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II. RESEARCH PROGRESS

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We have made substantial progress in improving potential-energy functions in transition metals and their aluminides. For elemental transition metals, we have developed a force code including angular forces, which has been supplied to several other workers in the field. For the aluminides, we have developed the first quantum-mechanically based pair potentials that describe structural energies. We have also continued to develop the basic theory of interatomic potentials, with particular emphasis on the physical consequences of nonorthogonality effects, and the effects of coordination number losses on alloy ordering energies. We have completed a substantial body of work on the stability of complex aluminide phases, including quasicrystals. These calculations have been performed with both pair potentials and *ab-initio* methodologies. Via *ab-initio* calculations, we have obtained some new insights into the nature of bonding in transition-metal oxides. We have made some initial explorations into the effect of the potential-energy function on crack properties, in particular the emission of dislocations from cracks. Finally, we have continued to push on the basic theory of interatomic potentials by evaluating the extent to which many-body interactions are caused by nonorthogonality effects. The significance of the results that have been obtained during this installment has been recognized by a number of invited talks at major meetings, as well as invited review papers.

A. Potential-Energy Functions for *d*-band Metals

(Publications 2, 6, 17, and 19)

We have made progress both for elemental bcc transition metals, and for generic surface ordering interactions (Ising-type parameters). Our method for the bcc transition metals is based on the basic physics of the Fermi-level "quasigaps" vs. peaks in the electron density of states (DOS). This can be best understood though the simplified analysis indicated in Fig. 2.

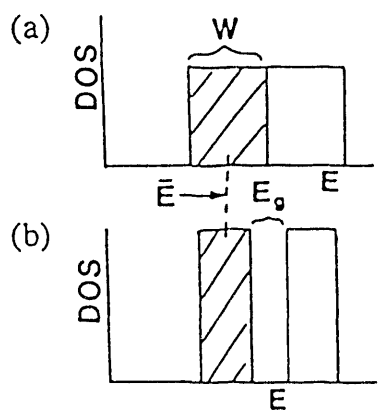

FIG. 2. Model electronic density-of-states distributions illustrating stabilizing effect of quasigap. $\bar{E}$ denotes average energy of occupied states.

In this picture, both DOS distributions are assumed to have the same value of μ_2, which is the mean-square value of E^2 when averaged over the electronic density of states (DOS). Thus μ_2 gives a way of quantifying the band-broadening contribution to the cohesive energy, and the contributions beyond μ_2 of interest here correpond to band-shape effects. For the top DOS, one sees that $\mu_2 = W^2/3$ (when normalized by the total weight of the DOS). In the half-filled band case (fairly appropriate for the bcc transition metals), the Fermi level lies in the gap of the right-hand-side DOS. In this case, the band energy (defined as the average energy per electron, relative to the center of the band) for the gapless DOS is simply $-W/2$. A simple calculation shows that the band energy for the DOS with a gap is approximately $-W/2 - E_g/8$. Thus the gap provides a stabilizing contribution to the structural energy, if the Fermi level lies in the gap. The same holds for a quasigap, or reduced value of the DOS. One can also readily show that μ_4 drops when the quasigap is created.

Using this physics, with the quasigap effects measured by the fourth moment μ_4 of the DOS, we have developed a semiempirical angular-force method for Group VI transition metals. This method is based on the electronic energy as a function of the moments

$$\mu_n = \int_{-\infty}^{\infty} E^n \rho(E) dE$$

up through μ_4 where $\rho(E)$ is the DOS. The key observation behind the method is that μ_n is rigorously given[14] in tight-binding models as as sum real-space path terms of order up to n. The method contains only four adjustable parameters, which is a much smaller number than is typically included in "embedded-atom" type methods. For the Group VI transition metals, these are least-squares fitted to five input quantities, which include the cohesive energy, the equilibrium lattice constant, and the three independent cubic elastic constants. The total-energy function is sufficiently transparent that one can obtain analytic expressions for the forces, *i.e.,* it is not necessary to virtually displace an atom in order to calculate the force on it.

The calibration tests that have been performed are quite encouraging. Both vacancy-formation energies and bcc-fcc structural-energy differences are obtained well by the method. The former result is expected, since a large part of the vacancy-formation energy is generally obtained already at the "μ_2" level. However the accuracy of the structural energies is surprising, since no information whatsoever about the fcc structure is included in the input database.

The method has been remarkably successful in studying the c (2×2) reconstruction that occurs on the W(100) surface. As seen in Fig. 3 a non-zero reconstruction amplitude is found (for all three different types of fitting methods that we have investigated). Although the amplitude depends on the fitting method, a value consistent with previous *ab-initio* calculations is obtained for sensible values of the parameters. The reconstruction is due to the μ_4-terms, which in an approximate fashion describe the destabilizing effect of a partly filled band of surface states in the unreconstructed surface. In intuitive terms, the driving force for the reconstruction may be described as a large bond-strength enhancement at the surface, which exceeds that obtained by

embedded-atom type methods. The success in such a subtle property as the surface reconstruction is truly surprising.

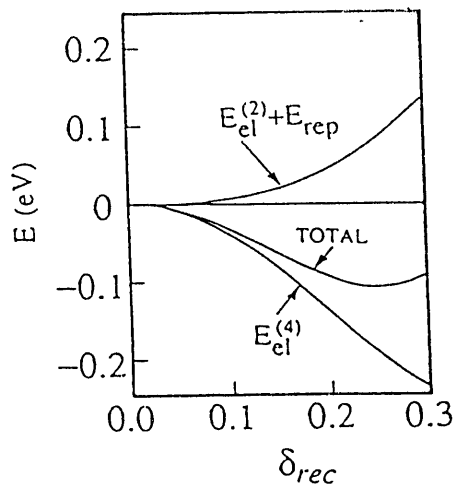

FIG. 3. Energetics of c(2×2) surface reconstruction for W(100) surface. Reconstruction amplitude is δ. Only lateral motions of first surface layer are allowed. Displacement is in Å; energy is per surface atom.

This μ_4-methodology has spawned a number of similar methods, developed by other workers. Kress and Voter[11] have developed an approach to the hcp-fcc energy difference based only on the matrix μ_2-part of the method, which already contains enough angular character to distinguish these structures. Professor James Adams and co-workers at the University of Illinois have developed[12] potentials for the Group V and Group VI transition metals, using a considerably larger input database including the phonon dispersion relations. EFese potentials also used a third-moment term. Dr. Steven Foiles at Sandia National Laboratories has applied[13] a modified version of the method to Mo and W. Applications are also proceeding apace. Roelofs and Foiles[19] have used potentials for Mo to develop a physical picture of the long-period reconstruction that occurs on the (100) surface. Professor Vitek's group at the University of Pennsylvania, in collaboration with the Principal Investigator, have applied[20] the μ_4 method to grain boundaries in W, and are now working on Mo as well. Professor Holzwarth and collaborators at Wake Forest University are using[21] a μ_4 method to treat the W(111) surface.

On the transition-metal alloy surfaces, we have completed a study of coordination effects on effective pair interactions (EPI) (or Ising-type parameters), which was begun in the preceding grant period. Our previous work[22] had established a scaling of the EPI with coordination number, and we have explored some more detailed effects. The additional effects that are explored are those of concentration (as manifested through the third moment μ_3 of the DOS), and surface orientation (as measured by μ_4). The surface orientation also changes μ_2, but this effect had already been treated.[22] A large value of μ_4 may be associated the presence of surface states. A pronounced shift in the range of band fillings for which ordering-type behavior is obtained was found with changing μ_3. It was shown that this type of effect would tend to promote surface-

ordering and bulk-clustering behavior, rather than the inverted case. We also found that the presence of surface states tends to increase the range of ordering. Professor Randall Brown of Luther College, who was previously supported under this Grant, will be continuing to explore more detailed implications of these results, with some (but not extensive) involvement of the Principal Investigator.

B. Potential-Energy Functions for Aluminides and Quasicrystals

(Publications 7, 8, 16, 18)

We have developed a pair potential for transition-metal aluminides which is based on simply immersing two transition-metal d-shells in a free-electron gas, and calculating the one-electron energy as a function of separation. The Hamiltonian includes couplings hybridizing the d-orbitals with the plane-wave states, but no direct d-d couplings. It is sufficiently simple that it can be solved exactly using Green's-function techniques. The parameters in the Hamiltonian are obtained from fits to *ab-initio* calculations for single impurities within a supercell approximation. The resulting pair potentials diaplay an oscillating behavior with amplitude much larger than that of, for example, Al itself. This large magnitude is due to both the strong scattering from the d-impurity, and the $(2l+1)$ degeneracy of the d-shell, which appears squared in an asymptotic expansion of the potential. The oscillations have a phase shift that varies systematically with the d-band filling. Because the model Hamiltonian (so far) has no direct d-d couplings, the potentials are applicable only to cases in which transition metal atoms are not nearest neighbors. The potentials are remarkably accurate for transition metals to the right of Group IV in the periodic table. As seen in Fig. 4 they agree to within 10-20% with *ab-initio* results for the DO_{22} vs. $L1_2$ energy differences. Since the structural-energy differences are closely related to antiphase-boundary energies, potentials of this type may be useful additions to embedded-atom type total-energy formulations. As yet, it is not possible to treat the Al-Ti system correctly with the potentials; possible improvements in this direction are discussed under Proposed Research.

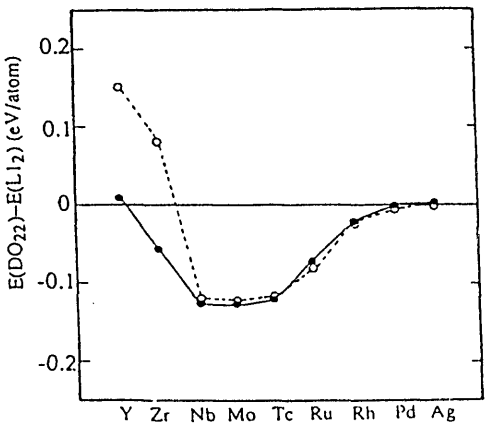

FIG. 4. Total energy differences between alternative Al_3M crystal structures, where M is a 4d transition metal. Open circle shows *ab initio* results. Solid circle is this work.

Some particularly exciting results have come from application to the Al-Mn system. The potentials were evaluated in the same way as for the earlier transition metals. For Al-Mn, the potential is stronger, because the *d*-band is half filled. The long-ranged oscillations in the potential are confirmed by a comparison with the experimentally obtained structure of liquid Al-Mn. A startling feature of the Mn-Mn system is the presence of a deep (almost -0.1 eV) minimum in the pair potential at about 4.7Å. As seen in Fig. 5, comparison with several observed complex structure show that these *invariably have a peak in the Mn-Mn distribution function close to this distance.* A hypothetical competing $L1_2$ structure Al_3Mn compound has the nearest Mn-Mn spacings out of the minimum in the pair potential, leading to a substantially higher energy. These results suggest that the origin of the complex structures in the Al-Mn system may be the 4.7Å-minimum in the Mn-Mn pair potential. Further work to prove or disprove this conjecture is desribed under Proposed Research.

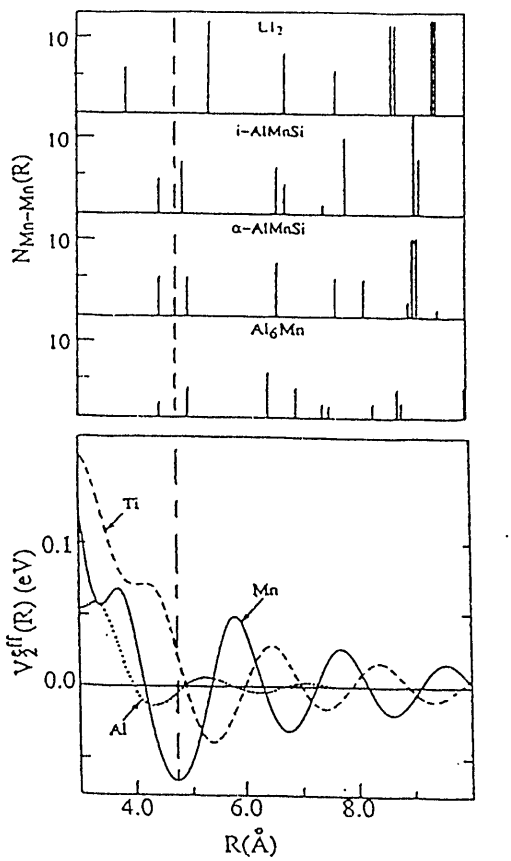

FIG. 5. Effective pair potentials for Mn pairs and Ti pairs in Al, and effective pair potentials between Al ions in pure Al. Distribution functions N_{Mn-Mn} indicate number of Mn-Mn pairs vs separation in Al-Mn intermetallic compounds. Vertical dashed line is placed at minimum of Mn-Mn potential.

C. Electronic Structure of Complex Structures and Quasicrystals

(Publications 1, 3, 4, 5, 9, 10, 11, and 12)

We have looked both at transition-metal containing materials and nearly-free-electron materials. A coherent picture is now beginning to emerge of the origins of quasigap effects around the Fermi level, and of their effect on cohesive properties. On the transition-metal containing materials, We have completed the work on the energy difference between the $Al_{12}W$ and Cu_3Au structures in transition-metal aluminides, that was begun in the preceding grant period. In order to evaluate long-ranged interaction effects between transition-metal impurities in Al, we have evaluated the energy of hypothetical $Al_{15}T$ compound (T=transition metal) on an underlying fcc lattice and compared it to the appropriate combination of Al and Cu_3Au-structure Al_3T. We find that there is a long-ranged interaction energy which is roughly half as large as the energy favoring the $Al_{12}W$ structure for nearly half-filled *d*-bands. Further *ab-initio* calculations have confirmed the importance of effects beyond the nearest-neighbor shell by comparing the electronic DOS distributions in two distinct A15-based structures, both of which have icosahedral coordination for the Mn sites, but different longer-ranged environments. Publication 9 is part of a public discussion with Dr. Linus Pauling about the relative important of atomic-size and electronic effects in stabilizing the $Al_{12}W$ structure.

We have also treated the structure and energy of transition-metal quasicrystals, in collaboration with Dr. Rob Phillips at Cornell University. With emphasis on the Ti-Mn system, we have developed a method for improving structures derived from 6d-3d projections. Such structures tend to have either short bond lengths, a low density, or many pairs of atoms having too few common neighbors. We have used this number of common neighbors, or "bond spindle", to locate positions for additional atoms. In the case of Ti-Mn, the original projected structure had a number of twofold bond spindles; in general, one expects to have mainly four- and five-fold spindles. The procedure is to locate the lowest bond spindles, and to add atoms in their vicinity via a simple geometric construction. This procedure greatly reduces the number of bad bond spindles, and significantly lowers an estimate of the total energy based on pair-potential calculations. We have also performed electronic total-energy calculations for this model using a *d*-orbital tight-binding method. These are the first electronic structural-energy calculations for transition-metal quasicrystals. They show a reduction in total energy which is roughly proportional to the number of twofold bond spindles that are removed. We expect that this annealing procedure should be useful in a variety of other problems, outside the quasicrystal field, involving incommensurate structures. In particular, grain boundaries contain regions of "bad" crystal, and this might be a useful way of finding such regions.

On the nearly-free-electron materials, we have explored in some detail the origins of the quasigaps that are seen in transport, specific-heat, and photoemission measurements. Most of the previous theories[23–26] of the enhanced quasigap formation in icosahedral materials had emphasized the effects of the high degeneracy of the shells of quasi reciprocal-lattice vector in icosahedral materials; such degeneracy leads to a more spherical quasi-Brillouin zone, and thus enhanced gapping effects. Our intent was to explore

the additional effects due to the angular distribution of the scattering wave vectors, *i.e.*, the effects of an icosahedral vs. a cubic distribution. The number of scattering wave vectors was held constant at twelve, and it was possible to distort a cubic arrangement continuously to an icosahedral one. We have used both numerical and analytic approaches to get at the underlying physics. In the numerical approach, exact electron density of states (DOS) distributions were obtained for "rational approximants". These correspond to orientations of the scattering vectors which approximate the icosahedral arrangement, but have rational direction cosines, so that in r-space they correspond to large unit-cell crystals. It is then straightforward, provided one has a kinetic-energy cutoff, to set up a secular matrix which can be numerically diagonalized to obtain a DOS distribution.

The numerical results for strong potentials, given in Fig. 6, showed that the cubic 1/1 arrangement has no gap in the density of states, no matter how strong the potential is. However, the rational approximants do, and the magnitude of the gap increases as the scattering vectors approach the icosahedral arrangement. For weaker potentials, there is no gap for any of the approximants (and likely not for the icosahedral arrangement either); however, quasigaps appear, and they become deeper as the icosahedral arrangement is approached. Another remarkable feature of the numerical results is that the band gap reduction in the low-order rational approximants (relative to the higher-order ones) comes not via uniform shifts of the valence and conduction band edges, but rather through the appearance of a narrow band of gap states. As icosahedral symmetry is approached, these states are gradually swept out of the gap.

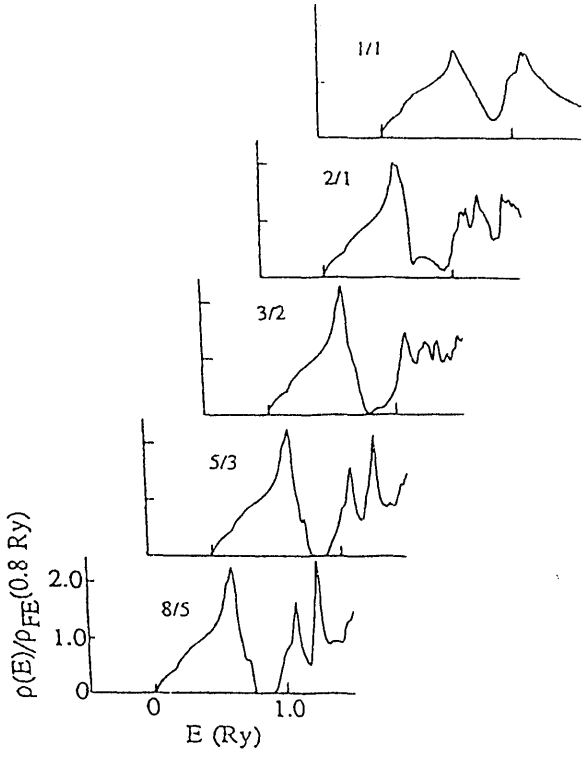

FIG. 6. Calculated DOS distribution ρ(E) for rational-approximant structures, for $V_0 = 0.25$ Ry. DOS given in units of the free-electron DOS at E = 0.8 Ry.

The results were interpreted via a two- and three-wave analysis of the energy eigenvalues at the centers and edges of the pseudo-Jones zone. This analysis showed that for reasons involving the *topology* of the band structure, it is impossible to have a gap in the cubic arrangement. The rational approximants can have gaps, and the magnitude of the gap increases as icosahedral symmetry is approached, basically because the splittings of the valence and conduction-band edges induced by cubic (vs. icosahedral) symmetry are reduced. It was also possible to perform an exact analytic calculation for the $k = 0$ point in the pseudo-Jones zone. The edge of the gap state distribution was found to correspond to a highly symmetric combination of either threefold or pseudo-threefold (depending on the order of the rational approximant) plane waves, with the threefold-based wave functions having different energies from those of the pseudo-threefold-based ones. As icosahedral symmetry is approached, the splitting between pseudo-threefold and threefold diminishes, and the gap states recede into the bulk bands.

These results have major implications for the modeling of the nearly-free-electron-like materials, namely that a pair-potential description of the usual pseudopotential-based variety will not suffice. The fact that (at least) a three-plane-wave model is necessary to describe the quasigap effects implies that, in real space, a model involving at least three-body interactions will be required. At the present, the only well established method for generating such three-body interations involves using third-order perturbation theory in pseudopotential.

D. Potential-Energy Functions in Transition-Metal Oxides
(Publication 13)

In an attempt to begin an expansion of our efforts in creating potential-energy functions to oxides, we have looked at the PdO and PtO systems. These materials have useful applications in electronics and catalysis (check). Rather than forming the NaCl structure, as many other monooxides do, they form a tetragonal structure in which the O environment has a different symmetry than the transition-metal environment. Our intent was to obtain some idea of the physical origins of this effect. The calculations were performed using the augmented-spherical-wave (ASW) method[27] used in some of the research discussed above. The results were that both of the systems have gap-like features induced by the reduced (tetragonal) symmetry. For PdO, one obtains only a dip in the electronic density of states (DOS), but PtO has a gap of approximately 1 eV. Because of inaccuracies in the local-density treatment of the band structure, one does not take the magnitude of the gap seriously, although it is in fortuitously good agreement with the observed gap. According to the quasigap physics discussed above, the gap-like features provide a stabilizing contribution to the total energy, perhaps partly explaining the preference for the tetragonal structure rather than the cubic NaCl structure. In more chemical terms, the bandfilling of Pd and Pt in their monooxides (eight d-electrons per atom) is such that a Jahn-Teller type splitting of tetragonal symmetry can produce a gap in the DOS at the Fermi level. Presumably the reason that this effect does not occur in NiO is that the p-d interaction is too weak for the Jahn-Teller interaction to dominate; instead magnetic-moment formation takes over.

The main impact of these results for our effort is that to treat these types of materials, it is necessary to include the quasigap effects that underly the angular forces for transition metals, and the pair potentials for aluminides, that we describe above. We believe that in oxides, the physics is similar to that of the "chemical grip" as discussed previously by Harrison.[28] Possible implementations of these ideas are discussed above under Proposed Research.

We have also been working on understanding the structure of the continually perplexing material $Fe_{1-x}O$. This work has been done in collaboration with Dr. Werner Schweika at KFA Jülich in Germany, where the Principal Investigator spent his sabbatical leave (the expenses were paid by the German government). Dr. Schweika has performed highly precise neutron-scattering measurements of the structure of this material, and the Principal Investigator has been modeling the measurements with various kinds of defect complexes. The calculations are based on the Kanzaki approach, in which a small number of input forces are used as parameters, and the long-ranged displacements in response to these forces are obtained via an elastic Green's function obtained by fitting the observed phonon spectrum. The major conclusion of the theoretical work is that a vacancy-only model cannot fit the data. It is instead necessary to have clusters containing both vacancies and interstitials. The calculations sugggest that a ratio of about three interstitials to each vacancy fits the experimental data best. We expect that this work will be completed fairly early on in the next Grant period.

E. Applications to Defect Structure and Mechanical Properties
(Publications 14, 15, 21)

Our efforts here have been directed at developing a practical methodology for treating defects with long-ranged strain fields, and also toward obtaining initial results for dislocation emission from crack tips. The methodology work is motivated by the fact that dislocations in solids have strain fields that decay as only $1/r$, and cracks are even worse, with a decay law of $1/\sqrt{r}$. This means that if one does molecular dynamics, then one needs to include a very large number of atoms in a simulation to obtain a satisfactory treatment of the boundary conditions. This can place great strains on CPU time and memory. We have collaborated with Dr. Robb Thomson at NIST in the implementation of a "Lattice Green's function" method, which treats such long-ranged strain fields more elegantly. The basic idea of the method is that the system is divided into an "active" region, in which the atomic coordinates are explicitly stored in the computer, and a "linear region". In the latter, the atomic coordinates are not explicitly stored; rather their effects on the active region are included basically as an effective Hamiltonian for this region. The only approximation that is made is that the atoms in the linear region experience forces that are linear functions of their displacements. The linear region can be made quite large, with the major constraint being that one has to store its reciprocal lattice in the computer memory; we have found that over a million atoms are easily treated even on a workstation-level computer.

To find a locally stable configuration, one needs to numerically find a zero-force point. This is done via a compact nonlinear iteration procedure which involves only the positions inside the active region. The point of Publication 14, on the methodology, is to

illustrate the practicality of crack and dislocation calculations with such a methodology. For a crack, one takes as the active region a thin slit around the crack; a crack length of several hundred atoms can be treated without major difficulties. Our comparisons with continuum theory indicate that a crack length of 100 atoms is sufficient to reproduce the "Griffith criterion"[1] relating the critical force required to propagate a crack to the surface energy. To treat dislocations, one adds more pieces to the active region, depending on the slip plane. If the dislocation moves along the crack plane, then one simply extends the active region parallel to the crack; if it moves in another plane, one adds a piece oriented at the appropriate angle. We have also demonstrated the applicability of the method to interfaces. Using various exactly-summed scattering series, one can first break the bulk material into slabs, then reattach these slabs to form a perfect interface, and finally put cracks on this interface.

Publication 15 (and to some extent Publication 21) describes initial applications to the criteria for dislocation emission from a crack tip in a model two-dimensional hexagonal lattice. These criteria are very important for the mechanical properties of a material: if dislocation emission is easy, one expects plastic deformation at a crack tip to blunt a crack before it propagates, and thus brittle fracture should be inhibited. If dislocation emission is hard, then one expects brittle behavior. The model hexagonal studies were motivated in particular by the existence of several continuum theories[29–31] of the emission process, which provide estimates of the critical force required. The latest of these,[31] by J. Rice of Harvard, finds that the critical force is proportional to $\sqrt{\gamma_{us}}$, where the "unstable stacking energy" γ_{us} may be thought of as a corrugation potential experienced under sliding of two semi-infinite blocks relative to each other. Via our Green's-function calculations, we were able to compare the atomistic results with the continuum predictions. The force laws used at this point were only simple pair potentials, but under Proposed Research applications of more complex force laws are outlined. For force laws with physically reasonable radial behavior, the agreement with continuum theory is remarkably good, at the 5% to 10% level, provided that the dislocation is emitted parallel to the crack plane. However, if the emission is at an angle relative to the crack plane, then the agreement is much worse. We were able to isolate a major factor reponsible for the disagreement, namely the extra surface that is created when the dislocation is emitted. Workers in Rice's group are now working on including this effect in their models.

F. Basic Theory of Interatomic Potentials

(Publication 20)

Although the basic theory developed in previous installments of the Grant have led to several promising types of potentials, this theory is still far from being completely understood. The tight-binding potentials described above have been based on orthogonal tight-binding models, and one issue that is very poorly understood is the effect of nonorthogonality on the form of the potential-energy function. It appears that the nonorthogonality will complicate the form of the interatomic potentials considerably, since the real-space description of the moments of the electronic DOS requires orthogonality. We have addressed the nonorthogonality effects within a simple s-band

tight-binding model. Since the original real-space description of the moments is invalid, we have devised a new methodology for obtaining a real-space description of the binding energy. This methodology is based on a combination of the nonorthogonal recursion method,[32] the extended Hückel method, and a Pade approximant for various matrix elements of the inverse of the overlap matrix. The main results of the calculations are real-space expressions for the first and second moments μ_1 and μ_2 of the electronic DOS. In the orthogonal case, these would be one-body and two-body terms respectively. In the presence of nonorthogonality, they have continued-fraction type forms, with, for example, μ_2 having important explicit three-body contributions. Thus nonorthogonality provides another source of many-body interactions in the tight-binding context. We find that expansions in powers of the overlap do not well approximate these many-body interactions. Some possible implementations of these effects, in Si, are outlined under Proposed Research.

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