View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by NASA Technical Reports Server

NASA-TM-112459

NDB

Reprinted from

surface science

Rele NASA
IN-26-TM
[illegible]
027661

Surface Science 315 (1994) 204–214

Multilayer relaxation and surface energies of metallic surfaces

Guillermo Bozzolo [a,*], Agustín M. Rodríguez [b], John Ferrante [c]

[a] Analex Corporation, 3001 Aerospace Parkway, Brook Park, OH 44142-1003, USA
[b] Departamento de Física, Universidad Nacional de La Plata, C.C. 67, 1900 La Plata, Argentina
[c] National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44135, USA

Received 14 March 1994; accepted for publication 20 April 1994

N·H
ELSEVIER

FOUNDING EDITOR: Harry C. Gatos

ADVISORY EDITORIAL BOARD

AUSTRIA:	K.D. Rendulic, *Graz*
CANADA:	P.R. Norton, *London, Ontario*
CHINA:	Xun Wang, *Shanghai*, Xie Xide, *Shanghai*
DENMARK:	J.K. Nørskov, *Lyngby*
FRANCE:	M. Bienfait, *Marseille*, L. Dobrzynski, *Villeneuve d'Ascq*, C.A. Sébenne, *Paris*
GERMANY:	E. Bauer, *Clausthal-Zellerfeld*, A.M. Bradshaw, *Berlin (Dahlem)*, G. Comsa, *Jülich*, D.M. Kolb, *Ulm*, D. Menzel, *Garching bei München*
ITALY:	G. Benedek, *Milan*
JAPAN:	Shinji Kawaji, *Tokyo*, Y. Murata, *Tokyo*, A. Yoshimori, *Okayama*
NETHERLANDS:	J.F. van der Veen, *Amsterdam*
RUSSIA:	V.A. Grazhulis, *Chernogolovka*
UK:	S. Holloway, *Liverpool*, R.M. Lambert, *Cambridge*, M.W. Roberts, *Cardiff*, P.D. Woodruff, *Coventry*
USA:	E.A. Carter, *Los Angeles, CA*, J.E. Demuth, *Yorktown Heights, NY*, P.J. Feibelman, *Albuquerque, NM*, M.G. Lagally, *Madison, WI*, T.E. Madey, *Piscataway, NJ*, R.L. Masel, *Urbana, IL*, J.W. Rabalais, *Houston, TX*, P.A. Thiel, *Ames, IA*, W.H. Weinberg, *Santa Barbara, CA*, R.F. Willis, *University Park, PA*, J.T. Yates, Jr., *Pittsburgh, PA*

EDITORIAL ADDRESSES:

Editor:

Dr. Charles B. Duke, Xerox Webster Research Center, 800 Phillips Road, Bldg. 0114-38D, Webster, NY 14580, USA
Telefax: +1-716-265-5080; Electronic mail: warthman.wbst128@xerox.com

Regional Editors:

Professor George Comsa, Institut für Grenzflächenforschung und Vakuumphysik, KFA Jülich, D-52425 Jülich, Germany
Telefax: +49-2461-58627

Professor Shinji Kawaji, Department of Physics, Gakushuin University, 1-5-1 Mejiro, Toshima-Ku, Tokyo 171, Japan
Telefax: +81-3-5391-1513

Dr. Richard M. Lambert, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK
Telefax: +44-223-336362; Electronic mail: rml1@cus.cam.ac.uk

All correspondence with the publisher regarding manuscripts accepted for publication should be addressed to:
Surface Science Technical Editors, P.O. Box 103, 1000 AC Amsterdam, The Netherlands
Telephone: +31-20-5862 526; Telefax: +31-20-5862 775; Electronic mail: hanraads@elsevier.nl

Please do not use telefax for the transmission of manuscripts.

Detailed information on submission and preparation of manuscripts may be found in the Requirements for swift publication on page 217.

Surface Science (including Surface Science Letters) (ISSN 0039-6028). For 1994, volumes 296–318 are scheduled for publication. Subscription prices are available upon request from the publisher. A combined subscription to Surface Science volumes 296–318, Applied Surface Science volumes 72–81, and Surface Science Reports volumes 18–20 is available at a reduced rate.
Subscriptions are accepted on a prepaid basis only and are entered on a calendar year basis. Issues are sent by surface mail except to the following countries where air delivery via SAL is ensured: Argentina, Australia, Brazil, Canada, China, Hong Kong, India, Israel, Japan, Malaysia, Mexico, New Zealand, Pakistan, Singapore, South Africa, South Korea, Taiwan, Thailand, USA. For all other countries airmail rates are available upon request.
Please address all your requests regarding orders and subscription queries to: Elsevier Science, Journal Department, P.O. Box 211, 1000 AE Amsterdam, The Netherlands. Telephone: +31-20-5803642, Telefax: +31-20-5803598. Claims for issues not received should be made within six months of our publication (mailing) date.
Books for review should be sent to Dr. C.B. Duke.

Elsevier Science B.V. All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the written permission of the publisher, Elsevier Science B.V., Copyright & Permissions Department, P.O. Box 521, 1000 AM Amsterdam, The Netherlands.
Special regulations for authors – Upon acceptance of an article by the journal, the author(s) will be asked to transfer copyright of the article to the publisher. This transfer will ensure the widest possible dissemination of information.
Special regulations for readers in the USA – This journal has been registered with the Copyright Clearance Center, Inc. Consent is given for copying of articles for personal or internal use, or for the personal use of specific clients. This consent is given on the condition that the copier pays through the Center the per-copy fee stated in the code on the first page of each article for copying beyond that permitted by Sections 107 or 108 of the US Copyright Law. The appropriate fee should be forwarded with a copy of the first page of the article to the Copyright Clearance Center, Inc., 27 Congress Street, Salem, MA 01970, USA. If no code appears in an article, the author has not given broad consent to copy and permission to copy must be obtained directly from the author. The fee indicated on the first page of an article in this issue will apply retroactively to all articles published in the journal, regardless of the year of publication. This consent does not extend to other kinds of copying, such as for general distribution, resale, advertising and promotion purposes, or for creating new collective works. Special written permission must be obtained from the publisher for such copying.

US mailing notice – Surface Science (including Surface Science Letters) (ISSN 0039-6028) is published three times per month by Elsevier Science, Molenwerf 1, P.O. Box 211, 1000 AE Amsterdam, The Netherlands. The annual subscription price in the USA is US$ 6104 (valid in North, Central and South America only), including air speed delivery. Second class postage paid at Jamaica, NY 11431.
USA POSTMASTERS: Send address changes to Surface Science, Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003. Airfreight and mailing in the USA by Publications Expediting.

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Although all advertising material is expected to conform to ethical standards, inclusion in this publication does not constitute a guarantee or endorsement of the quality or value of such product or of the claims made of it by its manufacturer.

∞ The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper).

Published three times per month
Printed in The Netherlands

ELSEVIER

Surface Science 315 (1994) 204–214

surface science

Multilayer relaxation and surface energies of metallic surfaces

Guillermo Bozzolo [a,*], Agustín M. Rodríguez [b], John Ferrante [c]

[a] Analex Corporation, 3001 Aerospace Parkway, Brook Park, OH 44142-1003, USA
[b] Departamento de Física, Universidad Nacional de La Plata, C.C. 67, 1900 La Plata, Argentina
[c] National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44135, USA

Received 14 March 1994; accepted for publication 20 April 1994

Abstract

The perpendicular and parallel multilayer relaxations of fcc (210) surfaces are studied using equivalent crystal theory (ECT). A comparison with experimental and theoretical results is made for Al(210). The effect of uncertainties in the input parameters on the magnitudes and ordering of surface relaxations for this semiempirical method is estimated. A new measure of surface roughness is proposed. Predictions for the multilayer relaxations and surface energies of the (210) face of Cu and Ni are also included.

1. Introduction

In the last few years there has been considerable interest in the study of the surface structure of high-index faces of metals [1–10]. Experimental evidence of both perpendicular (to the surface plane) and parallel (without loss of symmetry) relaxations in several open metal faces, provided the necessary background for theoretical studies [11–16]. Following the calculations of Barnett et al. [13], which first predicted the occurrence of significant interlayer spacing and registry relaxations, the surface structure of six fcc Al surfaces, including the (210) face, was studied by Jiang et al. [11] using the modified point-ion model. A low-energy electron diffraction (LEED) analysis by Adams et al. [3] provided the only experimental evidence to date of perpendicular and parallel relaxation of Al(210) surfaces. More recently, Sinnott et al. [10] reported corrected effective medium (CEM) results for the surface energies of several fcc metals and provided theoretical estimates for the perpendicular relaxation of the first two interplanar spacings. Finally, Chen and Voter [12] performed a calculation using embedded-atom potentials raising the issue of the possibility of reconstruction in fcc (n10) ($n = 1, 2, 3$) surfaces although none was found experimentally in such cases [3,9]. These theoretical studies, together with several other first-principles or semiempirical calculations for the determination of metallic surface structure, have provided not only large amounts of data but also some insight on the different mechanisms involved. However, some issues which could be considered somewhat minor given the success of most of these studies,

---

[*] Corresponding author.

0039-6028/94/$07.00 © 1994 Elsevier Science B.V. All rights reserved
SSDI 0039-6028(94)00256-9

have not enjoyed the same level of attention, the focus being in all cases up to what extent these techniques were able to reproduce the experimental results.

In this paper, we intend to open the discussion on some of these issues, by focusing on a multilayer relaxation calculation of the Al(210) surface by means of a semiempirical method which, in general, has been very successful in previous applications to surface phenomena, namely, equivalent crystal theory [14–16]. As opposed to the case of low-index surfaces, where ECT provides, in general, good results, the predictions for the Al(210) surface are not as good. Therefore, it serves as a useful example for answering the question of what ingredients of the theory are relevant, and which ones are not, in order to provide a physically accurate description of the problem at hand.

Like any of the methods available for the theoretical study of surface phenomena, whether it is a first-principles calculation or a semiempirical one, approximations are made and some external input is used, without a clear understanding of how these assumptions translate into the final results. Moreover, semiempirical techniques, which became the standard for simulations, oversimplify the problem in the attempt of making the computational aspects simple enough to allow for lengthy and complex calculations. Often, it is at the expense of introducing mechanisms whose roles, partly because of their generality, become obscure in that their influence on the final results is not well understood. The criteria used to interpret the results is also important: while the output may consist of a single quantity, easily identifiable (in the case of surface relaxation, the percentage changes in interplanar spacing), it is often the case that alternative solutions can still shed some light on the behavior of the system, even if they do not correspond to observed experimental results (i.e., alternative relaxation patterns which could correspond to local minima in the multidimensional energy surface). We therefore focus our attention on three aspects of the surface structure calculation: the input data used and its influence on the results, the energy algorithm and its ability to deal with the main physical effects that take place in the system, and the context in which the output data is analyzed.

In the particular case of ECT, although some of these features are common to other semiempirical techniques, it is important to analyze how uncertainties in the experimental data used as input affect the outcome of the calculation and, in the problem of multilayer relaxation, how that influences the ensuing relaxation pattern. We will find that very small uncertainties in the input data used in ECT (which is also the input of other semiempirical techniques) are amplified into large uncertainties in the final results. Secondly, we concentrate on the role of each of the terms that enter in the calculation of the energy by studying the results obtained under different parameterizations and therefore gaining some insight into their physical interpretation. In the study of multilayer relaxation, this relates to the mechanisms provided by the energy algorithm to describe the bond length anisotropies which ultimately dictate the structure of the surface. Finally, we generalize the concept of surface roughness thus establishing a more appropriate framework for the analysis of surface relaxation patterns theoretically obtained.

We organize the paper as follows: in Section 2 we briefly discuss the concepts of equivalent crystal theory. In Section 3 we concentrate on the first of the three main issues of this paper by introducing theoretical 'error bars' to the predictions of low-index surface relaxation, which we later generalize in Section 4 to the case of high-index surfaces. We discuss the dependence of the ECT results on the parameterization chosen for the bond-compression term in the ECT energy expansion. We also introduce a new concept to replace the definition of surface roughness and analyze the ECT results in this new framework.

2. Equivalent crystal theory

Equivalent crystal theory [15,16] is based on an exact relationship between the total energy and atomic locations and applies to surfaces and defects in both simple and transition metals as well as in covalent solids. Lattice defects and surface energies are determined via perturbation theory on a fictitious, equivalent single crystal whose lattice constant is chosen to minimize the perturbation. The energy of the equivalent crystal, as a function of its lattice constant is given by a universal binding energy relation [17].

Let ϵ be the total energy to form the defect or surface, then

$$\epsilon = \sum_i \epsilon_i, \tag{1}$$

where ϵ_i is the contribution from an atom i close to the defect or surface. ECT is based on the concept that there exists, for each atom i, a certain perfect, equivalent crystal with its lattice parameter fixed at a value so that the energy of atom i in the equivalent crystal is also ϵ_i. This equivalent crystal differs from the actual ground-state crystal only in that its lattice constant may be different from the ground-state value. We compute ϵ_i via perturbation theory, where the perturbation arises from the difference in the ion core electronic potentials of the actual defect solid and those of the effective bulk single crystal.

For the sake of simplicity, the formal perturbation series is approximated by simple, analytic forms which contain a few parameters, which can be calculated from experimental results or first-principles calculations. Our simplified perturbation series for ϵ_i is of the form

$$\begin{aligned}\epsilon_i = \Delta E\Big\{ & F^*[a_1^*(i)] + \sum_j F^*[a_2^*(i,j)] \\ & + \sum_{j,k} F^*[a_3^*(i,j,k)] \\ & + \sum_{p,q} F^*[a_4^*(i,p,q)]\Big\},\end{aligned} \tag{2}$$

where

$$F^*[a^*] = 1 - (1 + a^*)\mathrm{e}^{-a^*} \tag{3}$$

and ΔE is the cohesive energy. In this expression, we distinguish four different contributions to the energy of atom i and thus, the existence of four different equivalent crystals which have to be determined for each atom i.

The first term, $F^*[a_1^*(i)]$, contributes when average neighbor distances are altered via defect or surface formation. It can be thought of as representing local atom density changes. In most cases, this 'volume' term is the leading contribution to ϵ_i and in the case of isotropic volume deformations, it gives ϵ_i to the accuracy of the universal energy relation [17]. The value of $a_1^*(i)$, the lattice parameter of the first equivalent crystal associated with atom i, is chosen so that the perturbation (the difference in potentials between the solid containing the defect and its bulk, ground-state equivalent crystal) vanishes. Within the framework of ECT, this requirement translates into the following condition from which $a_1^*(i)$ is determined:

$$\begin{aligned}& NR_1^p \exp(-\alpha R_1) + MR_2^p \exp\left[-\left(\alpha + \frac{1}{\lambda}\right)R_2\right] \\ & \quad - \sum_{\text{defect}} r_j^p \exp\{-[\alpha + S(r_j)]r_j\} = 0,\end{aligned} \tag{4}$$

where the sum over the defect crystal or surface is over all neighbors within second-neighbor (NNN) distance. r_j is the actual distance between atom i and a neighbor atom j, N and M are the number of nearest-neighbors (NN) and next-nearest-neighbors, respectively, of the equivalent crystal (12 and 6 for fcc, 8 and 6 for bcc) and p, α and λ are parameters known for each atomic

Table 1
Computed constant and experimental input for ECT

Element	p	l	α	λ	$10^{-2}A_3/D$	$10^{-1}A_4/D$	$10^{-4}D$	ΔE	a_e
Al	4	0.336	2.105	0.944	7.822	2.104	591.4	3.34	4.05
Cu	6	0.272	2.935	0.765	5.784	2.530	99.74	3.50	3.615
Ni	6	0.270	3.015	0.759	7.382	2.793	100.1	4.435	3.524
Fe	6	0.277	3.124	0.770	9.183	1.887	60.62	4.29	2.86

The constant p is $2n - 2$, where n is the atomic principal quantum number, l (in Å) is a scaling length and λ (in Å) is a screening parameter (see text) The constants A_3 and A_4 are dimensionless. ΔE (in eV) is the cohesive energy and a_e (in Å) the equilibrium lattice constant.

species. Table 1 displays the values of these parameters for the fcc elements used in this work (see Ref. [16] for a complete list). $S(r_j)$ is a screening function and R_1 and R_2 are the NN and NNN distances in the equivalent crystal. The equivalent lattice parameter, a_1, is thus related to the scaled quantity a_1^* via

$$a_1^* = \left(\frac{R_1}{c} - r_{\text{WSE}}\right)/l, \tag{5}$$

where r_{WSE} is the equilibrium Wigner–Seitz radius, l is a scaling length and c is the ratio between the equilibrium lattice constant and r_{WSE}.

The higher-order terms are relevant for the case of anisotropic deformations. The linear independence attributed to these four terms is consistent with the limit of small perturbations which we assume for the formulation of ECT. The second term, $F^*[a_2^*(i, j)]$, is a two-body term which accounts for the increase in energy when NN bonds are compressed below their equilibrium value. This effect is also modeled with an equivalent crystal, whose lattice parameter is obtained by solving a perturbation equation given by

$$NR_1^p \exp(-\alpha R_1) - NR_0^p \exp(-\alpha R_0) + A_2 R_0^p \sum_j (R_j - R_0) \exp\left[-\beta(R_j - R_0)\right] = 0, \tag{6}$$

where $\beta = 4\alpha$ for the metals used in this work, and R_1 is the NN distance of the equivalent crystal associated with the deviation of NN bond length R_j from R_0, and R_0 is the bulk NN distance at whatever pressure the solid is maintained (generally, R_0 is the ground-state, zero-pressure value). A_2 is a constant determined for each metal (see Table 1 for a list of values of A_2 used in this work). The scaled equivalent lattice parameter is then

$$a_2^* = \left(\frac{R_1}{c} - r_{\text{WSE}}\right)/l. \tag{7}$$

The third term, $F^*[a_3^*(i, j, k)]$ accounts for the increase in energy that arises when bond angles deviate from their equilibrium values of the undistorted single crystal. This is a three-body term and the equivalent lattice parameter associated with this effect is obtained from the perturbation equation

$$NR_1^p \exp(-\alpha R_1) - NR_0^p \exp(-\alpha R_0) + A_3 R_0^p \exp\left[-\alpha(R_j + R_k - 2R_0)\right] \sin(\theta_{jk} - \theta) = 0, \tag{8}$$

where A_3 is a constant listed in Table 1 and θ_{jk} is the angle between the NN distances R_j and R_k with the atom i at the center. θ is the equilibrium angle, 70.5° for bcc and 90° for fcc. This term contributes only when there is a bond-angle anisotropy ($\theta_{jk} \neq \theta$). The scaled lattice parameter is then

$$a_3^* = \left(\frac{R_1}{c} - r_{\text{WSE}}\right)/l. \tag{9}$$

The fourth term, $F^*[a_4^*(i, p, q)]$, describes face diagonal anisotropies (see Ref. [16] for a detailed description, for each lattice type, of the structural effect associated with this term). The perturbation equation reads

$$NR_1^p \exp(-\alpha R_1) - NR_0^p \exp(-\alpha R_0) + A_4 R_0^p \frac{|d_p - d_q|}{d} \exp\left[-\alpha(R_j + R_k + R_l + R_m - 4R_0)\right] = 0, \tag{10}$$

where d is the face diagonal of the undistorted cube and A_4 is a constant adjusted to reproduce the experimental shear elastic constants (Table 1). Finally,

$$a_4^* = \left(\frac{R_1}{c} - r_{\text{WSE}}\right)/l.$$

Consider a rigid surface (i.e., no interlayer relaxation): all bond lengths and angles retain their bulk equilibrium values, thus $F^*(a_2^*) = F^*(a_3^*) = F^*(a_4^*) = 0$. The surface energy is therefore obtained by solving for the 'volume' term represented by $F^*(a_1^*)$ only. If we consider a rigid displacement of the surface layer towards the bulk, as is the case in most metallic surfaces, the higher-order terms become finite: some bonds are compressed, contributing to $F^*(a_2^*)$, the bond angles near the surface are distorted as well as the difference between face diagonals in some cases, generating an increase of energy via $F^*(a_3^*)$ and $F^*(a_4^*)$. For the case studied in this work, these additional contributions to ϵ_i are generally small, representing only 1% to 2% of the total energy. However, while these anisotropy terms are small for metals when there is no reconstruction, they play an important role in the energetics of these defects where the differences in energy between the rigid and relaxed configurations are also small. In what follows, we will refer to this ECT formalism as ECT II.

An earlier version of ECT [15], which we will refer to as ECT I, provides a simpler, although less accurate framework for a defect calculation. The second term in Eq. (2) is replaced by a simple expression, which allows for the direct calculation of the energy associated with bond-compression effects,

$$\epsilon_2 = \Delta E \sum_{n=1}^{N_s} \sum_{m=1}^{M_n} \frac{\theta_{mn}}{L_{mn}} F^*(a_{mn}^*), \tag{11}$$

where N_s is the number of atoms in the solid, $\theta_{mn} = 1$ if $a_{mn}^* \leq 0$ and $\theta_{mn} = 0$ otherwise, M_n is the number of nearest neighbors of atom n, L_{mn} is the number of nearest neighbors of atom m or n, whichever number is smaller, and a_{mn}^* is given by

$$a_{mn}^* = \frac{R_{mn}/c_1 - r_{\text{WSE}}}{l}, \tag{12}$$

with

$$l = \sqrt{\frac{\Delta E}{12\pi B r_{\text{WSE}}}}, \tag{13}$$

B is the bulk modulus of the crystal, R_{mn} is the distance between atoms m and n, c_1 is the ratio of the equilibrium nearest-neighbor distance in the crystal to r_{WSE}, and r_{WSE} is the equilibrium Wigner-Seitz radius. In ECT I [15], the third and fourth term of the energy expansion (Eq. (1)) are ignored. In what follows, we will list results as obtained with either one of the two versions of ECT. Those results obtained with the full energy expansion (ECT II) [16], will be analyzed in terms of the value of the parameter β which dictates the 'strength' of the bond-compression term therefore playing an important role in the energetics of surface relaxation as it will be seen that this term is mainly responsible for avoiding the collapse of the top layers onto each other.

3. Uncertainties in the prediction of multilayer relaxation

Before proceeding to the calculation of multilayer relaxation in high-index faces, we will discuss some features of theoretical calculations of these quantities. Ref. [14] provides a reasonably large sample of both experimental and theoretical results for changes in interlayer spacing in pure fcc and bcc crystals. In all cases, the semiempirical, theoretical techniques used, rely either on input data (generally experimentally determined) or on certain approximations for some of the variables of relevance. Necessarily, results will depend on such choices. Multilayer relaxations involve at best very small changes in position, with correspondingly, small changes in surface energy, whose minimization is the criterion used to determine the final interlayer spacings. Thus, the search for a minimum of the surface energy, as accurate as the minimization technique might be, will be strongly influenced by the approximations made, the error in input parameters and the shallowness of the minimum in the surface energy surface. As a consequence, to quote just one value for each of the changes in interlayer spacings as is ordinarily done, might not reflect the ambiguities in these calculations. In this paper we adopt a different path: to each theoretical prediction, we will attach an estimate of the possible errors due to any of the reasons mentioned above. Although there is no certain way to determine such errors (after all, the predictions are, within their own framework, exact), we will see that changes on the order of 1% in the surface energy can generate quite interesting variations in the relaxation schemes predicted. In particular, within the framework of ECT (I [15] or II [16]), such small changes in the surface energy can be easily obtained by changing any of the input parameters (lattice constant, cohesive energy, bulk modulus) by a similar amount, well below the usual experimental errors in the determination of such quantities.

To illustrate this issue, we will focus our attention on the surface structure of some fcc pure metals (Al, Cu and Ni). As can be seen in Tables 2–11 of Ref. [14], previous theoretical and experimental studies show a wide spread in the predictions of the changes in interlayer spacings for the (100) and (110) surfaces. Even results obtained within the same theoretical technique (embedded-atom method (EAM) [22], ECT) do not agree with each other (due to different fitting procedures of the embedding function in the case of EAM and different input data in both cases). Although there is general qualitative agreement, regarding the contraction or expansion pattern found for successive layers, in some cases the absolute theoretical values predict the wrong trend with respect to experimental results (see, for example, Al(100)). The ECT II results (from Refs. [14] and [16]) also highlight this inconsistency. The difference between the values obtained in this work and those from previous applications of ECT is easily traceable to slightly different values of some of the input parameters.

As mentioned above, in order to account for these and other ambiguities in the calculation, we investigated the change in predicted relaxations due to small changes in the rigid surface energy. We thus defined 'error bars' in such way that all the intermediate values so obtained predict variations in surface energies within a certain tolerance. In this work, we set the tolerance at 1% of the equilibrium surface energy σ_e. This defines a surface $\sigma(\Delta d_{12}, \Delta d_{23})$ and the allowed values for these parameters are such that $\sigma_e < \sigma(\Delta d_{12}, \Delta d_{23}) < 1.01\sigma_e$. Needless to say, this range of values does not include all the possible sets $(\Delta d_{12}, \Delta d_{23})$ that correspond to surface energies within the allowed values. It is interesting to note, however, that in most cases, all the experimental as well as theoretical predictions fall within the range of uncertainties in such procedure. This definition of the error bars is, of course, arbitrary and it was chosen as a means to simply illustrate the influence of uncertainties in the final results.

It should be noted that when comparing our theoretical predictions with available experimental results, the error bars quoted from experiment or theory are similar in that the optimum relaxations are determined by minimization of some property by varying the input parameters. To illustrate this point, we first discuss the surface energies and multilayer relaxations of the unreconstructed low-index surfaces of pure Al, Ni, and Cu crystals. In Table 2 we display the ECT II predictions for the surface energies and compare the results with typical experimental values for polycrystalline samples [18,19]. We note that experimental values for the surface energies are for polycrystalline surfaces, thus could be strongly dominated by the predominant surface plane. The experimental values from Ref. [21] have the advantages of the data being taken on solids (including low-temperature values), and the data being in much better agreement with modern, first-principles calculational results.

In Table 3 we compare results for the multilayer relaxations of the first two interlayer spacings for those cases for which recent experimental data are available [23,31]. The inclusion of the theoretical 'error bar', as mentioned above, allows for a better comparison with experiment as it shows that for most cases, small changes in the input parameters of the method may account for the whole range of possible experimental results. The exceptions are Al(100) and Al(111), where the outward relaxation of the surface layer has been attributed to an electron promotion effect [32]. Semiempirical methods (ECT, EAM, etc.), unless specifically designed to do so, do not generally allow for such fine electronic structure

Table 2
Experimental (Exp.) and relaxed ECT II surface energies of Al, Cu and Ni (in erg/cm^2)

Technique	Al	Cu	Ni
Exp. [18]	1200	1790	2270
Exp. [19]	1140	1780	2380
Exp. [19]	1180	1770	2240
Exp. [21]	1169	2016	2664
ECT(100)	1203	2309	2982
ECT(110)	1284	2373	3073
ECT(111)	856	1767	2274

Table 3
Surface relaxations of Al, Cu and Ni as percentages of the bulk interplanar spacings

Element	Face	Experiment			ECT II	ECT II (two-layers)	
		Δd_{12}	Δd_{23}	Ref.	Δd_{12}	Δd_{12}	Δd_{23}
Al	(100)	$+1.8$		[22]	-4.68 ± 1.62	-5.05 ± 1.58	$+3.35 \pm 0.80$
	(110)	-8.5 ± 1.0	$+5.5 \pm 1.1$	[23]	-8.29 ± 2.35	-9.53 ± 3.58	$+1.90 \pm 2.24$
	(111)	$+1.7 \pm 0.3$	$+0.5 \pm 0.7$	[24]	-3.67 ± 1.21	-3.94 ± 1.19	$+2.75 \pm 0.61$
Ni	(100)	-3.2 ± 0.5		[25]	-3.53 ± 1.68	-3.82 ± 1.68	$+2.48 \pm 0.85$
	(110)	-9.0 ± 1.0	$+3.5 \pm 1.5$	[26]	-6.32 ± 2.44	-6.55 ± 3.63	$+0.34 \pm 2.24$
	(111)	-1.2 ± 1.2		[27]	-2.89 ± 1.29	-3.10 ± 1.25	$+2.12 \pm 0.63$
Cu	(100)	-2.1	$+0.45$	[28]	-3.52 ± 1.74	-3.81 ± 1.70	$+2.47 \pm 0.86$
	(110)	-7.5 ± 1.5	$+2.5 \pm 1.5$	[29]	-6.31 ± 2.46	-6.51 ± 3.83	$+0.29 \pm 2.44$
	(111)	-0.7 ± 0.5		[30]	-2.88 ± 1.30	-3.10 ± 1.25	$+2.12 \pm 0.63$

The ECT II Δd_{12} column displays results for relaxations of the top layer only while the ECT II (two layers) columns display results for the case when the top two layers are allowed to relax.

effects, thus it is not surprising that our results for Δd_{12} in these cases predict surface layer contractions, even when the 'error bar' is taken into account. For completeness we also include results for the surface relaxation when only the top plane is allowed to relax, in order to single out correlations with subsequent interlayer spacing changes on the surface plane. Again, the agreement with available experimental data is good in all cases.

4. Results and discussion

As mentioned above, the bond length anisotropy term is of special importance as it models, in a straightforward fashion, the stiffness of the 'springs' between atoms, thus dictating the final configuration of the surface. The bond-compression term, as defined in Eq. (29) of Ref. [16], has a material-dependent parameter (β) which, although fixed in the original formulation, can be freely varied. In this work, in addition to using the original value of β, we studied the dependence of the interlayer relaxations and registry shifts on this parameter β. We also quote results obtained with ECT I, for a comparison of its effect on relaxation. Finally, being that this work is a continuation of our previous work on multilayer relaxation of high-index fcc and bcc surfaces [14], we will also compare our results with those quoted in Ref. [14], in order to highlight the effect of the inclusion of parallel relaxations in the energetics of fcc (210) surfaces.

We will now focus our attention on the Al(210) surface. Table 4 shows the results for the surface energy of Al(210) obtained with different approaches: ECT I [15], ECT II [16], embedded-atom method [22] and corrected effective-medium theory [10].

The different entries for ECT correspond to the unrelaxed case ("Rigid"), the perpendicularly relaxed case as obtained with the earlier version of the bond-compression term [15] ("ECT I ⊥") and the current (ECT II) version [16] ("ECT II-4 ⊥") for the stiffness parameter $\beta = 4\alpha$, with α defined in Ref. [20], and the case with perpendic-

Table 4
Surface energy of the Al(210) face (in erg/cm^2) (see text)

Method	$\sigma_{210}^{\mathrm{Al}}$
Rigid	1493
ECT I ⊥	1426
ECT II-4 ⊥	1405
ECT I ⊥ + ‖	1424
ECT II-4 ⊥ + ‖	1404
ECT II-3 ⊥ + ‖	1390
ECT II-2 ⊥ + ‖	1369
CEM-LMTO	1440
CEM-EMP	1330
MD/MC-CEM-LMTO	1150
MD/MC-CEM-EMP	1110
EAM	999

ular and parallel relaxation using the ECT I bond-compression term ("ECT I ⊥ + ∥") and the current version ("ECT II-n ⊥ + ∥") for $\beta = n\alpha$ ($n = 2$, 3, 4). The CEM entries are labeled according to the embedding functions used: semiempirical ("CEM-EMP") and those obtained from linear-muffin-tin-orbital calculations ("CEM-LMTO"), which is their best estimate. We quote results from Ref. [10] where the authors use approximate versions of CEM, used in molecular dynamics and Monte Carlo simulations ("MD/MC-CEM-LMTO" and "MD/MC-CEM-EMP") again with two different choices for the embedding functions. Substantial differences exist between the various results for the surface energies. We also include embedded-atom results as obtained by Chen and Voter [12]. These results are compared to experimental values of polycrystalline Al samples [18–21], which should correspond to an average of its highest density planes.

Table 5 reproduces the results obtained with the different variations of ECT described above, indicating the contributions from the different many-body terms included in surface energy σ. σ_i ($i = 1$, 2, 3, 4) indicate the i-body contribution to the energy. As is the case for perpendicular relaxations [14,16], the absence of reconstruction effects translates into σ_3 and σ_4 being much smaller than the first two contributions to the surface energy σ. This is an important issue, as a comparison between ECT I and II is justified only when σ_3 and σ_4 are very small.

When comparing the results for relaxed surfaces, we distinguish between those calculations that include parallel relaxations and those that do not. Table 6 displays results for the unrelaxed case and when only perpendicular relaxations of the interplanar spacings are included. Table 7 concentrates on the fully-relaxed case, for which LEED experimental data are available [3]. We also include results of pseudopotential calculations by Barnett et al. [13], and the values for the forces on the surface layers of the unrelaxed structure made using the point-ion model computed by Adams et al. [3], which can be taken as a representation of the trends of the relaxations. In this last set of results, it was assumed that the relaxations are linearly proportional to the forces in the limit of small relaxations and the actual forces are multiplied by an arbitrary factor in order to obtain numerical agreement with the value of Δd_{12}.

Table 5
Surface energy of Al(210) (σ) (in erg/cm^2) and the different ECT contributions (see text)

ECT	σ	σ_1	σ_2	σ_3	σ_4
ECT II-4	1404.31	1369.44	32.57	1.40	0.90
ECT II-3	1390.46	1348.24	39.12	1.75	1.35
ECT II-2	1369.33	1315.54	49.25	2.19	2.36
ECT I ⊥	1426.36	1371.13	53.26	0.71	1.26
ECT I ⊥ + ∥	1424.25	1366.83	54.90	1.55	0.89

The uncertainties in the experimental values, which are the results of a multivariable fit to LEED theory, for the parallel relaxations are large enough to make it difficult to extract a relaxation pattern to which theoretical predictions can be compared. If we are to take the trends of these results seriously, ECT predicts different trends from the experimental values for Al(210). However, certain features are common

Table 6
Percentage change in interlayer spacing perpendicular to the surface of Al(210)

⊥	ECT		CEM		MD/MC-CEM	
	ECT I ⊥	ECT II 4 ⊥	LMTO	EMP	LMTO	EMP
$\Delta d_{1,2}$	−9.5	−8.2	−19.7	−13.8	13.8	−18.9
$\Delta d_{2,3}$	−5.6	−7.5	−1.0	+3.2	−1.0	+2.8
$\Delta d_{3,4}$	+0.8	+2.1				
$\Delta d_{4,5}$	−3.3	−3.7				
$\Delta d_{5,6}$	+2.7	+4.0				

Table 7
Percentage change in interlayer spacing (Δd_{ij}) and registry shift (Δa_{ij}) of Al(210)

⊥ ‖	Experiment Ref. [3]	Barnett et al. Ref. [13]	ECT				PIM Ref. [3]
			ECT I	ECT II-4	ECT II-3	ECT II-2	
$\Delta d_{1,2}$	−15.5 ± 2.4	−27.7	−10.4	−8.1 ± 4.4	−10.9	−13.6	−15.5
$\Delta d_{2,3}$	−0.8 ± 2.9	−10.2	−5.8	−7.1 ± 3.8	−8.2	−10.6	−3.0
$\Delta d_{3,4}$	+8.9 ± 2.6	+25.9	+1.4	+2.9 ± 4.2	+2.4	+2.9	+1.5
$\Delta d_{4,5}$	−4.4 ± 3.6	−12.8	−3.9	−3.4 ± 5.8	−4.1	−3.5	−0.3
$\Delta d_{5,6}$	−1.2 ± 4.6	−2.4	+3.0	+4.2 ± 6.8	+4.5	+4.7	+0.1
$\Delta a_{1,2}$	−0.1 ± 3.4	−2.5	−0.3	−0.2 ± 2.4	−0.4	−0.4	+1.9
$\Delta a_{2,3}$	−3.2 ± 3.1	−10.0	+0.1	+0.0 ± 2.6	+0.1	−0.1	−3.2
$\Delta a_{3,4}$	+1.7 ± 3.1	+3.8	+1.2	+0.8 ± 2.9	+0.9	+0.9	+1.9
$\Delta a_{4,5}$	−2.0 ± 4.0	−1.0	+0.1	+0.0 ± 3.5	0.0	+0.1	−0.4
$\Delta a_{5,6}$	−0.9 ± 4.6	−2.0	−0.6	−0.5 ± 4.4	−0.7	−0.6	0.0

to all the results: a contraction of d_{12} and d_{23}, an expansion for d_{34} and a contraction of d_{45}. The theoretical predictions for d_{56} indicate a small expansion, which is not in complete disagreement with the experimental result, given the large uncertainty quoted. Although the trends agree, the ECT II–4 results seem to predict the magnitude of the contractions incorrectly. We can see (Table 7) that modifying this term allows the possibility of improving quantitative agreement with experiment. Such modifications await further experimental results with smaller scatter. It would be interesting to test the theoretical results for ECT and other theoretical predictions for the corresponding LEED R-factors in order to make a direct comparison with experimental results. The difference in the magnitude of the relaxations goes beyond the simple numerical appearance as they translate into quite different atomic rearrangements: while the experimental values suggest a 'filling' of the space between surface atoms, the ECT solution describes a highly symmetric distribution where the same effect is obtained by a larger net 'motion' of the surface atoms toward the bulk.

At this point, we find it convenient to extend the concept of roughness of a surface [2] by defining the *borocity* of a surface as

$$B_p = \frac{A_\mathrm{T}}{\sum\limits_{i=1}^{p} A_i \, \mathrm{e}^{-z_i/a}}, \tag{14}$$

where A_T is the unit surface area and A_i is the fraction of A_T including the projections of the hard spheres representing the atoms in layer i, of radius half the nearest-neighbor distance, not covered by similar 'disks' in layers above layer i. z_i is the location of layer i measured perpendicularly to the surface plane and a is the equilibrium lattice parameter (so defined, B_1 is the usual roughness of the surface [2]). This quantity provides a better measurement of the electronic smoothness of a surface by attempting to include, in a simple fashion, the contributions to the surface electron density by atoms below the surface plane. If the borocity of a surface is to be taken

Table 8
Borocity of low-index unrelaxed fcc faces

	(100)	(110)	(111)	(210)
B_1	1.2732	1.8006	1.1026	2.8467
B_2	1.0922	1.1691	1.0426	1.6116
B_3	1.0922	1.1691	1.0426	1.2820
B_4	1.0922	1.1691	1.0426	1.2360

Table 9
Borocity of the relaxed Al(210) face

	Rigid	Experiment	ECT I	ECT II
B_1	2.8467	2.8467	2.8467	2.8467
B_2	1.6116	1.5873	1.5984	1.5957
B_3	1.2820	1.2643	1.2634	1.2619
B_4	1.2360	1.2149	1.2177	1.2159

Table 10
Surface energy of the Cu(210) and Ni(210) face (in erg/cm^2) (see text)

Method	$\sigma_{210}^{\mathrm{Cu}}$	$\sigma_{210}^{\mathrm{Ni}}$
Rigid	2618	3407
ECT I ⊥ + ‖	2559	3330
ECT II-4 ⊥ + ‖	2540	3306
ECT II-2 ⊥ + ‖	2512	3270
CEM-LMTO	1820	2470
CEM-EMP	1660	2310
MD/MC-CEM-LMTO	2170	3010
MD/MC-CEM-EMP	1960	2810
EAM	1544	2082

as a measure of the smoothness of the surface, then the unrelaxed (210) surface is smoother than one would assume from its roughness value (B_1). Table 8 shows the borocity as a function of planes included for some low-index fcc faces.

The lower borocity of the (210) face accounts for the fact that, within the hard spheres scheme, the (110) face shows a certain degree of transparency as opposed to the complete coverage in (210) faces after a few planes are included. The borocity values for the rigid and relaxed Al(210) face show some interesting trends. Table 9 displays these results. While all 'solutions' predict a lower borocity than the one corresponding to the unrelaxed case, it is rather surprising to see that there is little change in borocity between the ECT and the experimental values. Although the relaxed distribution in each case is different, the overall surface effect is quite similar in both cases. The comparison between the ECT results with perpendicular relaxation only and the fully relaxed ones is consistent with the magnitudes of the parallel relaxations listed in Table 7.

Table 12
Percentage change in interlayer spacing (Δd_{ij}) and registry shift (Δa_{ij}) of Cu(210) and Ni(210)

⊥ ‖	Cu(210) ECT II-4	Ni(210) ECT II-4
$\Delta d_{1,2}$	-4.5 ± 5.1	-4.5 ± 5.0
$\Delta d_{2,3}$	-4.9 ± 4.2	-5.0 ± 4.1
$\Delta d_{3,4}$	$+1.0 \pm 4.4$	$+1.1 \pm 4.4$
$\Delta d_{4,5}$	-2.0 ± 5.8	-2.0 ± 5.8
$\Delta d_{5,6}$	$+3.2 \pm 6.8$	$+3.2 \pm 6.7$
$\Delta a_{1,2}$	$+0.0 \pm 2.4$	$+0.0 \pm 2.4$
$\Delta a_{2,3}$	$+0.0 \pm 2.5$	$+0.0 \pm 2.6$
$\Delta a_{3,4}$	$+0.5 \pm 2.8$	$+0.5 \pm 2.8$
$\Delta a_{4,5}$	$+0.1 \pm 3.5$	-0.1 ± 3.4
$\Delta a_{5,6}$	-0.5 ± 4.3	-0.4 ± 4.1

Since there is considerable experimental interest in stepped and kinked surfaces, we include predictions of multilayer relaxations for other fcc metals, Cu and Ni, in order to provide theoretical results for future comparison. Table 10 indicates the surface energy of Cu(210) and Ni(210) as obtained with different approaches, using the same notation as in Table 2.

As with Al(210), we single out the different contributions to the surface energy, as computed with ECT, in Table 11. Finally, Table 12 displays our predictions for the perpendicular and parallel relaxations for Cu(210) and Ni(210) usintg ECT II-4.

5. Conclusions

Based on the analysis of the experimental and theoretical results for multilayer relaxation of the

Table 11
Surface energy of Cu(210) and Ni(210) (σ) (in erg/cm^2) and the different ECT contributions as obtained with different formulations of the bond-compression effect (see text)

Surface	ECT	σ	σ_1	σ_2	σ_3	σ_4
Cu(210)	ECT II-4	2540.16	2508.93	29.30	0.96	0.96
	ECT II-2	2512.25	2465.42	43.09	1.76	1.97
	ECT I ⊥ +‖	2559.19	2510.25	46.98	1.00	0.95
Ni(210)	ECT II-4	3305.79	3264.75	37.78	1.82	1.44
	ECT II-2	3269.73	3208.40	55.11	3.29	2.93
	ECT I ⊥ +‖	3329.90	3265.54	60.91	1.97	1.48

Al(210) surface, we addressed several issues regarding the implementation of semiempirical approaches to the study of such phenomena. We noted that surface relaxations other than reconstruction involve small energy changes which may be difficult to determine accurately considering approximations used and the precision of the input parameters. In examining these issues for ECT applied to the Al(210) surface, we find that we obtain different results for experiment and considerable uncertainty in the theoretical predictions. The quality of the equivalent crystal theory results facilitates the discussion on the influence of several factors, both internal and external, on the ensuing results: the quality of the experimental input used, the mechanisms present in the algorithm for describing the behavior of the system and the analysis of the results in terms of relevant properties associated with the system under study. Therefore, at present we feel that conclusions based on theoretical values of surface relaxations are, at best, only meaningful to the extent that they refer to relaxation patterns and relative magnitudes.

Acknowledgements

Fruitful discussions with Dr. N. Bozzolo are gratefully acknowledged. This work was partially supported by the Engineering Directorate, NASA Lewis Research Center. A.M.R. would like to thank the Ohio Aerospace Institute, for partial financial support and the NASA Lewis Research Academy, where part of this work was done.

References

[1] J. Sokolov, H.D. Shih, U. Bardi, F. Jona and P.M. Marcus, J. Phys. C 17 (1984) 371.
[2] J. Sokolov, F. Jona and P.M. Marcus, Phys. Rev. B 31 (1985) 1929; B 29 (1984) 5402; Solid State Commun. 49 (1984) 307.
[3] D.L. Adams, V. Jensen, X.F. Sun and J.H. Vollesen, Phys. Rev. B 38 (1988) 7913.
[4] J.R. Noonan, H.L. Davis and W. Erley, Surf. Sci. 152 (1985) 142.
[5] D.L. Adams and C.S. Sorensen, Surf. Sci. 166 (1986) 495.
[6] D.L. Adams, W.T. Moore and K.A.R. Mitchell, Surf. Sci. 149 (1985) 407.
[7] P.R. Watson and K.A.R. Mitchell, Surf. Sci. 203 (1988) 323.
[8] P. Jiang, F. Jona and P.M. Marcus, Surf. Sci. 185 (1987) L520.
[9] X.-G. Zhang, M.A. Van Hove, G.A. Somorjai, P.J. Rous, D. Tobin, A. Gonis, J.M. MacLaren, K. Heinz, M. Michl, H. Lindner, K. Mueller, M. Ehsasi and J.H. Block, Phys. Rev. Lett. 67 (1991) 1298.
[10] S.B. Sinnott, M.S. Stave, T.J. Raeker and A.E. DePristo, Phys. Rev. B 44 (1991) 8927.
[11] P. Jiang, P.M. Marcus and F. Jona, Solid State Commun. 59 (1986) 275.
[12] S.P. Chen and A. Voter, Surf. Sci. 244 (1991) L107.
[13] R.N. Barnett, U. Landman and C.L. Cleveland, Phys. Rev. B 27 (1983) 6534; B 28 (1983) 1685; Phys. Rev. Lett. 51 (1983) 1359.
[14] A.M. Rodríguez, G. Bozzolo and J. Ferrante, Surf. Sci. 289 (1993) 100.
[15] J.R. Smith and A. Banerjea, Phys. Rev. Lett. 59 (1987) 2451; Phys. Rev. B 37 (1988) 10411.
[16] J.R. Smith, T. Perry, A. Banerjea, J. Ferrante and G. Bozzolo, Phys. Rev. B 44 (1991) 6444.
[17] J.H. Rose, J. Ferrante and J.R. Smith, Phys. Rev. Lett. 47 (1981) 675.
[18] W.R. Tyson and W.A. Miller, Surf. Sci. 62 (1977) 267.
[19] W.R. Tyson, J. Appl. Phys. 47 (1976) 459.
[20] L.Z. Mezey and J. Giber, Jpn. J. Appl. Phys. 21 (1982) 1569.
[21] H. Wawra, Z. Metallk. 66 (1975) 395.
[22] S.M. Foiles, M.I. Baskes and M.S. Daw, Phys. Rev. B 22 (1986) 7983.
[23] H.L. Davis, J.B. Hannon, K.B. Ray and E.W. Plummer, Phys. Rev. Lett. 68 (1992) 2632.
[24] J.R. Noonan and H.L. Davis, Phys. Rev. B 29 (1984) 4349.
[25] J.R. Noonan and H.L. Davis, J. Vac. Sci. Technol. A 8 (1990) 2671.
[26] J.W.M. Frenken, J.F. van der Veen and G. Allan, Phys. Rev. Lett. 51 (1983) 1876.
[27] S.M. Yalisove, W.R. Graham, E.D. Adams, M. Copel and T. Gustafsson, Surf. Sci. 171 (1986) 400.
[28] J.E. Demuth, P.M. Marcus and D.W. Jepsen, Phys. Rev. 11 (1975) 1460.
[29] R. Mayer, C. Zhang, K.G. Lynn, W.E. Frieze, F. Jona and P.M. Marcus, Phys. Rev. B 35 (1987) 3102.
[30] I. Stensgaard, R. Feidenhans'l and J.E. Sorensen, Surf. Sci. 128 (1983) 281.
[31] S.A. Lindgren, L. Walldén, J. Rundgren and P. Westrin, Phys. Rev. B 29 (1984) 576.
[32] P.J. Feibelman, Phys. Rev. B 46 (1992) 2532.