62, 4.57, 3.27
V	3.06	2.1	2.5, 1.83, 1.5, 3.06
Nb	2.61	2.75	3.2, 2.48, 1.78, 2.92
Ta	3.21	3.1	3.3, 2.87, 2.73, 3.49
Fe	2.12	1.8	2.31, 2.78, 2.44, 2.54, 2.34

distance, R_0 , and it is the most stable structure for all metals. The fcc lattice is stable at about $1.04R_0$ – $1.08R_0$ and the range of energy difference between fcc and bcc is from 0.03 to 0.33 eV. The values of ΔE_{f-b} agree quite well with the results of the CALPHAD method [3, 20] that is listed in table 1. The hcp phase is calculated by assuming the ideal c/a ratio is 1.633. The calphad method shows that the hcp structure is more stable than the fcc structure and the differences of energy are about 0.05–0.06 eV [20] or 0.023–0.047 eV [37] for bcc transition metals. However, the energy differences of this work are lower than 0.01 eV for Mo, W and Fe; moreover, the energy of the hcp structure is a few hundredths of an electronvolt higher than the fcc structure for V, Nb and Ta. The experimental values for the simple cubic and diamond structures are not available. The density functional calculation predicts that the energies of simple cubic and diamond structures of metals are on the order of electronvolts above the bcc structure [38]. This work predicts the same order of diamond structure except for Mo, that is 0.062 eV higher than the bcc structure. For the difference of energy between bcc and sc structures, this work predicts that it is as small as 0.05–0.3 eV.

The vacancy formation energies of bcc transition metals have been calculated and compared with experiments and other calculations. From table 4 we can see that the results from this work agree with experimental values well except for V. The value for V is larger than experiment by about 50%, and larger than most other calculations. This overestimate of V can be considered to be due to the uncertainty of some properties which be used to determine the parameters of the MEAM.

We have calculated the surface energies for low-index crystal faces and compared with the experimental values and other calculations (table 5). The experimental surface energy data in table 5 are for polycrystalline solids and these are obtained from high-temperature experimental data extrapolated to 0 K [27, 28]. Even though the surface energy of a polycrystalline solid has been described very well by using the local density approximation and jellium-like free-electron models [39, 40], the surface energies of a particular surface facet are not known well.

Table 5. Calculated surface energies for low-index crystal faces, in erg cm^{-2} . The experimental values are for polycrystalline solids and are those extrapolated from high-temperature experimental data to 0 K.

Element	Property	Present	2NN MEAM [3]	MEAM92 ^a	DFT [41]	<i>Ab initio</i> [42]	Expt [27, 28]
Mo	E_{100}	2892	3130	1712	3837		2900
	E_{110}	2745	2885	1818	3454	3180	
	E_{111}	2417	3373	1588	3740		
W	E_{100}	2947	3900	2217	4635		2990
	E_{110}	2620	3427	2123	4005	3840	
	E_{111}	2675	4341	1996	4452		
V	E_{100}	2810	2778	2188	3028		2600
	E_{110}	1975	2636	1717	3258	2550	
	E_{111}	2357	2931	1628	3541		
Nb	E_{100}	2709	2715	2055	2858		2300
	E_{110}	1928	2490	1721	2685	1640	
	E_{111}	2116	2923	1589	3045		
Ta	E_{100}	3329	3035	2827	3097		2780
	E_{110}	2182	2778	2104	3084	1790	
	E_{111}	2594	3247	2102	3455		
Fe	E_{100}	2895	2510	2170	2222		2360
	E_{110}	2131	2356	1609	2430	2660	
	E_{111}	2227	2668	1702	2733		

^a Calculated by using the MEAM potential proposed by Baskes in [2].

Most first-principles methods have been used only for particular cases, focusing on a few elements or on a special application for a given metal surface. Recently Vitos *et al* [41] have used the density functional theory to establish a database of surface energies for low-index surfaces of 60 metals, and Skriver and Rosengaard [42] performed an *ab initio* study of the surface energy for close-packed surfaces of 40 elemental metals. As shown in table 5, however, the value of the *ab initio* study is very small for Nb and Ta, and somewhat large for W and Fe, and the results of the DFT overestimate the surface energy except for Fe. For the MEAM results, the surface energies are comparatively underestimated using the MEAM92 potential [2] for all bcc transition metals, and both this work and the 2NN MEAM model [3] may describe the surface energy much better than other calculations.

Finally, the relation between atomic distance and energy per atom for dimers of bcc transition metals was also calculated (figure 3). For the bond length of bcc transition metals, the *ab initio* calculation results are 1.938 and 1.937 Å for Mo [33, 34], 1.703 and 1.774 Å for V [35, 36], 2.19, 2.01, 2.11 and 2.10 Å for Nb [34] and 2.01 Å for Fe [36]. In this work the dimer bond lengths are respectively shorter than the bulk nearest-neighbour distance values by 21.55% for Mo, 19.85% for W, 33.30% for V, 25.53% for Nb, 24.54% for Ta and 13.18% for Fe. The results give a good agreement with other calculations. Moreover the energy per atom is close to zero when the distance of the atoms increases to 5–6 Å. We can see that the proposed scheme and parameters are able to describe the dimer property very well. Because the electronic state of the dimer is most different from the bulk state, this strongly suggests that the new MEAM is a useful tool for non-bulk systems.

5. Conclusions

In order to increase the applicability of the MEAM to non-bulk systems, a new scheme of the MEAM has been developed. The potential parameters are determined by relating them

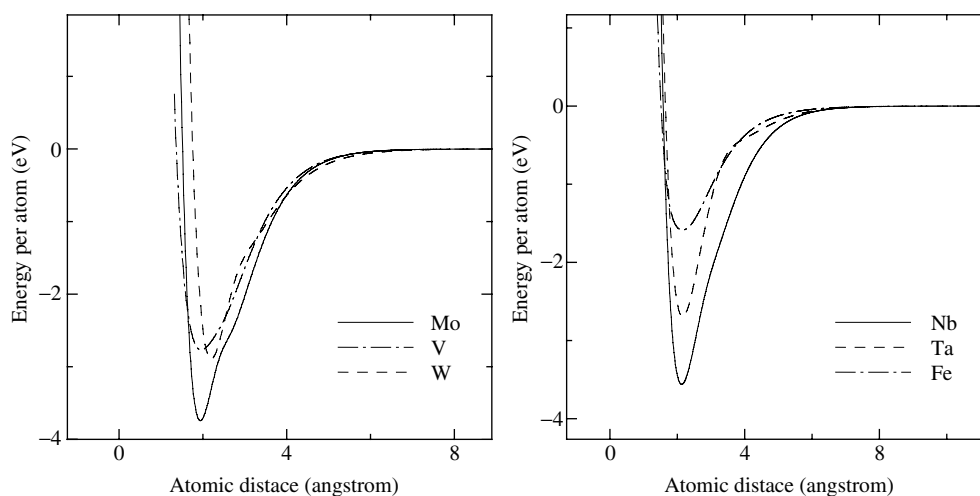


Figure 3. Relation between atomic distance and energy per atom for dimers of bcc transition metals.

with bulk, surface and dimer properties. We investigate many bulk and non-bulk properties of several bcc transition metals, Mo, W, V, Nb, Ta and Fe, with the new MEAM potential, and the results show that the new scheme and parameters work well for bcc transition materials.

References

- [1] Baskes M I, Nelson S J and Wright A F 1989 *Phys. Rev. B* **40** 6085
- [2] Baskes M I 1992 *Phys. Rev. B* **46** 2727
- [3] Lee B J, Baskes M I, Kim H and Cho Y K 2001 *Phys. Rev. B* **64** 184102
- [4] Baskes M I 1997 *Mater. Chem. Phys.* **50** 152
- [5] Pasianot R, Farkas D and Savino E J 1991 *Phys. Rev. B* **43** 6952
- [6] Baskes M I 1999 *Mater. Sci. Eng. A* **261** 165
- [7] Baskes M I and Johnson R A 1994 *Modell. Simul. Mater. Sci. Eng.* **2** 147
- [8] Chen D, Yan M and Liu Y F 1999 *Scr. Mater.* **40** 913
- [9] Yamagishi T, Takahashi K and Onzawa T 2000 *Surf. Sci.* **445** 18
- [10] van Beurden P and Kramer G J 2001 *Phys. Rev. B* **63** 165106
- [11] Takahashi K, Nara C, Yamagishi T and Onzawa T 1999 *Appl. Surf. Sci.* **151** 299
- [12] Baskes M I 1997 *Modell. Simul. Mater. Sci. Eng.* **5** 149
- [13] Yuan X, Takahashi K and Onzawa T 2002 *Q. J. Japan Weld. Soc.* **20** 63 (in Japanese)
- [14] Yuan X, Takahashi K, Yagi S, Yin Y and Onzawa T 2001 *Proc. 7th Int. Symp. Japan Welding Society (Kobe, Japan)* p 1259
- [15] Yuan X, Takahashi K, Yin Y and Onzawa T 2003 *Modell. Simul. Mater. Sci. Eng.* **11** 447
- [16] Rose J H, Smith J R, Gurnea F and Ferrante J 1984 *Phys. Rev. B* **29** 2963
- [17] Brandes E A 1983 *Smithells Metals Reference Book* (London: Butterworths)
- [18] Wadt W R and Hay P J 1985 *J. Chem. Phys.* **82** 284
- [19] Hay P J and Wadt W R 1985 *J. Chem. Phys.* **82** 270
- [20] Saunders N, Miodownik A P and Dinsdale A T 1988 *CALPHAD* **12** 351
- [21] Imbühl R, Behm R J and Ertl G 1982 *Surf. Sci.* **123** 129
- [22] Arnold M, Hupfauer G, Bayer P, Hammer L, Heinz K, Kohler B and Scheffler M 1997 *Surf. Sci.* **382** 288
- [23] Zhang B, Ouyang Y, Liao S and Jin Z 1999 *Physica B* **262** 218
- [24] Hu W, Shu X and Zhang B 2002 *Comput. Mater. Sci.* **23** 175
- [25] Kraftmakher Y 1998 *Phys. Rep.* **299** 79
- [26] Hoshino T and Mizuno T 2001 *Mater. Trans.* **11** 2206
- [27] Tyson W R and Miller W A 1977 *Surf. Sci.* **62** 267

-
- [28] Mezey L Z and Giber J 1982 *Japan. J. Appl. Phys.* **1** 21 1569
- [29] Beche A D 1988 *Phys. Rev. A* **38** 3098
- [30] Stevens P J *et al* 1994 *J. Phys. Chem.* **98** 11623
- [31] Pavlov M, Siegbahn P E M and Sandstrom M 1998 *J. Phys. Chem.* **102** 2189
- [32] Frisch M J *et al* 1998 (Pittsburgh, PA: Gaussian)
- [33] Baykara N A, McMaster B N and Salahub D R 1984 *Mol. Phys.* **52** 891
- [34] Morse M D 1986 *Chem. Rev.* **86** 1049
- [35] Langridge-Smith P R R, Morse M D, Hansen G P and Smalley R E 1984 *J. Chem. Phys.* **80** 593
- [36] Feibelman P J 1996 *Phys. Rev. B* **53** 13740
- [37] Dinsdale A T 1991 *CALPHAD* **15** 317
- [38] Paxton A T, Methgessel M and Polatoglou H M 1990 *Phys. Rev. B* **41** 8127
- [39] Wojciechowski K F 1999 *Surf. Sci.* **437** 285
- [40] Takahashi K and Onzawa T 1993 *Phys. Rev.* **48** 5689
- [41] Vitos L, Ruban A V, Skriver H L and Kollar J 1998 *Surf. Sci.* **411** 186
- [42] Skriver H L and Rosengaard N M 1992 *Phys. Rev. B* **46** 7157