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Abstract
Jiang *et al* (2004 *J. Phys.: Condens. Matter* **16** 521) present a model based on the traditional
broken-bond model for predicting surface energies of elemental crystals. It is found that bias
errors can be produced in calculating the coordination numbers of surface atoms, especially in
the prediction of high-Miller-index surface energies.

Jiang *et al* (JLZ) [1] present a method for estimating surface energies for elemental crystals based on the traditional broken-bond model. An interpolation approach, using the arithmetic mean of the two formulae created by Haiss [2] and Desjonquères [3], is adopted to predict γ values of elements with different facets. The calculated values are generally more accurate than those directly deduced from [2] and [3], though without providing new insight into the fundamentals of surface energy. After adding the contributions of next nearest neighbour bonds to the cohesive energy, JLZ rewrite the surface energy formula as follows [1]:

$$\gamma = \left\{ \left[2 - Z_S/Z_B - (Z_S/Z_B)^{1/2} \right] \right.$$
$$\left. + \beta \left[2 - Z_S'/Z_B' - \left(Z_S'/Z_B' \right)^{1/2} \right] \right\} E/(2 + 2\beta) \quad (1)$$

where Z_S and Z_S', Z_B and Z_B' are the coordination numbers of the nearest and next nearest neighbours of surface and bulk atoms, respectively. E represents the experimental cohesive energy. β shows the total bond strength ratio between the next nearest neighbour and the nearest neighbour. Calculations for elemental crystals including A1 (fcc), A2 (bcc), A3 (hcp), A4 (diamond like) and simple cubic (sc) structures show that the root mean square error is no more than 10% at the first-order approximation except for some A1 close-packed (111) surfaces and A3 crystals.

Unfortunately, the coordination numbers of the surface atoms dealt with by JLZ in [1] are open to question. Equations cited from [4] and [5] are undoubtedly appropriate for calculating the total broken-bond value for surface atoms

(not top layer atoms). However, directly applying the equation $Z_S = Z_B - Z_{(hkl)}$ to calculate coordination numbers of surface atoms (Z_S) is not rigorous; i.e., for A2 (111) surfaces, the top layer atoms on the A2 (111) surface have 4 and 3 for Z_S and Z_S'. Moreover, the second-layer and third-layer atoms have 7, 3 and 7, 6 for Z_S and Z_S', respectively. As a result, the total broken-bond values of the nearest and next nearest neighbour bonds are 6 and 6, which are consistent with the results deduced from [4]. Nevertheless, the approach in which coordination numbers of surface atoms are assumed as 2 ($8-6=2$) and 0 ($6-6=0$) according to $Z_S = Z_B - Z_{(hkl)}$ in [1] is inappropriate. The treatment has no effect on the results if only top layer atoms in corresponding surfaces have broken bonds; however, once the deeper layer atoms have broken bonds, like for the A2 (111) surface, this treatment will yield unphysical results. Furthermore, atoms on an ideal flat A2 (111) surface having $Z_S = 0$ is inconsistent with physical facts. For some high-Miller-index planes, e.g., the A2 (221) surface, the calculated Z_S is even negative, and so cannot be substituted into equation (1). This also explains, to some extent, why the surface energies calculated for A2 (111) deviate more significantly from the first-principles and experimental results in comparison with those for the other two surfaces. We suggest that equation (1) could be modified to

$$\gamma = E/(2 + 2\beta) \sum_i \left\{ \left[2 - Z_S^i/Z_B^i - \left(Z_S^i/Z_B^i \right)^{1/2} \right] \right.$$
$$\left. + \beta \left[2 - Z_S^{i\prime}/Z_B^{i\prime} - \left(Z_S^{i\prime}/Z_B^{i\prime} \right)^{1/2} \right] \right\} \quad (2)$$

where Z_S^i and $Z_S^{i\prime}$, Z_B^i and $Z_B^{i\prime}$ denote surface and bulk coordination numbers of the nearest neighbours and next

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Table 1. Parameters for calculating surface energies. The Z_S and Z_B values are coordination numbers of surface and bulk atoms for different surfaces (layers). S denotes the area of the two-dimensional surface unit cell; a is the lattice constant. β is generated from the LJ potential equation according to the nearest and next nearest neighbour bond lengths. 'Ref.' stands for reference. 'CN' stands for coordination number.

					Z_S		Z_B	
Structure	β	Surface	S	Layer	1st CN	2nd CN	1st CN	2nd CN
A1	0	(111)	$\sqrt{3}a^2/4$	1st	9		12	
				Ref. [1]	9		12	
		(100)	$a^2/2$	1st	8		12	
				Ref. [1]	8		12	
		(110)	$\sqrt{2}a^2/2$	1st	7		12	
				2nd	11		12	
				Ref. [1]	6		12	
A2	1/2	(110)	$\sqrt{2}a^2/2$	1st	6	4	8	6
				Ref. [1]	6	4	8	6
		(100)	a^2	1st	4	5	8	6
				2nd	8	5	8	6
				Ref. [1]	4	4	8	6
		(111)	$\sqrt{3}a^2$	1st	4	3	8	6
				2nd	7	3	8	6
				3rd	7	6	8	6
				Ref. [1]	2	0	8	6
A3	0	(0001)	$\sqrt{3}a^2/2$	1st	9		12	
				Ref. [1]	9		12	
		(10$\bar{1}$0)	$\sqrt{8/3}a^2$	1st	8		12	
				2nd	10		12	
				Ref. [1]	16/3		12	
A4	3/10	(110)	$\sqrt{2}a^2$	1st	3	7	4	12
				2nd	4	11	4	12
				Ref. [1]	3	6	4	12
SC	1/2	(100)	a^2	1st	5	8	6	12
				Ref. [1]	5	8	6	12
		(110)	$\sqrt{2}a^2$	1st	4	7	6	12
				2nd	6	11	6	12
				Ref. [1]	4	7	6	12

Table 2. Predicted surface energies of A1 metals based on the modified model which just considers the nearest neighbour broken-bond contributions to surface energies. 'JKL-Re': our theoretical values. Others are taken from [1] and references therein. 'Exp.' stands for experimental values.

	E (kJ mol^{-1})	a (Å)	(hkl)	γ (J m^{-2})			
				JKL	FCD	JKL-Re	Exp.
Cu	336	3.66	(111)	1.83	1.95	1.83	1.79, 1.83
			(100)	2.17	2.17	2.17	
			(110)	2.35	2.24	2.19	
Ag	284	4.18	(111)	1.20	1.17	1.20	1.25, 1.25
			(100)	1.40	1.20	1.40	
			(110)	1.51	1.24	1.42	
Au	368	4.20	(111)	1.52	1.28	1.52	1.51, 1.50
			(100)	1.80	1.63	1.80	
			(110)	1.94	1.70	1.82	
Ni	428	3.58	(111)	2.44	2.01	2.44	2.38, 2.45
			(100)	2.88	2.43	2.88	
			(110)	3.11	2.37	2.92	
Pd	376	3.85	(111)	1.85	1.92	1.85	2.00, 2.05
			(100)	2.15	2.33	2.15	
			(110)	2.35	2.23	2.22	
Pt	564	4.02	(111)	2.54	2.30	2.54	2.49, 2.48
			(100)	2.98	2.73	2.98	
			(110)	3.24	2.82	3.05	
Rh	554	3.87	(111)	2.70	2.47	2.70	2.66, 2.70
			(100)	3.15	2.80	3.15	
			(110)	3.41	2.90	3.24	
Ir	670	3.91	(111)	3.19	2.97	3.19	3.05, 3.00
			(100)	3.74	3.72	3.74	
			(110)	4.06	3.61	3.83	
Pb	196	5.11	(111)	0.55	0.32	0.55	0.59, 0.60
			(100)	0.64	0.38	0.64	
			(110)	0.70	0.45	0.66	
Al	327	4.05	(111)	1.45	1.20	1.45	1.14, 1.16
			(100)	1.68	1.35	1.68	
			(110)	1.84	1.27	1.74	
Ca	178	5.62	(111)	0.43	0.57	0.43	0.50, 0.49
			(100)	0.50	0.54	0.50	
			(110)	0.55	0.58	0.49	
Sr	166	6.17	(111)	0.33	0.43	0.33	0.42, 0.41
			(100)	0.39	0.41	0.39	
			(110)	0.43	0.43	0.38	
Mn	282	3.53	(111)	1.65	3.10	1.65	1.54, 1.60
Ac	410	5.79	(111)	0.90	0.97	0.90	
			(100)	1.03	0.73	1.03	
			(110)	1.14	0.68	1.07	
Th	598	5.19	(111)	1.61	1.48	1.61	1.50
			(100)	1.85	1.47	1.85	
			(110)	2.36	1.45	1.94	

nearest neighbours in the ith layer. All coordination numbers of atoms in different layers must be independently calculated until the atoms in the $(i + 1)$th layer have the same nearest neighbour and next nearest neighbour coordination numbers as bulk atoms. Table 1 lists all coordination numbers of different layer atoms in cleavage facets which have broken bonds (including nearest neighbours and next nearest neighbours).

Tables 2–4 give the new predicted γ values for A1–A4 and sc crystals in terms of the revised JLZ model (equation (1)). For comparison, experimental values, first-principles calculations and JLZ theoretical results are also shown. Generally, the predicted γ values after revision for A1 (111) metal surfaces are significantly lower than those yielded by the JLZ model (table 2). Compared with the first-principles calculations, the JLZ-revised γ values for A1 (111), A2 (100) and (111) are more satisfactory than those for the original JLZ model, as demonstrated in tables 2 and 3. In the prediction of surface energies for high-Miller-index surfaces, modification is especially necessary because Z_S may become a negative number according to the JLZ model. It can be seen in [1] that the energy difference between (0001) and (10$\bar{1}$0)

surfaces calculated from the JLZ model is abnormally greater than the first-principles calculation results. After revision, this difference can be effectively improved, as shown in table 4. The main reason for the reduction of the error is that the values of Z_S for different surface layers are distinguished.

In conclusion, a minor revision to JLZ's model is constructed, for predicting surface energies for different elemental crystals, which can effectively correct errors ensuing from the inappropriate method used in calculating

Table 3. Predicted surface energies of A2, A4 and sc elemental crystals based on the modified model which considers the next nearest neighbour broken-bond contributions to the surface energies. 'JKL-Re': our theoretical values. Others are taken from [1] and references therein.

	E (kJ mol^{-1})	a (Å)	(hkl)	γ (J m^{-2})			
				JKL	FCD	JKL-Re	Exp.
Li	158	3.99	(110)	0.50	0.56	0.50	0.52, 0.53
			(100)	0.58	0.52	0.57	
			(111)	0.72	0.59	0.62	
Na	107	4.20	(110)	0.29	0.25	0.29	0.26, 0.26
			(100)	0.34	0.26	0.35	
			(111)	0.41	0.29	0.38	
K	90.1	5.30	(110)	0.16	0.14	0.16	0.13, 0.15
			(100)	0.18	0.14	0.19	
			(111)	0.23	0.15	0.20	
Rb	82.2	5.71	(110)	0.12	0.10	0.12	0.12, 0.11
			(100)	0.15	0.11	0.15	
			(111)	0.18	0.12	0.16	
Cs	77.6	6.26	(110)	0.10	0.08	0.10	0.10, 0.10
			(100)	0.12	0.09	0.11	
			(111)	0.14	0.09	0.12	
Ba	183	5.03	(110)	0.36	0.38	0.36	0.38, 0.37
			(100)	0.41	0.35	0.42	
			(111)	0.51	0.40	0.45	
Ra	160	5.37	(110)	0.27	0.30	0.27	
			(100)	0.32	0.29	0.32	
			(111)	0.40	0.32	0.35	
Eu	179	4.58	(110)	0.43	0.49	0.43	0.45, 0.45
			(100)	0.50	0.46	0.49	
			(111)	0.61	0.52	0.54	
V	512	3.02	(110)	2.74	3.26	2.74	2.62, 2.56
			(100)	3.26	3.03	3.25	
			(111)	4.04	3.54	3.53	
Cr	395	2.85	(110)	2.39	3.51	2.39	2.35, 2.30
			(100)	2.83	3.98	2.82	
			(111)	3.50	3.89	3.05	
Fe	413	2.86	(110)	2.52	2.43	2.52	2.42, 2.48
			(100)	2.92	2.22	2.93	
			(111)	3.62	2.73	3.17	
Nb	730	3.76	(110)	2.58	2.69	2.58	2.66, 2.70
			(100)	2.99	2.86	2.99	
			(111)	3.72	3.05	3.24	
Mo	658	3.17	(110)	3.20	3.45	3.20	2.91, 3.00
			(100)	3.81	3.84	3.79	
			(111)	4.62	3.74	4.11	
Ta	782	3.35	(110)	3.40	3.08	3.40	2.90, 3.15
			(100)	4.05	3.10	4.04	
			(111)	5.01	3.46	4.38	
W	859	3.58	(110)	3.36	4.01	3.36	3.27, 3.68
			(100)	3.90	4.64	3.88	
			(111)	4.84	4.45	4.21	
Sb (sc)	265	3.36	(100)	0.66	0.61	0.66	0.60, 0.54
			(110)	0.77	0.66	0.83	
Bi(sc)	210	3.26	(100)	0.55	0.54	0.56	0.49, 0.49
			(110)	0.64	0.54	0.70	
Po(sc)	144	3.34	(100)	0.38	0.44	0.37	
			(110)	0.44	0.37	0.46	
Si(A4)	446	7.71	(110)	1.06		1.19	1.14
Ge(A4)	372	8.10	(110)	0.80		0.90	0.88

Table 4. Predicted surface energies of A3 metals based on the modified model which just considers the nearest neighbour broken-bond contributions to surface energies. 'JKL-Re': our theoretical values. Others are taken from [1] and references therein.

	E (kJ mol^{-1})	a (Å)	(hkl)	γ (J m^{-2})			
				JKL	FCD	JKL-Re	Exp.
Be	320	2.22	(0001)	2.40	1.83	2.40	1.63, 2.70
			(10$\bar{1}$0)	2.88	2.13	2.43	
Mg	145	3.20	(0001)	0.53	0.79	0.53	0.79, 0.76
			(10$\bar{1}$0)	0.65	0.78	0.55	
Zn	130	2.68	(0001)	0.66	0.99	0.66	0.99, 0.99
			(10$\bar{1}$0)	0.72		0.72	
Cd	112	3.06	(0001)	0.44	0.59	0.44	0.76, 0.74
			(10$\bar{1}$0)	0.47		0.49	
Tl	182	3.71	(0001)	0.49	0.30	0.49	0.60, 0.58
			(10$\bar{1}$0)	0.60	0.35	0.60	
Sc	376	3.30	(0001)	1.25	1.83	1.25	1.28
			(10$\bar{1}$0)	1.53	1.53	1.34	
Ti	468	2.95	(0001)	1.96	2.63	1.96	1.99
			(10$\bar{1}$0)	2.39	2.52	2.11	2.10
Co	424	2.53	(0001)	2.42	2.78	2.42	2.52, 2.55
			(10$\bar{1}$0)	2.95	3.04	2.64	
Y	422	3.55	(0001)	1.22	1.51	1.22	1.13
			(10$\bar{1}$0)	1.49	1.24	1.24	
Zr	603	3.25	(0001)	2.08	2.26	2.08	1.91, 2.00
			(10$\bar{1}$0)	2.54	2.11	2.26	
Tc	661	2.74	(0001)	3.22	3.69	3.22	3.15
			(10$\bar{1}$0)	3.93	3.90	3.45	
Ru	650	2.72	(0001)	3.20	3.93	3.20	3.04,
			(10$\bar{1}$0)	3.90	4.24	3.47	3.05
La	431	3.87	(0001)	1.05	1.12	1.05	1.02
			(10$\bar{1}$0)	1.28	0.92	1.19	
Lu	428	3.51	(0001)	1.27	1.60	1.27	1.23
			(10$\bar{1}$0)	1.55	1.42	1.37	
Hf	621	3.20	(0001)	2.22	2.47	2.22	2.19, 2.15
			(10$\bar{1}$0)	2.71	2.31	2.39	
Re	775	2.76	(0001)	3.72	4.21	3.72	3.63, 3.60
			(10$\bar{1}$0)	4.54	4.63	3.99	
Os	788	2.75	(0001)	3.80	4.57	3.80	3.44, 3.45
			(10$\bar{1}$0)	4.64	5.02	4.11	

the coordination numbers of surface atoms. This revision is especially indispensable if one is using the JKL model to calculate high-Miller-index surface energies for elementary crystals.

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