Electronic structure of the (130) symmetrical tilt grain boundary in an fcc metal

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We discuss the electronic structure of a grain boundary in a metal, using a tight-binding s-like Hamiltonian. We consider the symmetrical tilt boundary in an fcc crystal, with a misorientation angle of 36°52′ between the ⟨100⟩ axis of the grains. Two different microscopic models, obtained by computer simulation techniques, and corresponding to the same macroscopic boundary parameters, are studied. The calculation indicates the presence of localized states associated with the boundary. Rudimentary relaxation is introduced to restore charge neutrality at the boundary. The band-energy contribution to the specific boundary energy is evaluated.

I. INTRODUCTION

Grain boundaries form an important class of extended defects in metals. Their effect upon mechanical, e.g., fracture, and chemical, e.g., corrosion, properties of metals and alloys is well known. In the past decade, a considerable body of information has accumulated about them. The macroscopic characterization of grain boundaries, i.e., their geometries and energies of formation have been studied for a long time. Their microscopic structure has been the object of much speculation with many different models being proposed, such as the amorphous boundary, the dislocation array, the islands, the coincidence site lattice, and other models (for a review see Ref. 7). Recently, progress has been achieved along two directions. On the experimental side, the use of Auger electron spectroscopy has allowed the determination of the chemical composition of the boundaries in alloys, confirming the long held belief that the segregation of one of the atomic species to the boundary is responsible for many of the metallurgical properties of real materials, such as temper embrittlement of steels. On the theoretical side, computer simulations have been employed to provide better microscopic models for the atomic arrangements in the neighborhood of the boundary. Such studies also yield grain boundary energies. Although these computer simulations are still controversial, and there is no hope of experimentally detecting in the near future the atomic arrangements characteristic of a given macroscopic boundary geometry, they provide a less speculative starting point for grain boundary studies than previous models.

In the past decade, the great interest in surfaces and interfaces has resulted in the development of many theoretical tools for dealing with systems with reduced translational periodicities. These, combined with the available information concerning grain boundaries, allow us to study the electronic structure of such important defects. Yndurain and Falicov discussed already the electronic structure of a stacking fault in an fcc metal. The aim of the present work is to discuss the problem for a special grain boundary within a simple model, and completes a preliminary report by the author. We use the tight-binding formalism because many computational methods have been developed for it, and it is capable of yielding reasonable results. The particular method which we employ is discussed in Sec. II. It is most easily applied to symmetrical boundaries for which extensive use can be made of Bloch’s theorem. In Sec. III, we study the (130) symmetrical tilt boundary in an fcc lattice. This boundary has a misorientation angle of 36°52′ between the ⟨100⟩ axis of the grains. Two essentially distinct microscopic models, corresponding to the same macroscopic geometry, are examined. We calculate the electronic density of states in the neighborhood of the boundary and estimate the electronic contribution to its energy of formation. In Sec. IV we summarize the main results and present our conclusions.

II. GENERAL FORMALISM

In this section we develop the general formalism for the calculation of the density of states. Although it is basically the same as that discussed in Refs. 15 and 16, when dealing with grain boundaries there are some differences which must be taken into account. It is convenient to start by describing briefly the geometry of the boundary. In this work we limit ourselves to symmetrical tilt boundaries, an example of which is shown in Fig. 1. This boundary may be decomposed for the purposes of our calculation into two stepped surface half crystals separated by a mirror plane which contains a layer of atoms. As we shall see in the next section, there are different microscopic models compatible with the same macroscopic geometry of the boundary. The strict mirror symmetry, as well as the presence of atoms on
the mirror plane, are not absolutely necessary. Based on the decomposition above, the general Hamiltonian is written

$$H = H_{\text{be}}(+) + H_{\text{eb}} + H_{\text{be}}(-),$$

(2.1)

$$H_{\text{be}}(+) = \sum_{n=1}^{N} \sum_{\nu} \left( n_k \mu \right) H_{\nu n}(n, \vec{k})(n_k \nu) + \sum_{n' \neq n} \left( n' \vec{k} \mu \right) H_{\nu n}(n', \vec{n})(n \nu k),$$

(2.2)

$$H_{\text{eb}} = \sum_{n} \left( \sum_{\nu} \left( n \vec{k} \mu \right) H_{\nu n}(1, A, \vec{n})(A \vec{k} \nu) \right) + \left( n \vec{k} \mu \right) H_{\nu n}(1, -1, \vec{n})(A \vec{k} \nu) + \sum_{n'} \left( n' \vec{k} \mu \right) H_{\nu n}(1, -1, \vec{n})(-1 \nu k),$$

(2.3)

with an expression similar to (2.2)—summation over negative $n$'s—for $H_{\text{eb}}(-)$. In these equations $n$ is the layer index, $\vec{k}$ is a two-dimensional wave vector varying within the Brillouin zone corresponding to the layer periodicity, $\mu$ and $\nu$ refer to atom and orbital indices within a primitive cell of the layer, $A$ refers to the extra layer of atoms associated with the layer, and $\lambda$ to atom and orbital indices within the primitive cell of this layer. The various matrices $H(n, \vec{k})$, $H(n', n, \vec{k})$, etc., are constructed according to the rules discussed in Ref. 16. For $H_{\text{eb}}$ we make the further assumption that the overlap matrix elements are nonzero only between the extra layer and the top layers of the two half crystals and between these two top layers themselves. As in previous discussions, we choose a primitive cell in the layers such that the overlap matrices

$$H_{\nu n}(n', n, \vec{k}) = 0 \text{ for } |n' - n| > 1.$$  

(2.4)

In the bulk of the half crystals, that is, for $n$ and $n'$ sufficiently large, we have

$$H_{\nu n}(n, \vec{k}) = H_{\nu n}(-, \vec{k}) = H_{\nu n}(b, \vec{k}),$$

(2.5)

where $H_{\nu n}$ represent the Hamiltonians for the two isolated stepped surface half crystals and $H_{\nu n}$ includes all the terms which refer to the boundary and the coupling between the half crystals. These are thought to as being built by regularly stacking up layers of atoms in the direction normal to the average surface direction. The layers have full two-dimensional periodicity. In the case under discussion of a symmetrical tilt boundary, the layers have the same translational periodicity on both sides of the boundaries. (Notice that the half crystals may be displaced relatively to each other in the plane of the boundary without invalidating the preceding statement.) The extra layer of atoms of Fig. 1 also has a commensurate two-dimensional periodicity. All the electronic states may thus be classified by a unique set of Bloch wave vectors.

In the tight-binding approximation the Hamiltonian (2.1), after transforming to the two-dimensional Bloch representation, may be written

$$H_{\nu n}(n, n' + 1, \vec{k}) = H_{\nu n}(n, n - 1, \vec{k}) = H_{\nu n}(1, b, \vec{k}),$$

(2.6)

and

$$H_{\nu n}(n, n' - 1, \vec{k}) = H_{\nu n}(n, n + 1, \vec{k}) = H_{\nu n}(1, -1, \vec{k}),$$

(2.7)

with $H_{\nu n}(1, b) = H(1, b)$.

Our aim is to calculate the spectral density of states

$$\rho(\alpha, \vec{k}, \epsilon) = -(1/\pi) \text{Im} \langle \alpha \vec{k} | G(\epsilon + i0^+) | \alpha \vec{k} \rangle,$$

(2.8)

where $\alpha$ denotes all the other indices necessary to classify the orbitals and

$$G(z) = (z - H)^{-1}$$

(2.9)

is the resolvent of the Hamiltonian (2.1). The method of solution is based upon the transfer matrix formalism of Yndurain and Falicov and is illustrated below.

To begin with, let us solve the problem of one isolated half crystal by calculating the appropriate matrix elements of the resolvent (2.9) at the surface. The following abbreviation is used:
and the explicit k dependence of the Hamiltonian matrices is not written down. By rewriting (2.9) as
\[ zG(z) = I + HG(z) \]
and taking matrix elements we arrive at
\[
[zI - H(1)]G_{11}^0 = I + H(1, 2)G_{21}^0
\]
\[
[zI - H(b)]G_{21}^0 = H(2, 1)G_{11}^0 + H(1, b)G_{11}^0
\]
\[
[zI - H(b)]G_{11}^0 = H(-1, b)G_{n+1,1}^0 + H(1, b)G_{n+1,1}^0
\]
\[ + H(1, b)G_{n+1,1}^0 \quad \text{for } n \geq 3. \]

In writing these equations we make the assumption that relaxation effects are important only at the surface layer and between the surface layer and the layer immediately below it. The ansatz
\[ G_{n+1,m}^0 = S_{n+1,m}^0 \quad n > m \]
with
\[ [zI - H(b)]S = H(-1, b) + H(1, b)S \]
solves the set of equations (2.12), and we find
\[ G_{11}^0 = [zI - H(1) - H(-1, 2)[zI - \Sigma]^{-1}H(2, 1)]^{-1}, \]
where
\[ \Sigma = H(b) + H(1, b)S. \]

Similar, but algebraically more complicated expressions are obtained for \( G_{nm}^0. \)

We can now solve the problem for the grain boundary. This is illustrated by the calculation of \( G_{AA}. \) (Notice that the dimension of the matrix \( G_{AA} \) may be, and in general is, different from that of \( G_{nm}. \) We do not care to distinguish the two different unit matrices in the equations below, their dimension being uniquely determined by the context.) Taking matrix elements of (2.11) with the full Hamiltonian (2.1), we find
\[ [zI - H(b)]G_{nm,1}^A = H(1, b)G_{m-1,1}^A + H(-1, b)G_{m+1,1}^A \]
\[ [zI - H(-1)]G_{11,1}^A = H(-1, -2)G_{-1,1}^A + H(-1, 1)G_{11,1}^A \]

These equations are valid for \( n > 1. \) The solution for the set of equations for the two half crystals, because of the mirror symmetry of the boundary, reduces to the solution of the problem of a single half crystal. We may then easily see that

A similar calculation yields for the top layer of the half crystal in the presence of the boundary
\[ G_{11}^A = G_{0}^A - H(1, -1) \]
\[ - H(A, 1)G_{0}^A - H(-1, -1)G_{0}^A - H(1, -1) \]
\[ + H(-1, -1)G_{0}^A - H(1, -1) \]
\[ + H(-1, -1)G_{0}^A - H(1, -1) \]
\[ + H(-1, -1)G_{0}^A - H(1, -1) \]

which should be compared with (2.15), the equation in the case of a "free" surface. If there are no extra atoms in the boundary layer, then (2.18) is meaningless and (2.19) reduces to the first two terms on the right-hand side.

For the second layer we find
\[ G_{22} = zI - \Sigma - H(2, 1)(zI - Q)^{-1}H(2, 1), \]
where
\[ Q = H(1) + H(A, -1)G_{0}^A + H(-1, -1)G_{0}^A \]
\[ + H(-1, -1)G_{0}^A + H(1, -1)G_{0}^A \]

From Eqs. (2.18), (2.19), (2.21), and the definition of the spectral density of states (2.8) we are able to analyze the electronic structure of the grain boundary. This is done in the next section.
for a simple model Hamiltonian.

III. RESULTS

We consider the (130) symmetrical tilt boundary of an fcc lattice with a misorientation angle of 36°2' between the (100) axis of the grains. Our choice of this boundary is dictated by two considerations. First, it has been extensively studied by computer simulation techniques. Estimates of its energy (~1000 ergs/cm²) indicate that it is quite likely to occur. A boundary with the corresponding macroscopic geometric parameters has been observed. Second, it has a sufficiently small primitive cell—four atoms, as shown in Fig. 1—to allow an application of our method which is not too costly computationally. Although we limit ourselves in this work to an s-like tight-binding Hamiltonian, the size of the matrices involved in the calculation is such that we can extend it to a more realistic sd Hamiltonian.

We discuss separately the results for the models of Hasson et al. and for a version of the models of Weins and Smith et al. The relevant Hamiltonian matrices for the bulk, surface, and grain boundary are given in Tables I–V. In these tables

\[
\xi = \exp(ik_x a'), \\
\eta = \exp(ik_y a'),
\]

where \(a\) is the lattice parameter and \(a' = \sqrt{10} a/2\) is the long dimension of the primitive cell, parallel to the (130) plane.

For the bulk we take

\[
E_1 = 0, \\
V_{ij} = W_{ij} = -1, \quad i, j = 1, 4.
\]

This gives the standard s-like tight-binding Hamiltonian on an fcc lattice written in a convenient form for the solution of the surface and grain boundary problems. In Fig. 2 we present the dispersion curve along a particular direction of the three-dimensional Brillouin zone (BZ). It corresponds to the \((\pi/2, \pi/2)\) point of the two-dimensional (2D) BZ, which is the simplest choice for calculating averages over the zone. At this point, the bulk states projected onto the average surface direction extend from ~8.83 to 3.84 energy units. Naturally, there is no gap in the spectrum for a simple s band. Intrinsic surface or grain boundary states split off the top or the bottom of the band. The Fermi energy may be estimated from this single-point approximation to be \(E_F = 1.60\) for one electron per atom. The total band energy is \(U_3 = -2.60\) per electron. These results should be compared with the exact ones: \(E_F = 0.92\) and \(U_3 = -2.62\). Hence, in the estimates of total band energies below, we limit ourselves to a single averaging point in the irreducible part of the 2D BZ.

### Table I: Matrix elements of the intraslab Hamiltonian \(H(n, n-1)\). The elements not shown are zero. In the bulk, all parameters \(W_{ij} = V_4\).

\[
\begin{align*}
(1, 1) &= W_{11} \\
(1, 2) &= W_{12}(1 + \eta *) \\
(1, 3) &= W_{13} \\
(1, 4) &= W_{14}\xi^*(1 + \eta *) \\
(2, 2) &= E_2 \\
(2, 3) &= W_{23}(1 + \eta) \\
(2, 4) &= W_{24}\xi^* \\
(3, 3) &= E_3 \\
(3, 4) &= W_{34}(1 + \eta *) \\
(4, 4) &= E_4
\end{align*}
\]

### Table II: Matrix elements of the interlab Hamiltonian \(H(n, n - 1)\). The elements not shown are zero.

\[
\begin{align*}
(1, 1) &= W_{11} \\
(1, 2) &= W_{12}(1 + \eta *) \\
(1, 3) &= W_{13} \\
(1, 4) &= W_{14}\xi^*(1 + \eta *) \\
(2, 2) &= W_{22} \\
(2, 3) &= W_{23}(1 + \eta) \\
(2, 4) &= W_{24} \\
(3, 3) &= W_{33} \\
(3, 4) &= W_{34}(1 + \eta *) \\
(4, 4) &= W_{44}
\end{align*}
\]

### Table III: Matrix elements of the intergrain Hamiltonian matrix \(H(-1, 1)\). The matrix elements not shown are taken to be zero.

\[
\begin{align*}
(1, 1) &= U_{11} \\
(1, 2) &= U_{12}\xi^*(1 + \eta *) \\
(1, 3) &= U_{13}\xi^* \\
(2, 1) &= U_{21}(1 + \eta) \\
(3, 1) &= U_{31}
\end{align*}
\]
TABLE IV. The $2 \times 2$ matrix $H(1,1)$ which describes the extra layer of atoms in the grain boundary model of Fig. 1. The element not shown is obtained by Hermiticity.

$$(1,1) = E_1$$
$$(1,2) = V_{12}$$
$$(2,1) = V_{21}$$
$$(2,2) = E_2$$

A. Model I

This model is shown in Fig. 1. It is based upon the computer simulations of Hasson et al. The initial parameters for the numerical calculation are determined by attributing the bulk value to all atomic levels and either the bulk value or zero to transfer matrix elements across the boundary. The nonzero matrix elements are (cf. Tables III-V) $U_{11}$, $V_{12}$, $U_{12}$, $V_{21}$, $U_{22}$, $V_{23}$. This we call the no-relaxation model. It should be remarked that, due to the lack of empirical data concerning the actual positions of the atoms in and around the boundary, there is not much point in making an estimate for the values of the transfer matrix elements, especially in our simplified model Hamiltonian. We calculate in this model, the local density of states using a four-point approximation within the irreducible part of the 2D BZ: $\frac{1}{2}\pi(1,1)$, $\frac{1}{2}\pi(1,3)$, $\frac{1}{2}\pi(3,1)$, $\frac{1}{2}\pi(3,3)$. The charge transfer is evaluated in the standard manner by integrating $\rho(E)$ up to $E_F$. In this case we have used the corresponding four-point approximation in the bulk to evaluate $E_F$. In Fig. 3 we show the result for the spectral density of states at point $\frac{1}{2}\pi(1,1)$ for the no-relaxation model, averaged over the two atoms in the boundary (lower curve) and the four atoms in the first layer next to the boundary (upper curve). We find that roughly 0.2 electrons per atom are transferred from the bulk to the boundary. In order to restore charge neutrality, we change the site (atomic) energies of the atoms near the boundary until this charge transfer is reduced to zero. The energy relaxation is $\Delta = 0.5$.

The results for the relaxed model for the same $\frac{1}{2}\pi(1,1)$ point are shown in Fig. 4. Both results are characterized by a large peak near the top of the band, typical of the s-like fcc tight-binding band and a split-off state above the top of the band. In the relaxed model, since the atomic levels are

TABLE V. Matrix elements of the $4 \times 4$ matrix $H(1,1,1,1)$, representing the coupling between the atoms in the first slab below, or above, the boundary plane and the atoms in the extra boundary layer of Fig. 1. The elements not shown are taken to be zero.

$$(1,1) = U_{11}(1 \pm \eta)$$
$$(1,2) = U_{12}$$
$$(2,1) = U_{21}$$
$$(2,2) = U_{22}(1 \pm \eta)$$
$$(3,1) = U_{31}(1 \pm \eta)$$
$$(3,2) = U_{32}$$
moved up in energy, the structures in the continuum are also displaced in the same direction. As can be seen from Table VI, there is practically no change in the weight of the localized states. The relaxation mechanism adopted is not the only one possible; physically it is clear that changes in the overlap matrix elements are also necessary. However, the presence of a localized state associated with the boundary is probably independent of the choice of parameters, provided this is done within a reasonable interval. These states do not exist throughout the 2D BZ, but are concentrated near its center. In Fig. 5, we show the results for the relaxed model at the point \( \frac{1}{2} \pi (3,3) \). At this point, and also at \( \frac{1}{2} \pi (1,3) \) and \( \frac{1}{4} \pi (3,1) \), there is no evidence for split-off states. The electronic band-energy contribution to the grain boundary energy can be calculated within this approach. This is done by defining

\[
U_n = \int_{-\infty}^{\infty} dE \rho(n;E),
\]

where \( \rho(n;E) \) is the average local density of states for the nth layer, evaluated by summing (2.8) over all points in the 2D BZ and averaging the result over all sites in the primitive cell of the layer. The quantity \( U_n \) represents then the average band energy per site in the nth layer. The grain boundary band energy is calculated from

\[
U = \sum_{n=1}^{N} \frac{1}{\sigma} \sum_{\nu=1}^{v} \nu_n (U_n - U_{\infty}),
\]

where \( N \) is the total number of atoms in the layer. The energy density is obtained by dividing (3.4) by the total interface area

\[
\frac{U}{S} = \frac{1}{\sigma} \sum_{n=1}^{N} \nu_n (U_n - U_{\infty}),
\]

where \( \sigma \) is the area of the projection of the primitive cell onto the boundary plane and \( \nu_n \) is the number of atoms per primitive cell (\( \nu = 2 \) for the grain boundary plane and \( \nu = 4 \) for all other planes). In (3.4) and (3.5), \( U_{\infty} \) is the band energy per site in the bulk. Numerically, we expect these sums to converge quite rapidly, because \( U_n \)

\[
\begin{array}{c|c|c|c|c}
\text{Atom} & \text{Energy} & \text{Weight} & \text{Energy} & \text{Weight} \\
\hline
A & 4.20 & 0.28 & 4.65 & 0.31 \\
B & - & - & - & - \\
1 & 0.06 & 0.07 & - & - \\
2 & 0.00 & 0.00 & - & - \\
3 & 0.15 & 0.15 & - & - \\
4 & 0.09 & 0.10 & - & - \\
\end{array}
\]
tends to $U_{\text{e}}$ within a few layers of the boundary plane. We have not included in these expressions the electron-electron interaction contribution to the total energy. Since in the present calculation the electronic density is "rigid", this contribution cancels out exactly in the difference (3.5). We expect this feature of the calculation to cause a considerable increase in the energy of the boundary. For the model of Fig. 1, we find

$$\sigma = \sqrt{10}a^2/2$$

and

$$\sum \nu_s (U_s - U_{\text{m}}) = 6.4 |V|,$$

where we have reintroduced explicitly the energy unit.

Our model may be considered as an approximation to the monoatomic, monovalent, fcc noble metals Cu, Ag, and Au, at least as far as the s electrons are concerned. Hence, to estimate the grain boundary energy, we take $a = 4$ Å and $|V| = 0.8$ eV. The latter figure yields a total s bandwidth of 12.8 eV. With these parameters we find for the specific grain energy 3200 ergs/cm$^3$, a value which is considerably larger than that obtained by computer simulation studies.$^9$-$^{12}$ We comment upon this below.

B. Model 2

The second model which we consider is shown in Fig. 6. It differs from model 1 in two respects: There are no additional boundary atoms and the half crystals are displaced relative to each other. Such a model was proposed by Weins et al.$^{10}$ and more recently by Smith et al.$^{11}$ Macroscopically, the two boundaries are indistinguishable, and microscopically we still do not have the means to distinguish them experimentally.

![FIG. 6. Model for the (130) symmetrical tilt boundary based upon computer simulation results of Ref. 11.](image)

The intergrain matrix elements of the Hamiltonian, Table III, are all nonzero and taken equal to $-0.80$, hence slightly smaller in magnitude than the bulk ones. The absence of boundary atoms implies that the Hamiltonian matrices shown on Tables IV and V are not needed. In Fig. 7 we show the average density of states for the $\Gamma$ point of the 2D BZ, calculated in the no-relaxation model. The upper curve is the result for the atoms in the cell at the boundary. There is a split-off state at the top of the band of weight 0.09. The lower curve shows the result for the stepped surface; it is interesting to observe that no split-off state is seen in this case. Hence, the localized state mentioned above is characteristic of the grain boundary.

![FIG. 7. Average spectral density of states at point $\Gamma$ of the 2D BZ for model 2, without relaxation. Upper curve: atoms adjacent to grain boundary; lower curve: stepped surface results.](image)

We have performed a similar study as that described in Sec. IIIA for the density of states and electronic contribution to the total energy. The following points are worth remarking. (i) In the first three layers, without any relaxation, there is a charge excess of 0.0196 electron per atom, which, within the precision of our calculation means that these layers taken together are electrically neutral. The charge excess distribution per atom is the following. First layer: $+0.0781e$; second layer: $-0.0246e$; third layer: $+0.0053e$. The magnitudes of these numbers indicate the degree of convergence towards the bulk value of
zero charge excess. (ii) The total electronic band energies per atom are first layer: \(-2.38\); second layer: \(-2.55\); third layer: \(-2.52\). (iii) By relaxing the atomic levels of the individual atoms in the first and second layers we can reduce the charge excess of each atom essentially to zero. These relaxations are first layer, atom 1: 0.60; atom 2: 0.20; atom 3: 0.35; second layer, atom 2: \(-0.35\). (iv) The resulting total energies are first layer: \(-2.18\); second layer: \(-2.59\); third layer: \(-2.52\). Hence we see that, except for the first layer, imposing charge neutrality does not change considerably the energies. (v) The total energy per cell—cf. Eq. (3.6)—is \(2.80|V|\) for the unrelaxed model and \(4.08|V|\) for the relaxed model. The relaxed model has a higher band energy than the no-relaxation one because of the upward shift of the atomic levels. Coulomb corrections should lower the energy of the relaxed model. The respective specific grain energies are \(1400\) ergs/cm\(^2\) and \(2040\) ergs/cm\(^2\). In both cases, we find a result smaller than that of model 1.

It is interesting that model 2 predicts a smaller band energy than model 1. Although we may be tempted to conclude from this that model 2 is more likely the correct one, such a conclusion is not warranted because we have not evaluated total energies. In fact, we neglected both the Coulomb corrections and the Madelung contribution. The Coulomb correction is difficult to treat without our approach, although not hopeless, if an approach similar to that of Pei\(^{22}\) is used. The Madelung correction is easier to treat but falls outside the scope of the present paper. We believe that the present results make it worthwhile to try to improve these calculations with a view of deciding between different microscopic models of the same macroscopic boundary.

IV. CONCLUSIONS

We have presented a detailed study of the electronic structure of a model grain boundary in an s-like tight-binding fcc metal. We use two different microscopic models for the same macroscopic boundary parameters, based upon computer simulation studies. Both electronic densities of states and total band energies are evaluated. The main conclusions are: (i) There exist, within a limited domain of the two-dimensional Brillouin zone, localized states associated with the boundary; in the present case they lie above the top of the continuum of band states in an "absolute gap"; (ii) the band (electronic) energy contribution to the specific boundary energy is higher for model 1 (shown in Fig. 1) than for model 2 (shown in Fig. 6)—this result suggests that the latter may be the one actually realized in nature. The present calculation may be extended to treat other grain boundary geometries, more realistic Hamiltonians, and the Coulomb contribution to the total energy. We hope that such calculations will stimulate experimental work aimed at detecting the boundary states.

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