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Atomic-scale calculation of energies of Cu (001) twist boundaries*

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Unrelaxed energies for Cu (001) twist grain boundaries (GBs) are calculated using a Modified Analytical Embedded Atom Method (MAEAM). The results show that, except zero energy at 0° (perfect crystal), a small cusp exists at a twist angle of 36.87° corresponding to $\Sigma = 5$, which agrees with experimental results. For other misorientations, the GB energies keep almost constant even at a twist angle as small as 1.94°. Homogeneous expansion and the expansion perpendicular to the GB plane result in obvious decrease of energy, especially the latter.

Keywords: grain boundary energy, atomic-scale calculation, MAEAM, expansion
PACC: 6185, 6848, 7115, 7115M

1. Introduction

A detailed knowledge of the energy and structure of grain boundaries (GBs) is important for understanding many phenomena associated with grain boundary, such as grain growth,[1,2] impurity segregation,[3] atom migration across boundary,[4] deformation[5] and fracture[6] along boundary, etc. A number of experiments, rotating crystallites for example, have been conducted to determine the grain-boundary (GB) energy.[7−9] In addition, computer simulation methods have also been developed to calculate the GB energy and structure, especially for low index twist boundaries.[10,11] However, only 12 specific boundaries, corresponding to reciprocal planar density of coincidence site lattice (CSL) Σ lower than 73, have been considered for the (001) twist boundary.

Based on the density-functional theory, Daw and Baskes developed a semi-empirical means, namely embedded atom method (EAM).[12,13] In contrast to the central-force potential which considers only the potential energy of a system of particles, the EAM presents the energy of atoms in a system as a sum of electrostatic pairwise interactions of an atom with each of its near neighbours and an energy to embed the atom in the local electron density created by its near neighbours. It is believed that a many-body effect sensitive to the local environment of atoms makes possible the accurate treatment of defective structures such as surfaces, interfaces and grain boundaries.[11] In previous papers, we have made a calculation of the surface energy for materials with FCC,[14] BCC[15] and diamond cubic structures[16] by use of a modified EAM (MEAM), and the interface energy of Ag (001)/Ni (001)[17] by using a modified analytical EAM (MAEAM). MEAM[18] and MAEAM[19−22] are based on the initial EAM and analytical EAM (AEAM, developed by Johnson and his co-workers[23−26]) respectively with the directional bonding included.

In this paper, the unrelaxed energies of Cu (001) twist GBs for 50 configurations (including some small twist angles below 6°) have been calculated by use of MAEAM. The effects of the homogeneous lattice expansion and the expansion perpendicular to the GB plane (which has been detected experimentally in metal and ionic crystal[27,28]) on GB energy are discussed.

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2. MAEAM

In MAEAM, the total energy of a system $E_{\rm total}$ is expressed as[22]

$$E_{\rm total} = \sum_i F(\rho_i) + \sum_i \phi(r_{ij})/2 + \sum_i M(P_i), \quad (1)$$

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

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

where $F(\rho_i)$ is the energy to embed an atom at site i, ρ_i is the electron density at site i contributed by other atoms in the system, which is given by a linear superposition of spherical averaged atomic electron density $f(r_{ij})$; r_{ij} is the separation distance of atom j from i, $\phi(r_{ij})$ is the interaction potential between atoms i and j; $M(P_i)$ is a modified term that describes the energy change caused by the nonspherical distribution of electrons (P_i) and deviation from the linear superposition of atomic electron density. The embedding function $F(\rho_i)$, pair potential $\phi(r_{ij})$, modified term $M(P_i)$, and atomic electron density $f(r_{ij})$ can be written as[22]

$$F(\rho_i) = -F_0[1 - n\ln(\rho_i/\rho_{\rm e})](\rho_i/\rho_{\rm e})^n, \quad (4)$$

$$\phi(r_{ij}) = k_0 + k_1(r_{ij}/r_{1\rm e})^2 + k_2(r_{ij}/r_{1\rm e})^4 + k_3(r_{1\rm e}/r_{ij})^{12}, \quad (5)$$

$$M(P_i) = \alpha(P_i/P_{\rm e} - 1)^2 \exp[-(P_i/P_{\rm e} - 1)^2], \quad (6)$$

$$f(r_{ij}) = f_{\rm e}(r_{1\rm e}/r_{ij})^6, \quad (7)$$

where the subscript e denotes equilibrium and $r_{1\rm e}$ is the first nearest neighbour distance at equilibrium. In this study, the electron density at equilibrium $f_{\rm e}$ is chosen as

$$f_{\rm e} = [(E_c - E_{1\rm f})/\Omega]^{3/5}, \quad (8)$$

where $\Omega = a_0^3/4$ is the volume of an atom in a metal with FCC structure.

Seven parameters n, F_0, α, k_0, k_1, k_2 and k_3 in Eqs.(4)–(7) can be determined by fitting the cohesion energy $E_{\rm c}$, the mono-vacancy formation energy $E_{1\rm f}$, the lattice constant a_0, and the elastic constants of C_{11}, C_{12}, C_{44}. According to the principle that the energy vs separation distance curve should fit the Rose equation[29] as far as possible, we have

$$n = \sqrt{\Omega(C_{11} + 2C_{12})(C_{11} - C_{12})/(216E_{1\rm f}C_{44})}, \quad (9)$$

$$F_0 = E_{\rm c} - E_{1\rm f}, \quad (10)$$

$$\alpha = \Omega(C_{12} - C_{44})/32 - n^2F_0/8. \quad (11)$$

The potential parameters can be calculated with the following formulae:[22]

$$k_0 = -E_{1\rm f}/9 - \Omega(5481C_{44} + 2989C_{12} - 2989C_{11})/42840, \quad (12)$$

$$k_1 = \Omega(1311C_{44} + 939C_{12} - 939C_{11})/9520, \quad (13)$$

$$k_2 = \Omega(-33C_{44} - 32C_{12} + 32C_{11})/1020, \quad (14)$$

$$k_3 = 8\Omega(9C_{44} + C_{12} - C_{11})/5355. \quad (15)$$

The cut-off function is determined by Ref.[19] and the cut-off distance is chosen as

$$r_{\rm c} = r_{2\rm e} + 0.75(r_{3\rm e} - r_{2\rm e}). \quad (16)$$

Using E_i to show the contribution of atom i to the total energy $E_{\rm total}$ of a system, Eq.(1) can be rewritten as

$$E_{\rm total} = \sum_i E_i. \quad (17)$$

The GB energy is the superabundance relative to bulk material due to the existence of GB. Thus a contribution of atom i to the GB energy can be shown as $E_i - E_{\rm b}$, where $E_{\rm b}$ is the energy for each atom in a perfect crystal (equal to the negative value of cohesion energy $E_{\rm c}$). Summing the contributions of all atoms associated with boundaries and then dividing the obtained sum by the interface area A, we can obtain the GB energy density E:

$$E = \frac{1}{A}\sum_{l=1}^{L}\sum_i (E_i^l - E_{\rm b}), \quad (18)$$

where E_i^l is the energy of atom i in the lth lattice plane and L is the number of lattice planes in the boundary region. Inputting the lattice constant a_0,[30] cohesion energy $E_{\rm c}$, mono-vacancy formation energy $E_{1\rm f}$,[18] and the elastic constants C_{11}, C_{12} and C_{44} of copper[31], which are listed in Table 1, the parameters needed for energy calculation can be obtained, which are listed in Table 2.

Table 1. Parameters needed for fitting the pair potential of copper.

a_0/nm	$E_{\rm c}$/eV	$E_{1\rm f}$/eV	C_{11}/GPa	C_{12}/GPa	C_{44}/GPa
0.36147	3.54	1.14	168	121	75.4

Table 2. Calculated parameters of copper for energy calculation with MAEAM.

n	F_0/eV	α	k_0/eV	k_1/eV	k_2/eV	k_3/eV
0.2768	2.4	0.0822	–0.5966	0.4241	–0.0712	0.0696

Substituting the values of $k_i (i = 0-3)$ into Eq.(5), the interatomic potential for copper is calculated and plotted in Fig.1.

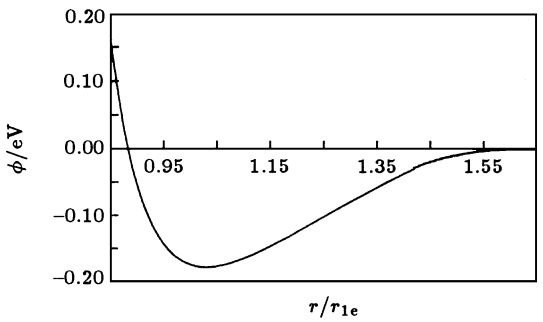


Fig.1. Interatomic potential for copper.

3. Determination of CSL

The periodic boundary condition can be employed to reduce the number of atoms for representing the structure of an infinite interface. For the (001) twist GB, the coincident site lattice (CSL) may be generated by rotating one of the two grains about their common [001] axis until its lattice vector $[kl0]$ in its own coordinate becomes coincident with the vector $[mn0]$ of the non-rotated one. Here m, n, k, l each are odd times of $a_0/2$. The reciprocal planar coincident density of crystal lattice can be described as

$$\Sigma = (m^2 + n^2)/A_0 = (k^2 + l^2)/A_0. \qquad (19)$$

The rotation angle is given by

$$\theta = \tan^{-1}(n/m) - \tan^{-1}(l/k), \qquad (20)$$

where $A_0 (= a_0^2/2)$ is the smallest unit cell area of perfect Cu (001) lattice plane, that is the area occupied by each atom in (001) plane, thereby the value of Σ equals the number of atoms in the smallest unit cell area of CSL in each (001) plane.

A computer code is compiled in MATLAB to evaluate the rotation angle θ, reciprocal planar density of coincident site lattice Σ, and corresponding lattice vector index m, n, k and l. The calculated results are listed in Table 3.

Table 3. Determined values of θ, Σ, m, n, k and l for (001) twist boundaries of FCC metals.

θ	Σ	m	n	k	l
1.94	1741	59	1	59	–1
2.55	1013	45	1	45	–1
3.47	545	33	1	33	–1
3.95	421	29	1	29	–1
4.24	365	27	1	27	–1
4.58	313	25	1	25	–1
4.98	265	23	1	23	–1
5.45	221	21	1	21	–1
5.72	401	19	21	21	19
6.03	181	19	1	19	–1
6.36	325	17	19	19	17
6.73	145	17	1	17	–1
7.15	257	15	17	17	15
7.63	113	15	1	15	–1
8.17	197	13	15	15	13
8.78	85	13	1	13	–1
9.53	145	11	13	13	11
10.39	61	11	1	11	–1
11.42	101	9	11	11	9
12.68	41	9	1	9	–1
13.42	293	15	19	19	15
14.25	65	7	9	9	7
15.19	229	13	17	17	13
16.26	25	7	1	7	–1
17.49	173	11	15	15	1
17.95	185	19	3	19	–3
18.92	37	5	7	7	5
20.02	149	17	3	17	–3
20.61	125	9	13	13	9
21.24	265	13	19	19	13
22.62	13	5	1	5	–1
24.19	205	11	17	17	11
25.06	85	7	11	11	7
25.99	89	13	3	13	–3
28.07	17	3	5	5	3
29.49	193	19	5	19	–5
29.86	241	11	19	19	11
30.51	65	11	3	11	–3
31.89	53	5	9	9	5
32.78	157	17	5	17	–5
33.40	109	7	13	13	7
34.21	185	9	17	17	9
36.87	5	3	1	3	–1
39.31	221	9	19	19	9
39.97	137	7	15	15	7
40.45	205	19	7	19	–7
41.11	73	5	11	11	5
42.08	97	13	5	13	–5
43.60	29	3	7	7	3
44.76	169	17	7	17	–7

4. Calculation of GB energy

4.1. Unrelaxed GB energy

The unrelaxed energies of Cu (001) GBs corresponding to 50 twist angles have been calculated with another computer program written in MATLAB. The variation of energy with twist angle θ is illustrated in Fig.2 by circles. The other two curves are for the energies after homogeneous expansion and perpendicular expansion, and will be discussed later. It can be seen that the unrelaxed energy of Cu (001) GB increases abruptly from zero to an almost constant value as the twist angle deviates slightly from 0° (corresponding to a perfect crystal) except a small cusp (about 200mJ/m^2 lower than the constant energy) at θ =36.87° (corresponding to the smallest value of $\Sigma = 5$). This result is different from that obtained using the equation of Read and Shockley,[32] which indicates that the GB energy increases monotonically with the twist angle from 0° to 15°. The cusp at θ =36.87° was also found in central-force potential calculation for Cu and Ni[33,34] and was verified in experiments for Cu, Al and Au metals[7−9] with the same FCC structure.

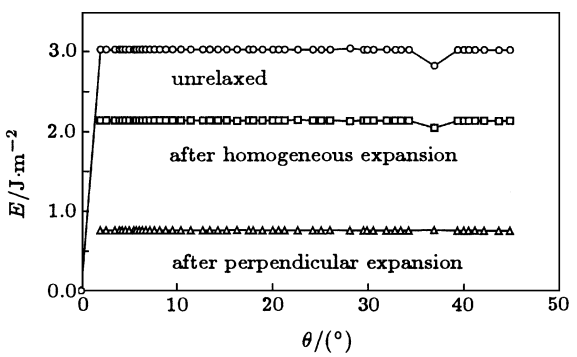


Fig.2. GB energy as function of the twist angle θ for Cu (001) GBs.

4.2. Effect of lattice expansion

A volume expansion near GB due to the introduction of the interface into the bicrystal has been detected experimentally for both $\Sigma = 5$ and $\Sigma = 13$ boundaries in metals and ionic crystal such as NiO.[27,28] This may be driven by the decrease of GB energy. To investigate it theoretically, a homogeneous lattice expansion in GB region is considered. The variation of GB energy as a function of the relative lattice expansion $\frac{\Delta a}{a_0} = \frac{a - a_0}{a_0}$ for $\Sigma = 5$ ($\theta = 36.87°$) and $\Sigma = 13$ ($\theta = 22.62°$) boundaries are shown in Fig.3. Here a_0 and a are the lattice constants of the perfect and expanded respectively. One sees that the GB energy decreases the lattice expansion with up to an expansion of about 6%; further expansion beyond this increases the energy. The minimum energies for $\Sigma = 5$ and $\Sigma = 13$ boundaries are 774mJ/m^2 and 877mJ/m^2 lower than those of unexpanded respectively. Such expansion is performed for all the twist boundaries and a similar result is obtained. All minimum energies appearing at $\Delta a/a_0 \approx 6\%$ are plotted in Fig.2 by squares. A nearly straight line parallel to the unrelaxed energy curve shows a close decrease (around 880mJ/m^2) in GB energy except $\Sigma = 5$ ($\theta = 36.87°$) boundary.

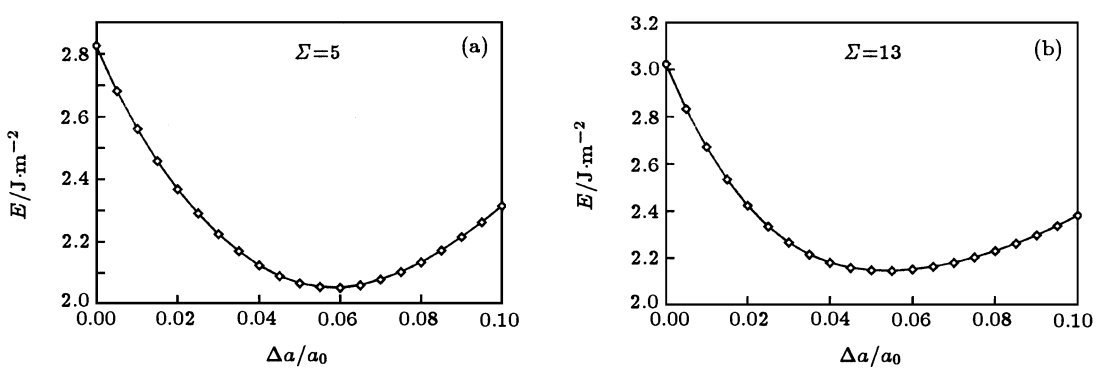


Fig.3. Variation of GB energy as function of relative lattice expansion $\Delta a/a_0$ for $\Sigma = 5$ ($\theta = 36.87°$) and $\Sigma = 13$ ($\theta = 22.62°$) Cu (001) GBs.

4.3. Effect of perpendicular expansion

In addition to homogeneous lattice expansion accounted above, the expansion perpendicular to the GB plane may be more important in that some distances between the atoms belonging to two slabs respectively may be shorter than those from them to their nearest-neighbours in an ideal crystal due to the relative rotation. According to Pauli principle, these atoms will strongly repel each other and will give rise to GB en-

ergy owing to the sharp increase of the interatomic potential with distance decreasing (Fig.1). Appropriate expansion perpendicular to GB plane can relieve this effect. For simplicity, we only investigate an increase of the distance between the two slabs (Δz, in units of a_0) while all atoms are held rigidly in their perfect lattice positions. Calculations of GB energy variation with Δz for all the twist boundaries are performed and listed in Table 3. And similar results are obtained. The results for $\Sigma = 5$ ($\theta = 36.87°$) and $\Sigma = 13$ ($\theta = 22.62°$) boundaries are shown in Fig.4 as an example. We find that GB energy could drop to about 760mJ/m^2 when Δz is near $0.12a_0$ for most boundaries and with further increase of Δz, energy increases and then reaches a constant value (1.9651J/m^2). It is interesting to note that, for all boundaries, both the minimum (about 760mJ/m^2) and the final constant value (1.9651J/m^2) of GB energy are independent of the twist angle, the former is illustrated in Fig.2 by triangles and the latter can be regarded as being twice the energy of the corresponding free surface.

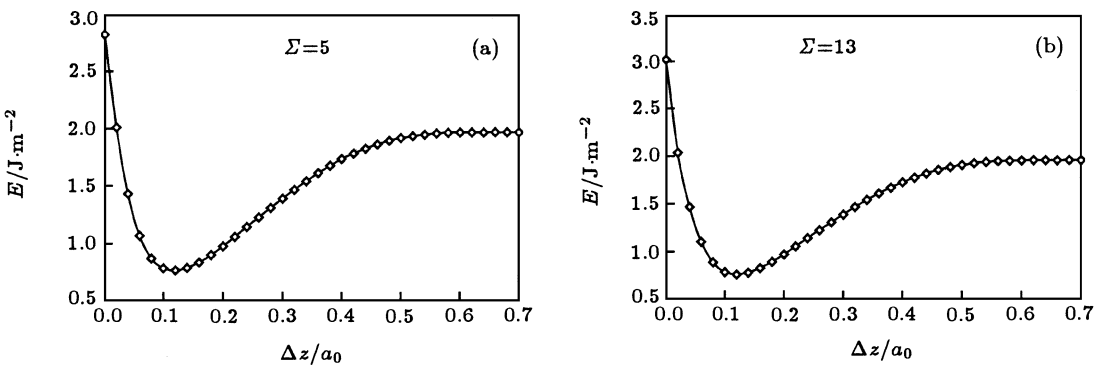


Fig.4. Variation of GB energy with Δz (in units of lattice-parameter a_0) for $\Sigma = 5$ ($\theta = 36.87°$) and $\Sigma = 13$ ($\theta = 22.62°$) Cu (001) GBs.

5. Conclusions

Unrelaxed energies of Cu (001) twist GBs have been calculated with MAEAM. The results show that the unrelaxed GB energies keep constant except a cusp at 36.87°. From GB energy minimization, the boundary configurations corresponding to $\theta = 0°$ (especially) and $\theta = 36.87°$ are preferable, which agrees well with the experimental results. Both homogeneous expansion and the expansion perpendicular to GB plane decrease the GB energy, especially the latter. The shorter distance caused by rotation between grains leads to the sharp increase of repulsive potential energy, thus GB energy, so that appropriate expansion could bring about a drop of energy. The significant energy drop resulting from the perpendicular expansion may be associated with the disorder of atoms in close contact with stacking defect mainly coming from the opposite sides of the boundary. For three-dimensional homogenous expansion, however, although the expansion perpendicular to GB plane results in energy decrease as above, the expansion parallel to GB plane destroys the perfect structure of each slab, and thereby the additional disorder and energy are produced.

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