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Modified lattice-statics approach to surface calculations in a monatomic lattice*

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The modified lattice-statics approach has been extended to the calculations of atomic relaxations resulting from the formation of (100), (110), and (111) surfaces in a monatomic semi-infinite lattice. This method allows anharmonic contributions to be included for atomic layers undergoing large displacements. As an example of this technique, displacements have been determined for atomic layers in the vicinity of high-symmetry surfaces in α-iron.

I. INTRODUCTION

When a surface is formed in a crystal the atoms in the vicinity of the surface generally become less tightly bound than those in the bulk and relax to new equilibrium positions such that the spacing between atomic layers near the surface may be considerably different from the bulk interlayer spacing. The calculation of these interlayer spacings near the surface is of fundamental importance to any attempt to understand how the surface interacts with other defects within the crystal and with adatoms on the surface itself.

Calculations of atomic configurations on and near the surface of metallic crystals have, for the most part, been done using the same sort of computer simulation techniques which have been employed in point-defect calculations in bulk crystals. This approach, in general, involves programming a computer to deal with a "model crystallite" consisting of several thousand atoms initially at their perfect lattice equilibrium separations and arranged such that at least one of the crystallite faces has the orientation of the surface under investigation. It is then assumed that the atoms interact with each other by means of a pairwise potential, which in surface calculations is generally a Morse potential or pseudopotential. The actual calculation consists of allowing the atoms or layers of atoms near the surface to relax, one by one, until the energy of the configuration is minimized (the net force acting on any given atom is zero within some specified tolerance). This "direct space" type of calculation has been used by Wynblatt and Gjostein,[1,2] Bonneton and Drechsler,[3] Jackson,[4] and Kato[5] in theoretical investigations of the surface properties of metals. One of the primary drawbacks of this type of calculation is the use of generally long-range potentials in a crystal model which may have dimensions on the order of only 100 Å. Moreover, the size of the crystallite is effectively limited by the number and complexity of interatomic force equations that can be handled by the computer facilities available.

An alternative method for calculating relaxations of atoms in the presence of defects is provided by the Green's-function approach. While there are some variations in the formalism used by various investigators, the underlying principles are the same. Using translational symmetry, the infinite lattice is subdivided into a number of identical "supercells" each containing a large number N of host atoms and one defect at the center. The $3N \times 3N$ direct-space force equations for the atoms in any given supercell are Fourier transformed to reciprocal space, resulting in N 3×3 decoupled equations which can be solved for the Fourier amplitudes by straightforward matrix inversion. The direct-space displacements can then be found by a back transformation. (It should be mentioned that in some formalisms, notably that of Tewary[6] and Tewary and Bullough[7] the entire calculation is done in reciprocal space without the direct-space potential being known explicitly. However, the information contained in the resulting Green's function is essentially the same as that which would be provided by the direct-space interatomic force equations.)

Green's-function techniques have been applied in qualitative surface calculations by Feuchtwang[8] and by Corciovei, Croitoru, and Grecu.[9] More recently the author[10] employed a Green's-function (or lattice statics) technique to determine numerical symmetry surfaces in α-iron and Cu.

The Green's-function approach allows extremely large "crystallites" or "supercells," the size of which can, in principle, be increased to infinity. Like the direct-space techniques, most Green's-function formalisms contain implicitly or explicitly the assumption of pairwise interactions between atoms (and between the defect and the host atoms). The major drawback of the Green's-function approach, however, is that Fourier transformations used are only valid in the harmonic approximation.

Hence the reliability of the results of a Green's-function calculation depends on the direct-space displacements of atoms in the vicinity of a defect being small, a condition which is not likely to be satisfied by the atomic layers forming the surface of a metal crystal.

The difficulties described above for the direct space and the Green's-function types of calculation can be avoided to a large extent by combining the two in such a way that the displacement of atoms near a defect (or surface) are computed in direct space and the relaxation of the remainder of the lattice, which is likely to be fairly small, is calculated in the harmonic approximation, using lattice statics. A "modified-lattice-statics" technique (hereafter referred to as the MLS method), embodying these features was developed by the author earlier[11] and applied to determine the displacement of host atoms around simple vacancies and octahedral carbon interstitials in α-iron.

The purpose of this paper is to apply the MLS formalism to determine the displacement of atomic layers in the vicinity of high-symmetry surfaces in monatomic lattices. As a numerical example of the application of the MLS technique to surface relaxations, calculations have been done for the (100), (110), and (111) surfaces in α-iron, using the short-range bulk potential developed by Johnson.[12] The use of a bulk potential in the vicinity of a surface of a metal crystal is, of course, completely unjustifiable and the numerical results of such a calculation must be regarded as qualitative at best. However, the same criticism may be made against virtually all surface calculations reported in the literature thus far. The point is that if one can reliably represent the interactions of atoms in the vicinity of a surface by means of a pairwise potential, the MLS method will provide a means of determining the relaxation of surface layers under the direct forces exerted by the "surface" on the remainder of the lattice.

In Sec. III, the MLS method is reviewed in more detail. Section III contains a discussion of how the MLS technique may be applied to surface relaxation calculations. In Sec. IV, the results of a calculation of atomic relaxations near high-symmetry surfaces in α-iron are presented.

II. GENERAL THEORY

The lattice-statics approach to surface relaxation calculations in cubic metals has been fully developed in an earlier paper,[10] therefore only the salient points of the formalism will be repeated here. It is assumed that the interaction between pairs of atoms can be described by means of a pairwise central potential $\phi(r)$. The lattice, originally assumed to be infinite, is subdivided into "supercells" each containing a defect at the center and a large number N of host atoms. Since the surface itself is considered to be the defect in the present context, the "supercells" take on the form of slabs with a plane of atoms missing in the center.

In the case of high-symmetry surfaces it has been shown quite generally[3] that the formation of the surface leads to relaxations which are entirely normal to the surface. It will be assumed that the interatomic spacings in the plane of the surface will not be altered from their values for the perfect lattice. The problem then becomes one-dimensional and can be formulated in terms of interlayer spacings and interlayer forces as in Ref. 10.

However, as pointed out earlier, the assumptions inherent in the harmonic approximation make its application to the first few surface layers of dubious validity. Therefore, in the modified lattice statics approach, those surface layers for which large displacements are anticipated, are allowed to relax in direct space using forces derived explicitly from a pairwise interatomic potential $\phi(r)$, rather than the series expansion used in the "pure" lattice statics approach.[10]

In most cases it appears necessary to treat in direct space only those surface layers which interact directly with the defect, which generally means only the first or first and second layers. Assuming that the first two layers are so treated, the modified lattice statics calculation proceeds in a three-step sequence. First, the top layer is allowed to relax in direct space holding all other layers fixed at their perfect lattice positions. Next, the second layer is relaxed, again holding all other layers fixed. These steps are repeated iteratively until the net force on each of the first two layers is below a specified tolerance level. The third step consists in determining the relaxation of the remainder of the lattice using essentially the same techniques as described above for the regular-lattice-statics calculation. In determining the force array for this portion of the calculation, only the harmonic portion of the direct-space defect-host interaction should be used since the dynamical matrix, $\vec{V}^{-\vec{q}}$ contains only harmonic terms.[13] Once the lattice has been relaxed the entire process must be repeated until self-consistency is attained, that is, until the results of two successive iterations are identical within some predetermined tolerance.

III. APPLICATION OF MLS TO SURFACES IN α IRON

The modified lattice statics technique has been applied to determine the relaxation of atomic layers in the (100), (110), and (111) surfaces in α-iron. The interatomic interaction used was that

TABLE I. Relaxation of atomic layers near a (100) surface in α-iron.

Layer	Relative displacements[a] (Å) MLS	LS
1	+0.095 5	+0.094 8
2	−0.020 4	−0.019 8
3	+0.004 15	+0.004 14
4	−0.000 87	−0.000 86
5	+0.000 18	+0.000 18
6	−0.000 038	−0.000 037

[a] Positive values indicate expansion; negative values indicate contraction.

developed by Johnson[11]:

$$\phi(r)=3.365(2.236-r)^3+0.886r-2.156\ \text{eV}.$$

This potential has been widely applied to other types of defect calculations in α-iron[14,15] with reasonable results. It is, nevertheless, a bulk potential which is being used only for lack of availability of pairwise interatomic potentials suitable for atoms on or near the surface. The results to be reported here, therefore, ought to be considered qualitative at best.

The coordinate systems and basic unit cells used in the present work were those used earlier in the exact-lattice-statics calculation fully described in Ref. 10. Since the interatomic potential used extends out to first and second neighbors, geometrical considerations show that the first two layers of the (100) surface interact directly with the surface and both layers were treated anharmonically. The (111) surface is even more complicated in that the first three layers interact directly with the surface, hence all three layers were relaxed in direct space. The atomic layers on the (110) surface interact only with nearest-neighboring layers.

The summations over wave vectors $\vec{q}$ were performed using the Gaussian quadrature technique employing 40 zeros of Legendre polynomials. Direct-space iterations proceeded until the net force acting on each of the layers treated anharmonically was less than 10^{-12} dyn and calculations were carried out until the lattice-statics displacements for two successive iterations were within 10^{-12} Å of each other.

Relaxations were obtained for the top 20 layers of the surface in each case using the KRONOS (CDC-6400) time-sharing system at the University of Nebraska at Omaha. Numerical results for the first six atomic layers of the (100) surface are shown in Table I. Relative displacements obtained from the modified-lattice-statics (MLS) approach are given along with the corresponding lattice statics (LS) results. Relative displacement indicates an increase or decrease in interlayer separation relative to that of the perfect lattice. Table II contains a similar comparison of LS and MLS results for relative displacements of the first ten layers of the (111) surface in α-iron.

Results are not tabulated for the (110) surface. In this case, only the top layer of atoms has a direct interaction with the "removed" layer and the effect of "forming" the surface is analogous to applying a force at the end of a spring; the result is simply a uniform expansion or contraction of the interlayer separation. Since the present calculation involves an extremely large (essentially infinite) number of layers, this uniform expansion is not detectable within the tolerance specified in the computer program, and for a straight lattice statics calculation the relative displacements of the atomic layers are all zero. However, in the MLS calculation the first layer was relaxed using direct space forces and a relative displacement of -2.02×10^{-7} Å was obtained.

IV. DISCUSSION

The extension of the lattice statics formalism to allow anharmonic effects to be included in calculating relaxations of atomic layers which are likely to be displaced significantly when a surface is formed, does not substantially alter the qualitative results obtained from exact lattice statics in the case of α-iron. This is perhaps not too surprising since the displacements obtained by direct lattice statics were not extremely large to begin with. The displacements of layers on the (100) surface consist of alternate expansions and contractions of the interlayer separations and die out rapidly with increasing distance from the surface. Displacements of (111) surface layers tend to die out far less rapidly than in the ⟨100⟩ direction. It should also be noted that the anharmonic contributions to

TABLE II. Relaxation of atomic layers near a (111) surface in α-iron.

Layer	Relative displacements[a] (Å) MLS	LS
1	+0.007 001	+0.005 712
2	−0.017 56	−0.011 035
3	+0.005 529	+0.005 549
4	+0.000 492	+0.000 424
5	−0.002 53	−0.002 44
6	+0.001 59	+0.001 59
7	−0.000 133	−0.000 147
8	−0.000 534	−0.000 523
9	+0.000 437	+0.000 435
10	−0.000 109	−0.000 112

[a] Positive values indicate expansion; negative values indicate contraction.

the first and second layer displacements are relatively greater for the (111) surface than for the (100) surface. Both of these effects can most likely be attributed to the fact there is a direct nearest-neighbor bond between an atom at the (111) surface and an atom lying beyond the $z = 0$ plane, which is normal to the surface and which is "broken" when the surface is formed. Hence, as Jackson[4] points out, geometry dictates that the displacements at the (111) surface ought to be larger than at either of the other two high-symmetry surfaces. The α-iron "model" used here is perhaps not typical in this respect, however, since the magnitudes of the first- and second-neighbor radial force constants, Bi, which in the harmonic approximation determine the interlayer forces *before* relaxation, are opposite in sign and nearly equal in magnitude. In the case of the (111) surface, this condition yields rather small surface forces before relaxation takes place.

It must be stressed again that the present calculations have employed a bulk interatomic potential, as appears to be true for all other calculations of surface displacement which have been reported,[1-5] although most other workers have employed Morse or Mie potentials. The results of any of these calculations, including the present work, must therefore be regarded as qualitative, at best, since it seems evident that the electronic distributions, which dominate interatomic interactions in metals, differ significantly at a surface from those in the bulk.

The most important aspect of the present work, however, lies not in the numerical results which have been obtained, but rather the development and presentation of an analytic technique which, given the proper pairwise potentials, will produce reliable values for the relaxations of surface layers. The modified lattice statics formalism allows calculations to be done on a semi-infinite surface model in which most of the atomic layers are relaxed simultaneously, yet allows the incorporation of anharmonic effects for as many layers as necessary.

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