

Generalization of Equivalent Crystal Theory to Include Angular Dependence

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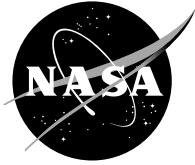
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Acknowledgments

We would like to thank the Tribology and Surface Science Branch, NASA Glenn Research Center, where part of the work was performed. We also thank Dr. Phillip Abel for fruitful comments.

This work was sponsored by the Low Emissions Alternative Power Project of the Vehicle Systems Program at the NASA Glenn Research Center.

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Abstract

In the original Equivalent Crystal Theory, each atomic site in the real crystal is assigned an equivalent lattice constant, in general different from the ground state one. This parameter corresponds to a local compression or expansion of the lattice. The basic method considers these volumetric transformations and, in addition, introduces the possibility that the reference lattice is anisotropically distorted. These distortions however, were introduced ad-hoc. In this work, we generalize the original Equivalent Crystal Theory by *systematically* introducing site-dependent directional distortions of the lattice, whose corresponding distortions account for the dependence of the energy on anisotropic local density variations. This is done in the spirit of the original framework, but including a gradient term in the density. This approach is introduced to correct a deficiency in the original Equivalent Crystal Theory and other semiempirical methods in quantitatively obtaining the correct ratios of the surface energies of low index planes of cubic metals—(100), (110), (111). We develop here the basic framework, and apply it to the calculation of Fe (110) and Fe (111) surface energy formation. The results, compared with first principles calculations, show an improvement over previous semiempirical approaches.

Introduction

Equivalent Crystal Theory (ECT) is a method to calculate energies of atomic conglomerates. It has been very successful in predicting formation energies of bulk defects. Bozzolo, Ferrante and Smith (BFS) have extended it to multicomponent metals, and have successfully used it to predict the ground state structures and surface properties of various alloys.

The basic idea of the original Equivalent Crystal Theory (OECT) rests on the fact that the total ground state energy of a quantum system is a functional of the electron density [1]. Therefore, OECT requires that, at the atomic site under consideration, the density be the same for both the real lattice and the equivalent, defect-free lattice. That provides a value for the equivalent lattice parameter a_{eq} at that site. The energy contribution from that site is obtained by using the Universal Binding Energy Relation (UBER) curve. The UBER provides binding energy as a

function of average atomic separation (or in this case, lattice parameter). In this work, we generalize OECT without losing its original flavor, that is, by keeping the assumption that the electron density must remain the same for both the real and the equivalent crystal. However, here we extend it to include non-local effects by requiring that both, the real and equivalent crystal densities be the same not only at the center of the atomic site into consideration, but also in a neighborhood around that point. Concretely, we will impose that the density at an atomic site and its gradient be the same for the real and the equivalent crystal. These density variations in the neighborhood can be estimated from recent ab initio calculation for surface binding curves for Fe. The reference crystal now includes both isotropic distortions and separation of the solid in two pieces normal to a given surface plane.

In this new framework, the reference crystal at an atomic site will be assigned two (instead of one) parameters: the equivalent lattice parameter *and* the relative separation, γ , between two hypothetical surfaces. The direction of the separation, and the separation itself, do not have to be the same for all the real atoms in the crystal. We will call that, potentially variable, direction z . The two parameters are obtained from two requirements, which are: the site density and its gradient at each location are assumed the same for both the real and the equivalent crystal.

Development of the Ideas

In this modified version of ECT (MECT), the reference crystal is not just a perfect lattice with $a \neq a_0$, but, in addition, it incorporates a pair of surface-terminated bulks with $a \neq a_0$, separated by a distance γd , where d is the interplanar distance normal to a particular plane.

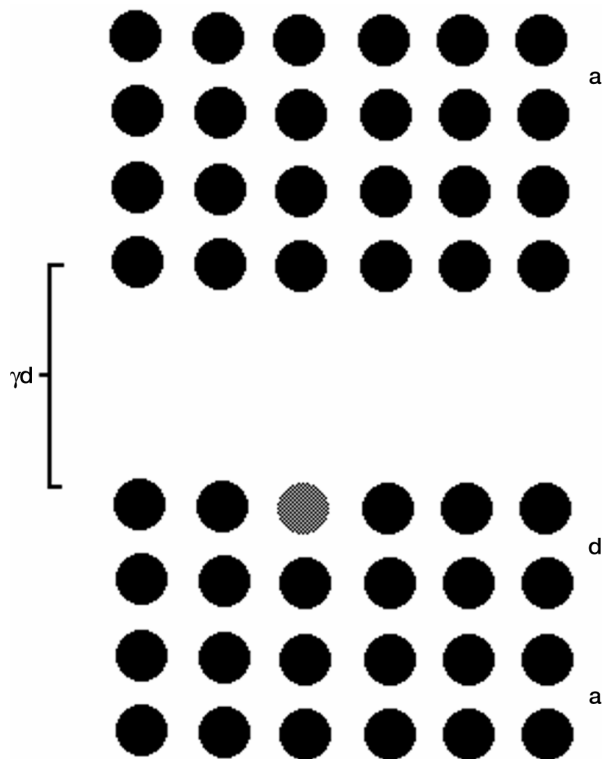


Figure 1.—Reference crystal.

Figure 1 shows the reference crystal in a generic configuration. Clearly, as opposed to the original ECT (OECT), not all atoms in this reference crystal contribute the same amount to the total energy. We will consider the local energy contribution coming from a reference atom in the (quasi) surface (QS), shown in red in the figure. The quasi-surface becomes a bona fide surface in the limit $\gamma \rightarrow +\infty$. An atom in QS (AQS) contribution to the total energy is now a function of both the lattice parameter \underline{a} , and the relative distance γ , between the two QS. This differs in form from OECT which expands the energy in a series containing a volume term, plus two-, three-, and four-body terms. In this formulation, the next term beyond the volume's would be the gradient of the density, and the next beyond that would be the curvature.

In OECT, \underline{a} was found by requiring that the total electron density at the center of a given atom be the same for both the real defect crystal and the reference crystal. That condition will remain valid in MECT, but we will impose a second constraint. The motivation for the additional equation is to also look at the density close to the center of the given atom, not only at the center. We will impose that the real and reference densities must be equal in that small (but not zero) region. As in OECT, we take the densities from each atom to be given by $\rho(\vec{r}) = \sum_{\vec{R}} |\vec{R} - \vec{r}|^p e^{-\alpha|\vec{R} - \vec{r}|}$, with standard notation. Consider the atom for which we want to calculate the energy contribution, to be located at the origin. We expand $|\vec{R} - \vec{r}|$ taking into account that $r \ll R$:

$$\rho(\vec{r}) = \rho(\vec{0}) + \vec{r} \cdot \nabla \rho(\vec{r})|_{\vec{r}=\vec{0}} + \dots \quad (1)$$

Then, expanding the power and the exponential,

$$\rho(\vec{r}) \approx \sum_{\vec{R}} R^p e^{-\alpha R} + \vec{r} \cdot \sum_{\vec{R}} (\alpha R - p) R^{p-1} e^{-\alpha R} \frac{\vec{R}}{R} \quad (2)$$

From this expression, we will impose:

$$\sum_{\vec{R}_{\text{equivalent}}} R^p e^{-\alpha R} = \sum_{\vec{R}_{\text{real}}} R^p e^{-\alpha R} \quad (3)$$

$$\left[\sum_{\vec{R}_{\text{equivalent}}} (\alpha R - p) R^{p-1} e^{-\alpha R} \frac{\vec{R}}{R} \right] \cdot \hat{n}_e = \left[\sum_{\vec{R}_{\text{real}}} (\alpha R - p) R^{p-1} e^{-\alpha R} \frac{\vec{R}}{R} \right] \cdot \hat{n}_r \quad (4)$$

where \hat{n}_e and \hat{n}_r are fixed directions in the respective spaces.

Both right-hand sides are explicit functions of γ and \underline{a} and will be obtained by solving (3) and (4).

Generalization of UBER

The most critical issue to stress in MECT is the fact that, as opposed to what happens in OECT, not all atoms in the reference crystal are equivalent and therefore contribute a different amount to the total energy.

Let us assign the energy contribution from each atom to the total energy

$$E_n = E_{AQS} + (E_B - E_{AQS})[1 - e^{-\lambda(n-1)}] \quad (5)$$

where all atoms in the same plane n will be weighted equally, but atoms in different layers will have a different contribution. Here E_B is the contribution from bulk (which is given by the OECT UBER), E_{AQS} is the (still unknown) contribution from AQS, $\lambda \approx 1/M$ (M is the number of layers in which atoms are substantially different from bulk), finally n is the layer's depth ($n = 1$ corresponds to the top layer, our QS). Here we have assumed an exponential form for the contribution to the energy as a function of depth. Hung et al [2] have shown that the electron density in slabs of increasing widths rapidly approaches its bulk value .

The total energy E_{tot} can be calculated as:

$$E_{Tot} = N_A \sum_{n=1}^{+\infty} E_n = N_A \cdot N_D \cdot E_B + N_A \cdot (E_{AQS} - E_B) \cdot \sum_{n=1}^{+\infty} e^{-\lambda(n-1)} \quad (6)$$

Where N_A is the number of atoms in-plane, N_D is the number of layers (although the sum goes to infinity here, in practice N_D is very large but not infinite).

Calling $N = N_A \cdot N_D$, the total number of atoms, we obtain:

$$E_{Tot} = N \cdot E_B + \frac{N_A \cdot (E_{AQS} - E_B)}{1 - e^{-\lambda}} \quad (7)$$

Hung et al [3] have done a first-principles density functional theory calculation where they obtained the energy as a function of separation of two surface-terminated bulks. Call that energy curve $E(\gamma d_0)$, where $d_0 = ca_0$ is the equilibrium interplanar distance, a_0 is the equilibrium lattice parameter, and c is a geometric factor that depends on the orientation and the crystal structure. Ferrante and Smith [4] defined the adhesive energy as the energy two surfaces have referred to the energy they have when infinitely separated. Since reference [1] reports energy per unit area (A), we have, for one QS:

$$E_{ad}(\gamma) \equiv \frac{E(\gamma) - E(+\infty)}{A} \quad (8)$$

We now make the identification $E_{Tot} = 2E$ in equations (7) and (8), since they both correspond to total energies of the two QSs, calculated independently. Then,

$$E_{ad}(\gamma) = \frac{2N_A}{A} \left[\frac{E_{AQS}(\gamma) - E_B}{1 - e^{-\lambda}} - \frac{E_{AQS}(+\infty) - E_B}{1 - e^{-\lambda}} \right] \quad (9)$$

When $\gamma = 1$, the two QSs are separated by their equilibrium distance, and then $\lambda = 0$ and $E_{AQS} = E_B$. Thus, in that case:

$$E_{ad}(1) = \frac{2N_A}{A} \frac{E_B - E_{AQS}(+\infty)}{1 - e^{-\lambda}} \quad (10)$$

and

$$E_{AQS}(+\infty) = E_B + \frac{A}{2N_A} (e^{-\lambda} - 1) E_{ad}(1) \quad (11)$$

Substituting (11) into (9):

$$E_{ad}(\gamma) = \frac{2N_A}{A} \frac{E_{AQS}(\gamma) - E_B}{1 - e^{-\lambda}} + E_{ad}(1) \quad (12)$$

Solving for $E_{AQS}(\gamma)$, which is the energy of the reference atom AQS,

$$E_{AQS}(\gamma) = E_B + \frac{A}{2N_A} (1 - e^{-\lambda}) [E_{ad}(\gamma) - E_{ad}(1)] \quad (13)$$

Call Γ the area occupied by an AQS, that is $\Gamma \equiv \frac{A}{N_A}$. If E_B is the energy per atom, then the energy per 2D Wigner-Seitz area is:

$$E_{AQS}(\gamma) = \frac{E_B}{\Gamma} + \frac{1}{2} (1 - e^{-\lambda}) [E_{ad}(\gamma) - E_{ad}(1)] \quad (14)$$

The term E_B has been parameterized [5] by the Universal Binding Energy Relation (UBER):

$$E_B(x) = E_c \left[1 - \left(1 + a^* e^{-a^*} \right) \right] \quad (15)$$

where $x = \frac{a}{a_0}$, is the relative lattice parameter of the reference crystal, E_c is the bulk cohesive energy, and:

$$a^* = \frac{a}{\ell_B} \left(\frac{3}{8\pi} \right)^{\frac{1}{3}} (x - 1) \quad (16)$$

for BCC structures. Here ℓ_B is related with the bulk modulus and is known for metals [6,7], and a is the lattice parameter.

$E_{ad}(\gamma)$ in equation (12) has also been parameterized by a UBER in reference [1]:

$$E_{ad}(\gamma) = -2\gamma_s \left[1 + \frac{d}{\ell_s}(\gamma - 1) \right] e^{-\frac{d}{\ell_s}(\gamma - 1)} \quad (17)$$

It is important to note that the last expression is valid only for $a = a_0$ since that is the calculation performed in reference [1]. We need to extend it to any value of γ and a .

If they had done the same (adhesion) calculation for a crystal with a larger lattice parameter, the energy (for a given relative separation) would have been smaller. In particular, in the limiting case $a \rightarrow +\infty$, the energy of the system tends to zero, for any separation. On the other hand, the first principles calculation $A(\gamma)$ (explicitly written in terms of the relative separation) has a minimum for $\gamma = 1$, that is for a separation equal to the lattice parameter (or the corresponding interplane distance). Finally, we write the excess (referred to the bulk ground state) energy of the reference atom AQS as:

$$\Delta E_{AQS} = E_c \left[1 - \left(1 + a^* e^{-a^*} \right) \right] + \gamma_s \left\{ 1 - \left[1 + \frac{x d_0}{\ell_s}(\gamma - 1) \right] e^{-\frac{x d_0}{\ell_s}(\gamma - 1)} \right\} e^{-a^*} \quad (18)$$

This expression is built in such a way that the ground state of the system corresponds to $\gamma = 1$ and $x = 1$, that is an undistorted crystal with the equilibrium lattice parameter. Any configurational change, away from that structure, can only increase the energy.

Setting the Reference QS (100)

In this section, we build a reference crystal as a BCC (100) QS.

Figure 2 shows the geometry for the BCC (100) QS. We take a “unit cell” in which the atoms below the QS are allowed to move under isotropic transformations. The atoms above the QS, can support both volume and surface-surface separation transformation. Nearest neighbors to AQS are denoted \vec{R} and \vec{R}_γ . A typical \vec{R}_γ (out of four) is $\vec{R}_\gamma = a(1,1,\frac{1+\gamma}{2}) - \frac{1}{2}a(1,1,1) = \frac{a}{2}(1,1,\gamma)$. In order to use equation (4) we will compare the gradient terms along the z direction that is, we take

\hat{n}_r and \hat{n}_e both equal to \hat{z} . We need to evaluate $\cos(\theta) \equiv \hat{R}_\gamma \cdot \hat{z} = \frac{\frac{\gamma}{2}}{\sqrt{\frac{1}{2} + \frac{\gamma^2}{4}}}$. For the neighbors \vec{R} , we

use the previous expression with the sign changed (because they point opposite to the z direction) and with $\gamma = 1$. Then the left hand side of equation (3) becomes (there are four contributions of each kind):

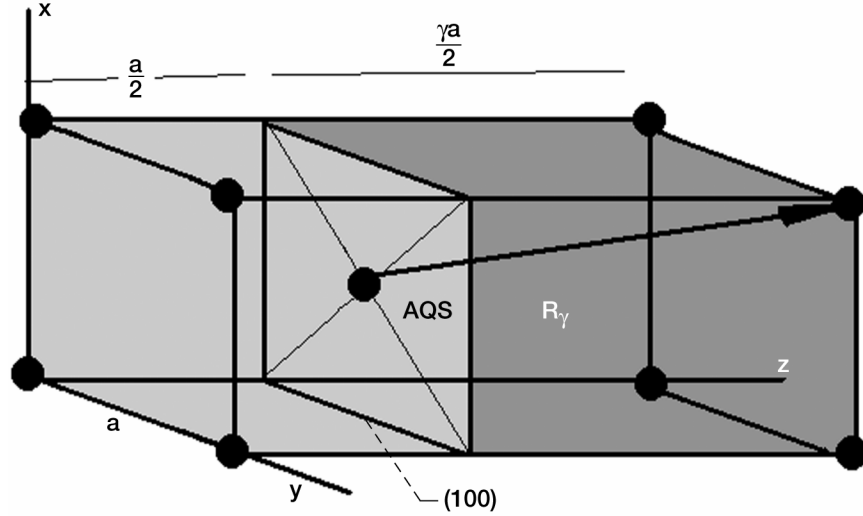


Figure 2.—The AQS in the quasi-free surface (100). The dark volume can only experience dilations controlled by x . The light volume can experience both dilations and separations controlled by γ .

$$\text{Equivalent Gradient} = -\frac{4}{\sqrt{3}}(\alpha R - p)R^{p-1}e^{-\alpha R} + \frac{2}{\sqrt{\frac{1}{2} + \frac{\gamma^2}{4}}}(\alpha R_\gamma - p)R_\gamma^{p-1}e^{-\alpha R_\gamma} \quad (19)$$

where $R = \frac{\sqrt{3}}{2}a_0x$, and $R_\gamma = a_0x\sqrt{\frac{1}{2} + \frac{\gamma^2}{4}}$.

The left hand side of equation (3) can be derived more simply in a similar way:

$$\text{Equivalent Density} = 4R^p e^{-\alpha R} + 4R_\gamma^p e^{-\alpha R_\gamma} \quad (20)$$

Application of the Method

We use the method described in the Generalization of UBER section to predict surface energy formations of Fe (110) and (111). It is necessary to select the reference surface which has the largest density gradient, that is the second term in equation (1). Fortunately, this information is available from reference [2]. With the advent in new ab initio techniques such information can be available for other surfaces of interest.

In order to solve equations (3) and (4) we need evaluate the density and gradient terms for the real crystals of interest and compare them with expressions given in equations (19) and (20).

1) Fe (110) surface energy formation.

Iron's ground state structure is BCC. Figure 3 shows a typical atom. When creating a surface (110) passing through that atom, two near neighbor atoms are lost.

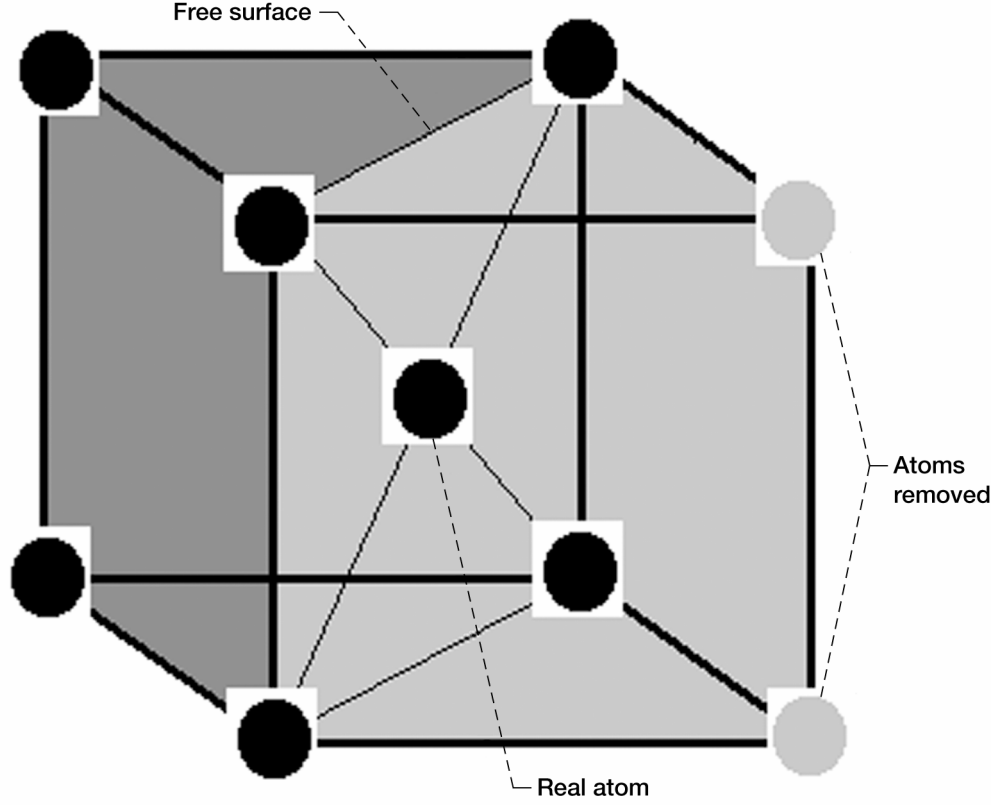


Figure 3.—An atom in the real crystal loses two near neighbors when creating a (110) BCC surface.

The contribution to the density from neighboring atoms is

$$\text{Density}(110) = 6R_0^p e^{-\alpha R_0} \quad (21)$$

with $R_0 = \frac{\sqrt{3}}{2}a_0$, and a_0 the equilibrium lattice parameter.

To calculate the gradient term for BCC (110), we refer to figure 3. We notice that by symmetry the individual gradient terms from neighboring atoms in the (110) plane, when added together, cancel. Then the gradient term reduces to the contributions from the two remaining neighbors in the first layer below the free surface. By symmetry (they make the same angle with respect to the normal to the (110) plane) they both contribute to the sum on the right-hand side of equation (3)

the same amount. One of those neighbors is at $\vec{R} = -\frac{a_0}{2}(1,1,1)$. The direction of the normal to

(110) is $\hat{n} = \frac{(110)}{\sqrt{2}}$. Then $\frac{\vec{R}}{|\vec{R}|} \cdot \hat{n} = -\sqrt{\frac{2}{3}}$. Since the two atoms contribute the same, the gradient term becomes

$$\text{Gradient}(110) = -2\sqrt{\frac{2}{3}}(\alpha R_0 - p)R_0^{p-1}e^{-\alpha R_0} \quad (22)$$

Next we use equations (19), (20), (21) and (22) and substitute in (3) and (4). From that we find the values of γ and x that satisfy the equations. Define

$$\Delta(x, \gamma) = \sqrt{[\text{Equivalent Density} - \text{Density}(110)]^2 + [\text{Equivalent Gradient} - \text{Gradient}(110)]^2}$$

Figure 4 shows a gray level plot of $\Delta(x, \gamma)$ for the parameters of iron. From there a pair of roots is identified at $x = 0.959$ and $\gamma = 1.119$. Substituting these values in equation (18) provides $\Delta E_{\text{AQS}} = 2.49 \text{ J/m}^2$, which compares well with 2.247 J/m^2 from first principles [2, 3].

2) Fe (111) surface energy formation.

Figure 5 shows a typical atom. When creating a surface (111) passing through that atom, four near neighbor atoms are lost.

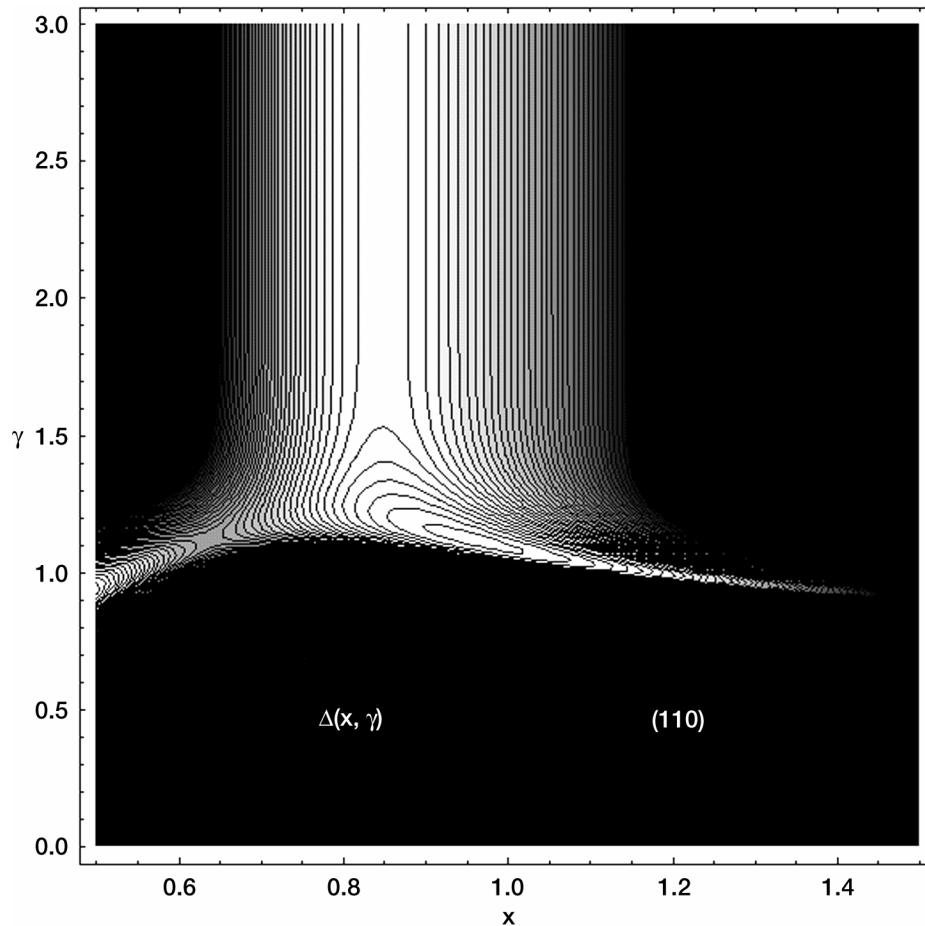


Figure 4.—Function to find the optimal values of x and γ .

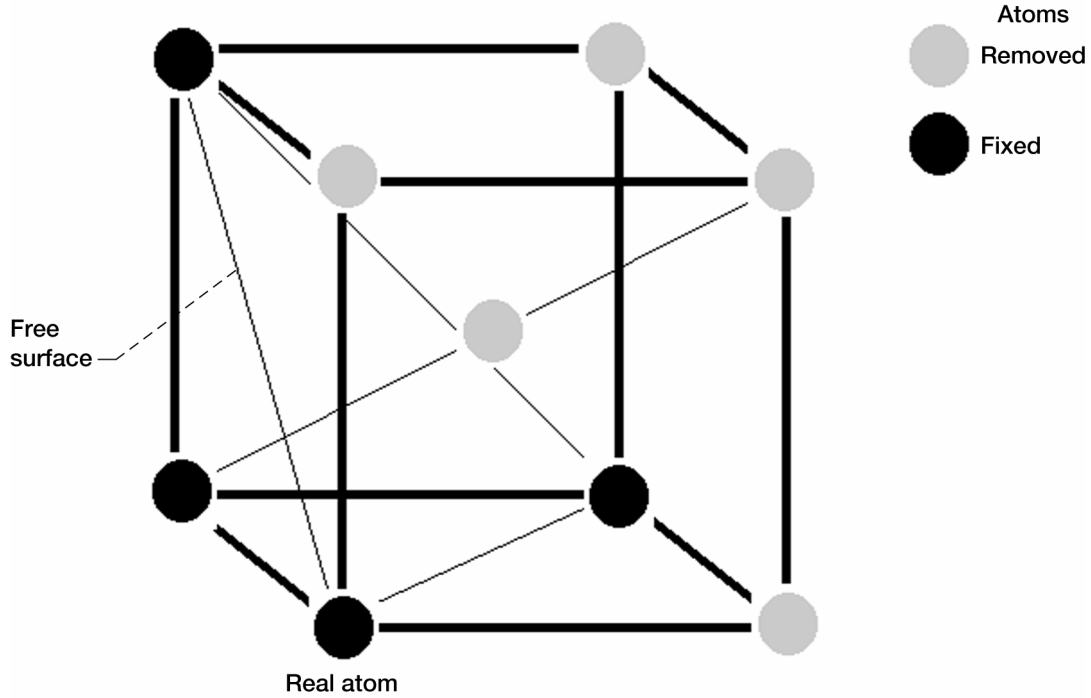


Figure 5.—An atom in the (111) Fe surface loses four near neighbors as compared with bulk.

The gradient term involves three atoms in the first layer below the surface with $\frac{\vec{R}}{|\vec{R}|} \cdot \hat{n} = -\frac{1}{3}$, and one atom in the second layer below the surface with $\frac{\vec{R}}{|\vec{R}|} \cdot \hat{n} = -1$. Then

$$Gradient(111) = -\left(3\frac{1}{3} + 1.1\right)(\alpha R_0 - p)R_0^{p-1}e^{-\alpha R_0} = -2(\alpha R_0 - p)R_0^{p-1}e^{-\alpha R_0} \quad (23)$$

and

$$Density(111) = 4R_0^p e^{-\alpha R_0} \quad (24)$$

Next we use equations (19), (20), (23) and (24) and substitute in (3) and (4). From that we find the values of γ and x that satisfy the equations. Define as in 1)

$$\Delta(x, \gamma) = \sqrt{[Equivalent \ Density - Density(111)]^2 + [Equivalent \ Gradient - Gradient(111)]^2}$$

Figure 6 shows a gray level plot of $\Delta(x, \gamma)$ for the parameters of iron. From there a pair of roots is identified at $x = 1.07006$ and $\gamma = 1.19797$. Substituting these values in equation (18) provides $\Delta E_{AQS} = 2.59 \text{ J/m}^2$, which also compares well with 2.62 J/m^2 from first principles [2, 3].

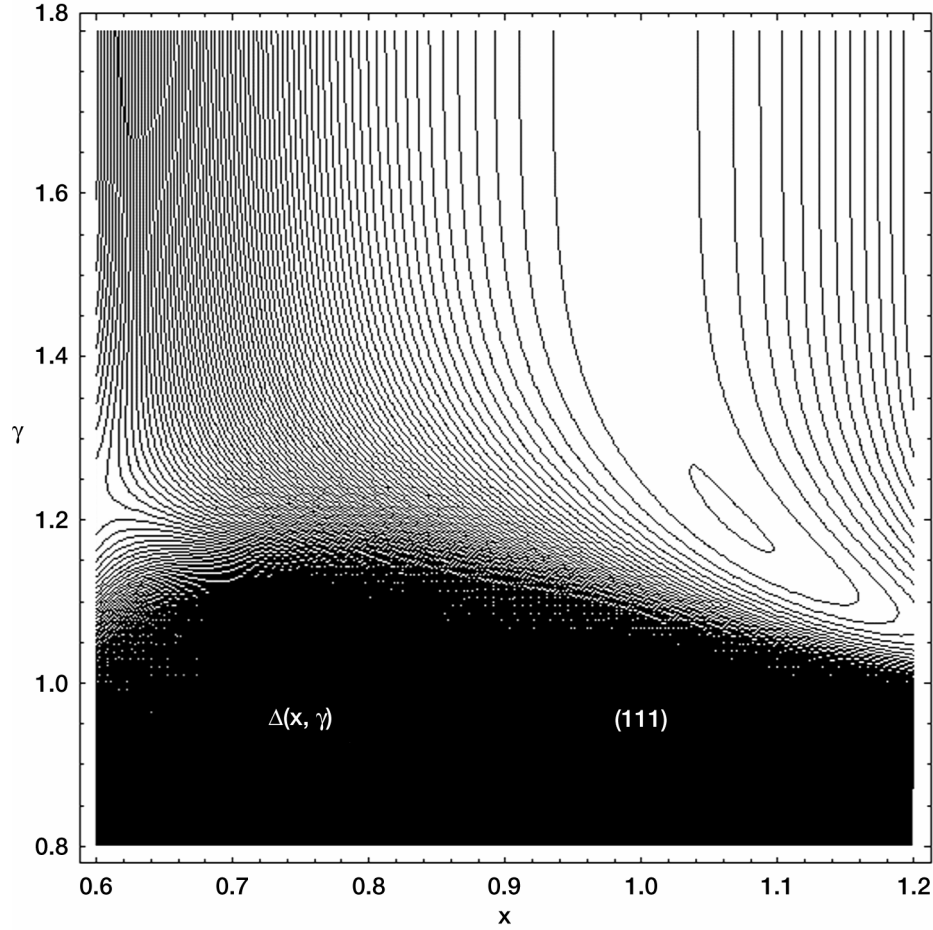


Figure 6.—Function to find the optimal values of x and γ for the formation of the (111) surface.

Table 1 shows results for Fe low index energy formation calculated by various methods. In addition, the table shows the ratios between (110) and (111) surface energies. This number is relevant because it has been used in the past as a gauge of the predictive power of a theory. It is known [8] that the ratios of surface energies are lower than expected from simple geometrical arguments based on surface roughness. This is due to the smoothing of the electron density parallel to the surface. Our results for the (111) to (110) energies are within 10% of the ab initio results.

Table I.—Comparison of surface energies calculated from various method.

J/m^2	OECT [5]	AB INITIO [2,3]	MEC (This work)
$Fe(110)$	1.78	2.25	2.49
$Fe(111)$	2.48	2.62	2.59
$\frac{Fe(110)}{Fe(111)}$	1.39	1.16	1.04

Conclusions

This paper introduced MECT, whose main features are the introduction of a gradient term in the density and the possibility for anisotropic deformations of the equivalent lattice. This approach is of interest in the calculation of surface energies in particular, and more generally for low symmetry geometries in which the gradient of the density is significant and therefore makes an important contribution to the total energy. We have applied the method to calculate low index surface energy formation of Fe and found an improved agreement with ab initio results.

References

- [1] W. Kohn, L. J. Sham, “Self-Consistent Equations Including Exchange and Correlation Effects”, *Phys. Rev.* **140**, A1133–A1138 (1965)
- [2] M.J.S. Spencer, A. Hung, I.K. Snook, I. Yarovsky, “Density functional theory study of the relaxation and energy of iron surfaces”, to appear in *Surface Science* (2002)
- [3] A. Hung, I. Yarovsky, J. Muscat, S. Russo, I. Snook, R.O. Watts, “First-principles study of metallic iron interfaces”, to appear in *Surface Science*.
- [4] J. Ferrante, J.R. Smith, “A theory of adhesion at a bimetallic interface: overlap effects”, *Surface Science* **38** (1973) 77-92
- [5] A.M. Rodríguez, G. Bozzolo, J. Ferrante, “Multilayer relaxation and surface energies of fcc and bcc metals using equivalent crystal theory”, *Surface Science* **289** (1993) 100-126
- [6] J. R. Smith, A. Banerjea, T. Perry, J. Ferrante, G. Bozzolo, “Equivalent Crystal Theory of Metals and Semiconductors Defects”, *Phys. Rev.* **B44** (1991) 6444
- [7] A. Banerjea and J.R. Smith, “Origins of the universal binding-energy relation”, *Phys. Rev. B* **37**, 6632–6645 (1988)
- [8] M. Methfessel, D. Hennig, and M. Scheffler, “Trends of the surface relaxation, surface energies, and work functions of the 4d transition metal”, *Phys. Rev.* **B 46**, 4816-4829 (1992)

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE March 2004		3. REPORT TYPE AND DATES COVERED Technical Memorandum
4. TITLE AND SUBTITLE Generalization of Equivalent Crystal Theory to Include Angular Dependence			5. FUNDING NUMBERS WBS-22-708-04-03	
6. AUTHOR(S) John Ferrante and Fredy R. Zypman				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration John H. Glenn Research Center at Lewis Field Cleveland, Ohio 44135-3191			8. PERFORMING ORGANIZATION REPORT NUMBER E-14443	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-2004-212970	
11. SUPPLEMENTARY NOTES John Ferrante, NASA Glenn Research Center (retired); and Fredy R. Zypman, Yeshiva University, Department of Physics, 2495 Amsterdam Avenue, New York, New York 10033. Responsible person, Phillip B. Abel, organization code 5960, 216-433-6063.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Categories: 72, 76, and 77 Distribution: Nonstandard Available electronically at http://gltrs.grc.nasa.gov This publication is available from the NASA Center for AeroSpace Information, 301-621-0390.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) In the original Equivalent Crystal Theory, each atomic site in the real crystal is assigned an equivalent lattice constant, in general different from the ground state one. This parameter corresponds to a local compression or expansion of the lattice. The basic method considers these volumetric transformations and, in addition, introduces the possibility that the reference lattice is anisotropically distorted. These distortions however, were introduced ad-hoc. In this work, we generalize the original Equivalent Crystal Theory by <i>systematically</i> introducing site-dependent directional distortions of the lattice, whose corresponding distortions account for the dependence of the energy on anisotropic local density variations. This is done in the spirit of the original framework, but including a gradient term in the density. This approach is introduced to correct a deficiency in the original Equivalent Crystal Theory and other semiempirical methods in quantitatively obtaining the correct ratios of the surface energies of low index planes of cubic metals - (100), (110), and (111). We develop here the basic framework, and apply it to the calculation of Fe (110) and Fe (111) surface energy formation. The results, compared with first principles calculations, show an improvement over previous semiempirical approaches.				
14. SUBJECT TERMS Crystal structure; Metals; Iron; Surface energy; Anisotropy			15. NUMBER OF PAGES 18	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	