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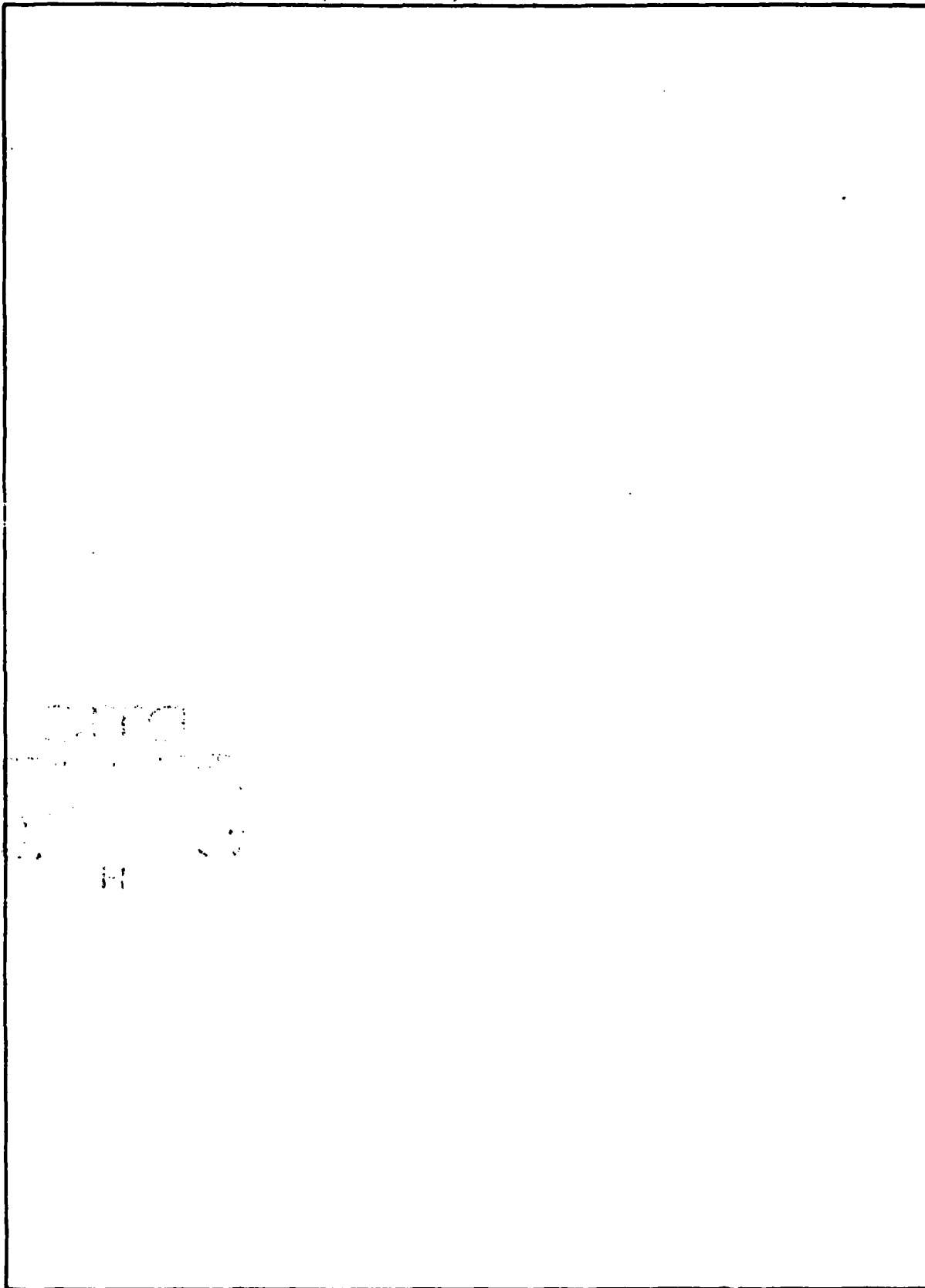
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I. Overview

I believe the research carried out under U.S. Air Force sponsorship as Grant AFOSR-77-3114 has resulted in a number of significant advances in our fundamental understanding of materials science. The general approach was to apply theoretical solid state physics and quantum chemistry techniques to problems of concern in materials. An overview/summary will be presented first, followed by a list of publications with a more detailed synopsis. As may be seen, the emphasis shifted from ceramic to metallic systems.

Hydrogen Embrittlement - a new mechanism that may play a role in hydrogen assisted failure was proposed. We recognize the abundance of existing theories. But this mechanism is one of the few based on ab initio calculation rather than enlightened empiricism. Our quantum chemical cluster calculations implied that absorbed hydrogen induced large tensile stresses at the very surface of a metal (and compressive stresses when hydrogen is in the interior). Implications for experiments in both low carbon and high strength steels were discussed.

Oxidation - the very early stages of oxidation of aluminum was modeled, again using quantum chemical cluster calculations. They resolved a discrepancy between work function measurements and LEED and EXFAS measurements. Such studies should enhance our understanding of the oxidation process.

Grain Boundaries - again quantum chemical cluster methods were used to model the close-packed Bernal polyhedra structure now thought to be typical in grain boundaries. The influence of hydrogen on the structure was investigated and, again, the results suggested significant stresses were induced.

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Stacking Faults - the textbook model of a stacking fault is a hard sphere interface between fcc and hcp stacking. We modeled these faults with computer simulation techniques. The important details (choice of input interatomic forces, relaxation procedure, boundary effects) will be discussed later. Suffice to say that we demonstrated that small relaxations could completely obviate the conventional stacking fault energy expressions. In addition, contributions from the cores of the dissociated partial dislocations can be significant and even dominating. Peculiar, and perhaps suggestive, results were obtained for aluminum (where, in agreement with experiment, little dissociation occurred). The structure of the stacking fault will be needed in the interpretation of the recent very sensitive lattice imaging and weak beam microscopy experiments.

Brittle Fracture - thermodynamic and kinetic aspects of crack propagation in brittle materials were analyzed from an atomistic viewpoint.

Interatomic Forces - In the last decade, there has been a surge of computer simulation calculations. Almost all were carried out by individuals whose training was in mechanics. As a result, the assumptions in the mechanical model - specifically the choice of interatomic forces - were not always examined as critically might be desirable. We have evaluated the methodology proposed for a class of pair potentials in transition metals by applying the same approach to derive pair potentials for simple metals (alkali metals, aluminum). In the latter case reliable ab initio calculations provide benchmark potentials. The agreement was poor. We proposed extracting pair potentials using experimental phonon spectra data and generated potentials for essentially all metals with fcc or bcc structures. The results for the simple metals compared favorably with the ab initio results.

II. Publications

1. Modified Lattice-Statics Approach to Dislocation Calculations. I. Formalism. D. M. Esterling, J. Appl. Phys. 49, 3954-3959 (1978).
2. Modified Lattice-Statics Approach to Dislocation Calculation. II. Application. D. M. Esterling and J. d. Moriarty, J. Appl. Phys. 49, 3960-3966 (1978).
3. Equilibrium and Kinetic Aspects of Brittle Fracture, D. M. Esterling, Int. Journ. of Fracture 14, 417-427 (1978).
4. Equivalence of Macroscopic and Microscopic Griffith Conditions for Subcritical Crack Growth, D. M. Esterling, Int. Journ. of Fracture, 17, 321-325 (1981).
5. Interatomic Potentials From Experimental Phonon Spectra. I. Prototype, D. M. Esterling and A. Swaroop, Phys. Stat. Sol. (b) 96, 401-411 (1979).
6. Interatomic Potentials From Experimental Phonon Spectra. II. General Results, A. Swaroop and D. M. Esterling, Phys. Stat. Sol. (b) 96, 691-696 (1979).
7. Reliability of Various Empirical Potential Methods, D. M. Esterling and A. Swaroop, Phys. Stat. Sol. (b) 97, 101-104 (1980).
8. Realistic and Reliable Pair Potentials from Transition Metals and Alloys, Published in Theory of Alloy Formation, TMS-AIME Conference Proceedings (New Orleans, LA, 1979), Edited by L. A. Benett.
9. Dislocation Dissociation in Some FCC Metals, D. M. Esterling, Acta. Met. 28, 1287-1294 (1980).
10. Lattice Statics Approach to Fracture and Plasticity, D. M. Esterling, Comments on Solid State Physics, 9, 105-114 (1979).
11. Alloying, Chemisorption and Hydrogen Embrittlement of Steel, D. M. Esterling, Materials Science and Engineering, 16, 113-117 (1980).
12. Surface Relaxation and Induced Stress Accompanying the Adsorption of H upon Be (0001), B. N. Cox and C. Bauschlicher, Jr., Surf. Sci. 102, 295-311 (1981).
13. Cluster Calculations of Hydrogen in the Grain Boundaries of Nickel, B. N. Cox and C. Bauschlicher, Jr., Surf. Sci. 108, 483-502 (1981).
14. A Cluster Model of the Chemisorption of Atomic Li, O and Na by the (111) Surface of Al, B. N. Cox and C. Bauschlicher, Jr., Surf. Sci. 115, 15-36 (1982).

III. Technical Synopsis

A. Advances in Computer Simulation Techniques

1. Modified Lattice-Statics Approach to Dislocation Calculations.
I. Formalsim. D. M. Esterling, J. Appl. Phys. 49, 3954-3959 (1978).
2. Modified Lattice-Statics Approach to Dislocation Calculation.
II. Application. D. M. Esterling and J. Moriarty, J. Appl. Phys. 49, 3960-3966 (1978).

Virtually all previous work that simulated extended defects assumed that beyond a suitable distance from the defect center that the displacement field could be obtained from continuum elasticity theory. Practical computer limits lead to placement of an elastic boundary (rigid or flexible) at modest distances from the defect center. The back stress due to the (artificial) rigid boundary can lead to serious errors in estimating the yield stress for the model system. The modified lattice-statics method permits the extension of the discrete lattice to infinity. Beyond a certain distance the detailed interatomic forces are assumed to become linear restoring forces. This is a much weaker assumption than taking the displacements as continuum elasticity results: The discrete/continuum boundary is replaced by a harmonic/anharmonic boundary. The modified lattice statics method does have the disadvantage of complexity in comparison with more conventional modeling approaches. We employed the method in modeling studies in references 1, 2, 3, 4 and 8. The method was reviewed in reference 9.

B. Theory of Brittle Fracture

3. Equilibrium and Kinetic Aspects of Brittle Fracture, D. M. Esterling, Int. Journ. of Fracture 14, 417-427 (1978).
4. Equivalence of Macroscopic and Microscopic Griffith Conditions for Subcritical Crack Growth, d. M. Esterling, Int. Journ. of Fracture, 17, 321-325 (1981).

It is now well established that sizeable deviations from classical Griffith theory can occur for fast fracture. These are due to "lattice-trapping" effects first studied in detail by Hsei and Thomson and later

elaborated by Esterling. Recently Fuller and Thomson, as well as J. Rice, have suggested that the classical Griffith result is valid for prediction of subcritical crack growth (crack creep). There was an apparent conflict with some earlier results of Esterling. The suggestion was made that a numerical error existed in the program. This has since been shown not to be the case. However, Esterling, as well as Hsei and Thomson in an earlier paper, did not use the correct continuum limit in obtaining the Griffith result (Specifically the simple "bond-snapping" model of Hsei and Thomson has a non-zero Poisson ratio). We have recently completed numerical results for a non-linear force law for a two-dimensional crack face and also obtained some exact analytical results for the "bond-snapping" models. All the corrected results are in accord with the Fuller-Thomson argument that the Griffith prediction can be applied to subcritical crack growth.

C. Interatomic Potentials

5. Interatomic Potentials From Experimental Phonon Spectra.
I. Prototype, D. M. Esterling and A. Swaroop, Phys. Stat. Sol. (b) 96, 401-411 (1979).
6. Interatomic Potentials From Experimental Phonon Spectra.
II. General Results, A. Swaroop and D. M. Esterling, Phys. Stat. Sol. (b) 96, 691-696 (1979).
7. Reliability of Various Empirical Potential Methods, D. M. Esterling and A. Swaroop, Phys. Stat. Sol. (b) 97, 101-104 (1980).
8. Realistic and Reliable Pair Potentials from Transition Metals and Alloys, Published in Theory of Alloy Formation, TMS-AIME Conference Proceedings (New Orleans, LA, 1979), Edited by L. A. Bennett.

Computer simulation of microstructure can only be as valid as its input. A major concern for us has been the almost universal use of Johnson empirical potentials. We have always been concerned about the assumptions used in deriving these short-ranged potentials. During the funding period

we authored three manuscripts dealing with the systematic derivation of empirical potentials from neutron scattering data (References 5, 6 and 8).

The pair potentials obtained with this straightforward and systematic approach originally proposed by Brosens, Cornelis, Wallace and Devreese deviated substantially from the associated Johnson potentials. The first paper (Reference 5) was designed to establish their reliability through comparison with liquid metal results (when available) and with pseudopotential theory results for simple metals. In addition, the internal consistency as the assumed range was increased provided additional evidence that Nature was tracing out a pair potential for us. The second paper (Reference 6) presented results for a large range of fcc and bcc metals. In Reference 8, we propose extension of the method to alloy systems.

In addition, in Reference 7 we have gained some further insights into the problem with the Johnson empirical potentials and related potentials. These potentials use the vacancy formation energy as an input parameter. They assume that this energy can be derived wholly from the pair potential portion of the total energy. This is incorrect. The situation has been clearly established by Popovic, Carbotte, and Piercy. They showed that the change in electron density due to the formation of the vacancy (more accurately the shift in the Fermi wavevector k_F) leads to contribution from the structure independent portion of the total energy which is quite large and cannot be ignored. This effect is in addition to any relaxation or any volume dilational effects. The procedure developed by Johnson and others places the entire burden for the formation energy on the pair potential portion of the total energy. This severely distorts the form of the derived pair potential, frequently leading to a spurious deep well near

the nearest neighbor distance. We applied the Johnson-like procedure to derive a pair potential for aluminum - a case where the pair potential is already well known from pseudopotential theory. The agreement was poor as anticipated suggesting in the acceptance of Johnson potentials for transition metals where there are no benchmark comparisons available.

D. Stacking Fault Configuration in FCC Metals

9. Dislocation Dissociation in Some FCC Metals, D. M. Esterling, Acta. Met. 28, 1287-1294 (1980).

The dissociation of a perfect screw dislocation into a stacking fault in an fcc lattice was modeled by the modified lattice statics technique. The interatomic potentials were those derived in References 3 and 4. Hence, the only input information for the empirical potentials was phonon spectra data. The calculated stacking fault widths for Al, Cu, and Ag were in good agreement with the experimental results from weak beam microscopy. This is a non-trivial result (although by no means should be viewed as an absolute confirmation of the validity of our pair potentials!). In an NSF/NATO sponsored study we employed potentials from other authors (for the same three metals) and in that case, the stacking fault widths deviated strongly from the measured values - even though the latter potentials included a "stacking fault energy" as an input parameter. As mentioned in the above summary, the textbook stacking fault energy expressions neglect core effects and relaxations from a hard sphere stacking configuration. These considerations may not be neglected in any theoretical study. Further, a complete interpretation of the weak beam microscopy results must include corrections due to configuration relaxations including core effects.

E. Review Paper

10. Lattice Statics Approach to Fracture and Plasticity, D. M. Esterling, Comments on Solid State Physics, 9, 105-114 (1979).

The Editors of Comments on Solid State Physics asked Esterling to write a review of the lattice statics method and its applications. The paper surveys some representative work on the computer simulation of microstructure, including some semidiscrete model work. However, considerable emphasis is placed on future needs in such areas as: reliable pair potentials, finite temperature effects (including entropy), additional defect studies (e.g. grain boundaries) and the critical need for the study of defect-defect interactions (solute atom-dislocation, impurity atom-crack tip).

F. Environmental Embrittlement of Steel

11. Alloying, Chemisorption and Hydrogen Embrittlement of Steel, D. M. Esterling, Materials Science and Engineering, 16, 113-117 (1980).

In Reference 11, we proposed that the embrittling behavior of hydrogen or iron and its alloys could be correlated with its chemisorption energy. This is based on the "reduction in surface energy" models recently proposed by Fuller and Thomson and by I. C. Howard. To complete our analysis, we would need to know the effect of alloying iron on its chemisorption energy. This has not been determined experimentally. Instead we use auxiliary experiments and some recent theories of alloying to suggest that the chemisorption energy will be essentially unchanged on alloying, even at large concentrations or with exotic elements. Hence we conclude that alloying does not appear to offer an effective remedy for reducing the intrinsic embrittling process. This is in contrast to the influence of alloying in modifying the fracture path (e.g. temper embrittlement elements leading to intergranular fracture). In the latter case, alloying may significantly influence the importance of hydrogen embrittlement by symbiotic effects such as weakening internal bonds or changing local microstructure to one more susceptible to embrittlement.

G. Applications of Quantum Chemistry to Surface/Interfacial Effects Including Embrittlement

12. Surface Relaxation and Induced Stress Accompanying the Adsorption of H upon Be (0001)₁, B. N. Cox and C. Bauschlicher, Jr., Surf. Sci. 102, 295-311 (1981).
13. Cluster Calculations of Hydrogen in the Grain Boundaries of Nickel, B. N. Cox and C. Bauschlicher, Jr., Surf. Sci. 108, 485-502 (1981).
14. A Cluster Model of the Chemisorption of Atomic Li, O, and Na by the (111) Surface of Al, B. N. Cox and C. Bauschlicher, Jr., Surf. Sci. 115, 15-36 (1982).

Ab initio cluster calculations have been performed to provide a basic understanding of possible mechanisms of the hydrogen embrittlement of nickel, and the early stages of the oxidation of the close-packed surface of aluminum. The first calculations performed were of relaxation induced by hydrogen absorbed on the close-packed (0001) surface of beryllium described in Reference 12. The total Hartree-Fock energy of clusters of seven, ten, and fourteen beryllium atoms was calculated as a function of the substrate's lattice parameter, both in the presence and absence of an adsorbed hydrogen atom. The equilibrium lattice parameters thus obtained demonstrated that hydrogen draws together the nearest surface beryllium atoms with great force. The nearest surface bond lengths are shortened by one to two percent. A simple computer simulation of the effect of a random, low coverage of hydrogen then showed that, at a coverage of ~10% of a monolayer, surface stresses on the order of magnitude greater than the bulk yield stress of beryllium would be induced. If a similar effect exists in engineering metals, especially steels, the induced stresses are clearly large enough to be an important factor in their being damaged by hydrogen. Several experiments relating to the influence of hydrogen upon dislocation initiation and void initiation and growth in steels can be interpreted in terms of induced surface stresses. Specifically the void density in low carbon steel fractured in the presence of hydrogen is much enhanced. We suggest that this might be due to a "drawing

together" of the surface of the void by the adsorbed hydrogen (in contrast to the usual void pressurization ideas). The drawing together might inhibit growth at the expense of enhanced nucleation leading to a higher void population density.

The induced contraction of a surface is in contradistinction to the expansion caused universally by hydrogen absorbed into a metal's bulk. The radical difference between surface and bulk responses suggested the investigation of the effect of hydrogen on the grain boundaries of a metal as described in Reference 13. Nickel was chosen for study, since it is next to iron on the periodic table and shares with steels the qualitative features of hydrogen embrittlement, yet is amenable to a simplified treatment of the d-bands. Grain boundaries were modeled by clusters in the form of close-packed Bernal polyhedra, which enclose a volume ranging from that of a tetrahedral interstice up to that of a vacancy. It was found that a single enclosed hydrogen atom caused expansion of the smallest polyhedra, in agreement with the expansion caused by hydrogen in nickel-hydrogen solid solutions, but a contraction of 1.7 to 2.8% in the linear dimensions of the largest, most open polyhedra. Once again it may be expected that a random presence of hydrogen throughout such structural units of a grain boundary will induce very large stresses, which may well be related to the fact the hydrogen embrittlement in un-notched nickel is always manifested by inter-granular fracture. It was also found that, as for beryllium, hydrogen causes a shrinkage of similar proportions in the close-packed (111) surface of nickel. The shrinkage induced in the larger Bernal polyhedra was interpreted in terms of the calculated charge transfers.

A question of great current interest is the initial reaction of oxygen with a clean (111) surface of aluminum. This central problem of corrosion

has been widely studied since the discovery that formation of the amorphous oxide phase of exposed aluminum (111) is preceded by the formation of an ordered (1x1) overlayer. However, some dispute has arisen between various experiments over the character of this overlayer, and previous theoretical work has not resolved the situation. Therefore cluster calculations were made of a single oxygen atom adsorbed to nineteen aluminum atoms in Reference 14. The bonding geometry was determined accurately and should settle the experimentalist's dispute. The chemical nature of the bond was shown to be appreciably covalent. Because of this covalence, the calculated dipole moment induced by the adsorbed oxygen atom is anomalously small, in agreement with null measurements of the change in work function accompanying the first exposure of Al(111) to oxygen. These work function measurements were not previously understood, since they seemed to imply that the oxygen was adsorbed within the surface layer, in contradiction of LEED and EXAFS measurements.

Calculations were also performed for atoms of lithium and sodium adsorbed on Al(111) in Reference 14. They were found to form quite ionic bonds, with the calculated dipole moments for sodium in good agreement with work function measurements. Both sodium and lithium adsorbates were found to have very low activation energies for diffusion over the Al surface.

IV. Personnel

This grant provided support for the Principal Investigator, D. M. Esterling, and three postdoctoral research associates. The three associates were:

Dr. Anand Swaroop, currently with Systems and Applied Sciences, Washington, DC.

Dr. Brian Cox, currently with Rockwell International Science Center,
Thousand Oaks, CA.

Dr. Ian Boswarva, currently with JIAFS, The George Washington
University, NASA-LRC, Hampton, VA.

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