MOLECULAR DYNAMICS APPROACH OF THE [001] TWIST GRAIN BOUNDARIES ENERGY IN Cu
E. Doni, G. Bleris

To cite this version:

HAL Id: jpa-00230265
https://hal.archives-ouvertes.fr/jpa-00230265
Submitted on 1 Jan 1990

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
MOLECULAR DYNAMICS APPROACH OF THE [001] TWIST GRAIN BOUNDARIES ENERGY IN Cu

E.G. DONI and G.L. BLERIS

Department of Physics, Aristotle University of Thessaloniki, GR-540 06 Thessaloniki, Greece

Abstract - Using the Molecular Dynamics technique the energy E vs the misorientation \( \theta \) has been calculated for the CSL [001] twist grain boundaries in Cu. Two potentials have been used; the Morse potential and a spline potential constructed by Englert and Tompa for Cu. In each case the low and high angle grain boundary regions have been clearly distinguished by using the relation \( E = E_0 \theta (A - \theta \eta) \), valid for low angle grain boundaries. To this relation a polynomial has been added, in order to describe the energy vs misorientation dependence in the range \( (0, 45^\circ) \).

1 - INTRODUCTION

During the last two decades a lot of work has been done on the study of the relaxed structure and energy of Grain Boundaries (GBs) on the basis of the Coincidence Site Lattice (CSL) model. Many applications have been reported using the CSL model in different energy minimization procedures /1-6/. Brokman and Balluffi have shown that a plot of the energy \( E \) of the [001] twist GBs as a function of the misorientation \( \theta \) appears as a smooth line which can be distinguished in two regions with respect to the magnitude of the misorientation /5/. In the low angle region a steep increase of \( E \) with \( \theta \) exists, while in the high angle region the \( E(\theta) \) curve reaches a level. Cusps may appear in the region of low \( \Sigma \) boundaries due to secondary relaxations. On the other hand Read and Shockley in 1950 have analytically derived a relation giving the GB energy as a function of the misorientation on the basis of the dislocation model of a GB /7/. This relation is valid for low angles, where the spacing of the dislocations is rather big and the dislocations do not overlap. The aim of this paper is to show that the Read and Shockley relation could be extended by adding some terms in order, the general characteristics of the energy vs the misorientation for a GB to be analytically described. For this purpose a computational procedure /8/ based on the Molecular Dynamics (MD) technique /9,10/ has been applied in order the energy of the CSL [001] twist GBs in Cu to be estimated. For our generic study the calculations were carried out at \( T = 0 \) K and two different potentials, the Morse potential /11,12/ and a spline potential /13/ for Cu have been used.

2 - COMPUTATIONAL PROCEDURE

Computational cells have been constructed for some of the CSL [001] twist GBs. In Table 1 the [001] twist GBs and their misorientations \( \theta \), up to \( \Sigma = 99 \), are tabulated in an increasing \( \Sigma \) value. The CSLs used in this study are emphasized.

<table>
<thead>
<tr>
<th>( \Sigma )</th>
<th>5</th>
<th>13a</th>
<th>17a</th>
<th>25a</th>
<th>29a</th>
<th>37a</th>
<th>41a</th>
<th>53b</th>
<th>61a</th>
<th>65a</th>
<th>65b</th>
<th>73c</th>
<th>85a</th>
<th>85b</th>
<th>89a</th>
<th>97c</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta )</td>
<td>36.87</td>
<td>22.62</td>
<td>28.07</td>
<td>16.26</td>
<td>43.60</td>
<td>18.92</td>
<td>12.68</td>
<td>31.89</td>
<td>10.39</td>
<td>14.25</td>
<td>30.51</td>
<td>41.11</td>
<td>8.80</td>
<td>25.06</td>
<td>25.99</td>
<td>42.08</td>
</tr>
</tbody>
</table>

The computational cells have been constructed by applying periodic boundary conditions and they are considered as square prisms with cross-sections defined by the unit cells of the CSLs. The cross-sections are

(1) Work supported by the Greek Research Foundation No 87EA 269
the (001) planes, the GB is located in the middle of the computational cell and twelve successive (001) planes are taken into account. The models are allowed to relax by using the MD method and two potentials have been used. The first one is the classical Morse potential adapted for Cu /11,12/ and its use for a generic study has been already discussed elsewhere /14/. The second one is a spline potential consisted of ten splines and constructed by Englert and Tompa for Cu /13/. The values of the elastic constants are derived by its derivatives and it is fitted to many physical data as to the best value of vacancy formation energy, to the force constant data and to the experimentally observed intrinsic stacking fault energy. A similar potential for Cu consisted of nine splines has been used earlier /1/. The idea of using empirical interatomic potentials has been extensively discussed /15/. There is a general agreement that these potentials have a physical meaning if they describe interactions between atoms in an environment similar to that the adaption was carried out. Along this line of approach they could be used for defects which change a little the density of the material, i.e. GBs and dislocations. However for our generic study the two potentials truncated at the third neighbor allow a comparative examination of the results in the available literature.

3 - [001] TWIST GRAIN BOUNDARIES ENERGY

The general expression of the GB energy \( E \) as a function of the misorientation \( \theta \) derived by Read and Shockley /7/ from the dislocation model of a GB is

\[
E = E_0 \theta \left( A - \ln \theta \right)
\]

where \( E_0 \) and \( A \) are constants. \( E_0 \) depends on the elastic distortion, and it can be calculated from the dislocation model and the elastic constants of the material. \( A \) depends on the nonelastic core energy of the dislocation and its evaluation requires the calculation of the forces between atoms in the bad material of the dislocation core /16/. This formula has been analytically derived for tilt boundaries and it has been properly modified for twist boundaries also. Actually, it is valid for all kinds of small angle boundaries (not only tilt boundaries) if the constants \( E_0 \) and \( A \) are modified correspondingly /17/. The first term, \( E_0 \theta \), in relation (1) gives the core energy of the dislocation and it is directly proportional to the misfit angle \( \theta \). The second term, \(-E_0 \theta \ln \theta\), comes from the elastic energy and gives the elastic energy of the dislocations in their surroundings. In relation (1) the higher order terms expressing the elastic stress field of the dislocations have been neglected. As \( \theta \) increases, the higher order terms become important in the area where the stress fields of the dislocations overlap. In order to calculate the elastic energy, we have to sum the higher order terms as an infinite series of powers of \( \theta \). This could be alternatively done by fitting the variation of \( E \) in the high angles regime as a function of the variation of \( A \).

A plot of \( E/\theta \) vs \( \ln \theta \) according to relation (1) is a straight line. The slope of this line is \(-E_0\) and the zero-energy intercept is \( A \). A plot of \( E \) vs \( \theta \) according to the same relation (1) is a curve which reaches a maximum of magnitude \( E_m \) at an angle \( \theta_m \). The parameters \( E_m \) and \( \theta_m \) are related to \( E_0 \) and \( A \) by the equations:

\[
E_m = E_0 \theta_m, \quad \theta_m = e^{A-1}
\]

In Fig. 1 the plots of \( E/\theta \) vs \( \ln \theta \) are given as a result of the application of the MD relaxation procedure in a variety of \( \Sigma \), represented by special marks, for the two potentials used for Cu. The linear dependence is obvious for low values of \( \theta \). In each case the line expressing the fair linear correlation has been drawn. The resulting values from this correlation for the parameters \( E_0 \) and \( A \) and consequently for \( E_m \) and \( \theta_m \) are given in Table 2 for the two potentials used. These results are in good agreement with the data existed for copper /16/.

| Table 2 - Values of the parameters \( E_0, A, E_m \) and \( \theta_m \) for Cu. The energies are in erg/cm\(^2\) and the angles in degrees. |
|---|---|---|---|
| \( E_0 \) | \( A \) | \( E_m \) | \( \theta_m \) |
| Morse Potential | 1456 | .046 | 561 | 22.1 |
| Spline Potential | 1651 | .108 | 677 | 23.5 |

For higher values of \( \theta \) a deviation from the Read and Shockley behavior is also obvious. This deviation becomes noticeable in Fig. 2 where relation (1) with the set of parameters given in Table 2 and the computational results have been depicted together, for each of the two potentials used. The computational results show clearly the plateau-like behavior in the high angles regime, as it has been described in /5/. In each case the deviation \( \Delta E \) between the dashed interpolation curve representing the computational results and the solid
Fig. 1 - Plots of $E/\theta$ vs $\ln \theta$ for the two potentials used for Cu. The different $S$ are represented by special marks. The linear relationship between $E/\theta$ and $\ln \theta$ is shown for low angles. The line expressing the fair linear correlation has been drawn.

Fig. 2 - Plots of $E$ vs $\theta$ for the two potentials used for Cu. The solid curves represent relation (1) with parameters taken from Table 2, the dashed curves represent the computational results.
curve (relation (1)), gives a measure of the divergence of the high angle GB energy from the GB energy described by the Read and Shockley relation.

By considering $E_0$ as a constant depending only on the elastic properties of the material, relations (2) imply that a continuous variation of $E_m$ and $\theta_m$ could describe the $E(\theta)$ behavior beyond the low angles regime. Thus for high angles $\theta$, $A$ has to be considered from the second of the relations (2) as an implicit function of $\theta$.

For a given angle $\theta$ the deviation $\Delta A$ can be expressed as a function of the deviation $\Delta E$ and the parameters $E_m$ and $\theta_m$, by means of the relation:

$$\Delta A = \frac{\theta_m}{\theta} \frac{\Delta E}{E_m}.$$  

$\Delta A$ has been expressed as a function of $\theta$ by making a polynomial fit. In each case the polynomials up to the 8th order have been searched. Between them only the 3rd order ones describe the variation of $A$ as a function of $\theta$, up to $\theta = 45^\circ$, giving the necessary symmetrical behavior of the energy around this limit. Their coefficients are given in Table 3. It should be noticed that other polynomials are fitted well in the low angle region but they show a rather high divergence about the $45^\circ$ limit, failing to describe the plateau-like behavior of the energy in the high angle region and its necessary symmetrical form.

Table 3 - The coefficients of the polynomials of the 3rd order used to fit the difference $\Delta A$ between the corresponding two curves of Fig. 2.

<table>
<thead>
<tr>
<th></th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Potential</td>
<td>.03569</td>
<td>-.46703</td>
<td>1.56702</td>
<td>-.83351</td>
</tr>
<tr>
<td>Spline Potential</td>
<td>.02224</td>
<td>-.32398</td>
<td>1.20022</td>
<td>-.66706</td>
</tr>
</tbody>
</table>

From relations (2) and (3) it is obvious that the energy difference $\Delta E$ is given by the relation:

$$\Delta E = E_0 \theta A.$$  

Fig. 3 - Plots of $E_1/E_0$ (relation (6)) vs $\theta$ for the two potentials used for Cu.
By considering the GB energy $E_{GB}$ as the sum of a Read and Shockley part given by relation (1) and a part obtained from relation (4) as a function of $\Delta A$, we have:

$$E_{GB} = E + \Delta E$$

$$= E_0(\bar{A} - \ln \theta + a_1 \theta + a_2 \theta^2 + a_3 \theta^3),$$

(5)

where the constant polynomial term $a_3$ has been added to $A$.

Taking into account the polynomial coefficients of Table 3 relation (5) can be written in the form:

$$E_{GB} = E_1 + E_2$$

$$= E_0(\bar{A} + a_2 \theta^2) + E_0(\bar{A} - \ln \theta + a_1 \theta + a_3 \theta^3).$$

(6)

The first term, $E_1$, gives the atomic misfit energy on the boundary, while the second term, $E_2$, the elastic misfit distortion away from the boundary. Their relative variation $E_1/E_2$ as a function of the misorientation $\theta$ is given in Fig. 3 for each of the two potentials used.

**DISCUSSION**

The MD method has been used in order to provide a model for CSL [001] twist GBs energy $E$ as a function of the misorientation $\theta$. Two main aspects have been taken into account; the low angle energy model given by Read and Shockley /7/ and the high angle constant-energy plateau described by Brokman and Balluffi /5/. Although the limits of the validity of both models are not clearly defined the available information allows some predictions. Using two different potentials for Cu, numerical results which show a satisfactory linear character for the low angle region have been obtained and the constants of the Read and Shockley relation (1) have been found. A polynomial fit of the computational results has also been made. The numerical procedure used in this study justifies quantitatively the computational results but hardly constitutes a rigorous derivation of the $E(\theta)$ function. Nevertheless it shows clearly that the whole variation of the boundary energy can be treated on the basis of the variation of the parameter $A$. The direct consequence of this approach is that in the high angle region the boundary is characterized by a high atomic misfit energy, given by the first term, $E_1$, of relation (6) and a relatively low elastic misfit distortion far away from the boundary, given by the second term, $E_2$, of relation (6). In conclusion we wish to emphasize that the purpose of this paper is to investigate the $E(\theta)$ function. The general accepted behavior of the twist GB energy in the low and high angle regime has been taken into account. The observed good consistency of the 3rd order polynomials obtained, might not be altered as far as the general form of the energy vs misorientation does not change. Indeed, the results reported by other authors using either theoretical procedures or experimental measurements show that the overall view of the energy function is the one used. However, the values of the coefficients of the polynomial might be changed.

REFERENCES