

COMPUTATIONAL STRUCTURES TECHNOLOGY

Section 2COMPUTATIONAL TECHNIQUES IN MATERIAL SCIENCE AT
THE ATOMIC LEVEL

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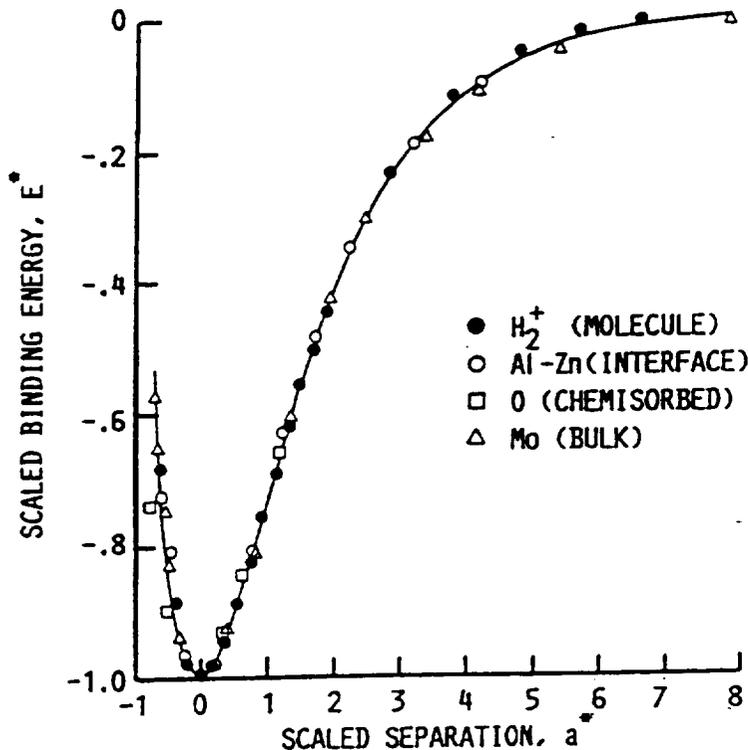
There is a great deal of overlap in the problems of interest to the solid state physicist and the material scientist. To date, however, many of the properties of most interest to material scientists such as the strength of materials or their defect energetics have not been amenable to accurate calculation by physicists because of the complexity of these phenomena. Accurate models for material properties, such as the band structure, transport, and magnetic properties, have been limited to relatively simple systems. However, the results of such calculations were impressively successful for the simple systems in that accurate agreement with experiment was obtained. To a considerable degree, such atomic-level treatments have relied on lattice periodicity (Ref. 2) in order to reduce the calculation to one over a single (and relatively small) unit cell. The properties of interest to the material scientist generally are related to "defects" in atomic structure producing a partial loss of periodicity and thus involving calculations over a large number of atoms. For example, dislocations, grain boundaries and interfaces between different materials can involve calculations over hundreds of atoms. The breakdown of periodicity and the involvement of many atoms clearly complicates such problems. Until recently, the lack of

adequate affordable computing power combined with the lack of efficient methods for performing the quantum mechanical calculations made it difficult to tackle such complex problems. For example, it was only fairly recently (Refs. 16, 25) that it became possible to determine which of the simple structures, fcc, bcc, or hcp for an elemental metal had the lowest energy and thus was the most stable. These structures involve only small differences in energy. Since the cohesive energy is obtained from the difference in total energy between an ion in the metal and the energy of an isolated atom, this difference in total energies (each of which is a large number) made the small differences in structural energy difficult to calculate.

These limitations have lead the material scientist to the use of simplified approaches to approximate properties of interest. Pair-potentials (two-body forces), such as Van der Waals interactions, have long been used to treat some problems of interest in material science (Refs. 2, 8). However, the pair potential approach has some serious shortcomings. Perhaps the most serious is its inability to describe the angular effects associated with covalent bonding which requires at least three-body forces. Also, it is not clear that the pair potential approach adequately treats the many-bcody effects that occur in real materials, especially metals (Ref. 17). For example, the significant changes in the electron gas in a metal with changes in atomic positions greatly affects the energetics of a defect. Some attempts have been made to correct for these effects by including angular dependent terms (Refs. 20, 22, 5) in the potentials whose parameters are adjusted to give certain material properties correctly. The potentials are then used to calculate other properties of interest. The emphasis in this review is on modern computational techniques that go beyond pair-potentials including many body effects and not a review of calculations for specific defects (such as grain boundaries). All pertinent references which could serve as a starting point for a literature search in modern techniques are included. With the space limitations for this review, no attempt is made to make it a comprehensive review of the literature.

APPLICATIONS

New semi-empirical and more efficient versions of earlier first principles methods have been developed which enable the treatment of a complex defect including obtaining its total energy. The new semi-empirical embedded atom method (EAM) (Ref. 10) and equivalent crystal theory (ECT) (Ref. 18) have shown considerable promise in describing defects in metals. These approaches go beyond pair potentials in including electron redistribution and many body effects. Both methods make use of the "universal binding energy relation" (UBER) (Refs. 14, 15, 24). It has been established that with an appropriate scaling of the length, binding energy, and equilibrium separation, the shape of the binding energy distance curve is the same for many types of bonding (Fig. 1). EAM represents the energy for embedding an atom in a solid by an electron density dependent term obtained by overlapping atomic densities and a pair repulsion term with parameters selected from physical properties along with fitting the total expression to the UBER. ECT uses perturbation theory, the perturbation being the difference in energy between a solid with a defect and a fictitious ideal "equivalent crystal" described by the energy change in the



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FIG. 1 \square BINDING ENERGY AS A FUNCTION OF INTERATOMIC SEPARATION FOR FOUR TYPES OF BINDING

119 UBER. Requiring the perturbation terms to vanish leads to a simple analytic relation
 120 for the lattice parameter of the equivalent crystal. This value is then used in the
 121 UBER to calculate the energy of an atom in a defect. Both methods are almost as
 122 simple to apply as the pair potential approach and have the advantage of including
 123 many-body terms. The difficulties involved in locating the minimum energy configura-
 124 tion and carrying out a molecular dynamics calculation to include temperature
 125 effects are mitigated by the simplicity of these semi-empirical approaches. In two
 126 cases which have been tested for surface energy determinations, the surface energy
 127 and surface relaxation of metals (Table 1), ECT is more quantitatively accurate than
 128 the EAM scheme. However, EAM is presently more versatile than ECT, which is in
 129 an earlier stage of development. Another approach that should be noted utilizes the
 130 so-called tight-binding bond model (Refs. 9, 21). Significant progress has recently
 131 been made in justifying and implementing this approach in the framework of density
 132 functional theory (Ref. 11). For ceramics and ceramic-metal interfaces, pair potentials
 133 still dominate as a calculation technique. In some cases the form of the pair po-
 134 tential includes a term accounting for the charge transfer between anions and cations
 135 (Ref. 19).

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TABLE 1
SURFACE ENERGIES FOR SOME SELECTED METALS
(In erg/cm²)

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Element	Crystal Face	ECT	First Principles LDA	EAM	Experiment ^a
Al	(111)	920			
	poly				1169
	(100)	1280			
Ni	(100)	1310	1090 ^b		
	(111)	2400		1450 ^c	
	poly				2664
	(100)	3120	3050 ^d	1580 ^c	
Cu	(100)	2980		1730 ^c	
	(111)	1830	2100 ^a	1170 ^c	
	poly				2016
	(100)	2380	2300 ^d	1280 ^c	
Ag	(100)	2270		1400 ^c	
	(111)	1270		620 ^c	
	poly				1543
	(100)	1630	1650 ^d	705 ^c	
Fe	(110)	1540		770 ^c	
	(110)	1810			
	poly				2452
W	(100)	3490	3100 ^d	1693 ^f	
	(110)	3330			
	poly				4435
	(100)	5880	5100 ^g	2926 ^f	

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^aWawra, H. Z. *Metallk.* 66, 1975, 396, 492.

^bHo, K. M., Bohnen, K. P. *Physical Review B* 32, 1985, 3446.

^cFoiles, S. M., et al., *Physical Review B* 33, 1986, 7893.

^dGay, J. G., et al., *Journal of Vacuum Science Technology, A* 2, 1984, 931.

^eAppelbaum, J. A.; Hamann, D. R. *Solid State Communications*, 27, 1978, 881.

^fFinnis, M. W.; Sinclair, J. E. *Phil. Mag. A*, 50, 1984, 45.

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The well-known improvements in computers, combined with more efficient theoretical techniques, have made some problems of interest in material science amenable to first principle studies. Most often the defect problems have been recast into closely related periodic problems, since those are most readily handled by the efficient band structure methods. This is accomplished by using large unit cells, the so-called "super cells" (Refs. 13, 23). For example, interfaces can be treated by large cells with each half of the cell occupied by one of the two materials involved. When the cell becomes sufficiently large (in practice surprisingly small) the behavior around the plane separating the two materials converges to that of an isolated interface. At this stage, defects of the order of several hundred atoms can be treated practically by this approach. (Note, typical numbers are about 64 atoms for point defects and 56 for interfaces. The actual limit depends on the availability and cost of computer

TABLE 2
INTERFACE ENERGY IN eV NORMALIZED PER
INTERFACE UNIT CELL AREA (I.U.C.A.) FOR
DIFFERENT BONDING CONFIGURATIONS

Interface	Bonding	γ (eV/I.U.C.A.)
SiC/AlN	Si-N, C-Al	0.45
SiC/BP	Si-Al, C-N	8.10
	Si-P, C-B	3.57
	Si-B, C-P	0.50

148 time). Self-consistent first-principles calculations are generally carried out using the
149 density functional theory (Ref. 11) in the local density approximation. A few brief
150 comments on this theory are given in Appendix 1. It should also be stated that there
151 are essentially no material limitations in applying first-principle methods, i.e., met-
152 als, semiconductors or ceramics or interfaces between them.

153 These first-principles techniques are now at a stage where they can treat the
154 energetics and electronic properties of ceramic interfaces (see, e.g., Ref. 3). In
155 Table 2 we show the results of examining the possible bonding combinations at ce-
156 ramic interfaces (Ref. 12) using the first-principles LMTO (linear muffin tin orbital)
157 method (Ref. 1) which shows which configurations are energetically preferred.
158 Therefore, it is now possible to provide information of interest in interfaces involving
159 ceramic-matrix composites.

160 A second important problem, mentioned earlier, is determining the minimum
161 energy configuration for a defect. This problem is significant, no matter what ap-
162 proach is used. For example, a tilt boundary is often treated simply as a geometric
163 construction. It is necessary, however, to consider the atomic relaxations which yield
164 the minimum total energy configuration. Since there may be many subsidiary min-
165 ima, finding the absolute minimum by varying the configurations may require sub-
166 stantial computer time in first-principles calculations. A new approach, unifying
167 state-of-the-art electronic structure theory with molecular dynamics methods has re-
168 cently been developed. It allows one to minimize the total energy as a function of
169 electronic degrees of freedom and atomic position simultaneously and even allows
170 the study of dynamics and temperature dependent phenomena (Ref. 6).

171 The future for first-principles and semi-empirical calculations in material science
172 is quite bright. A brief description of EAM and ECT are presented in the Appendix
173 sections Embedded Atom Methods and Equivalent Crystal Theory 1c. To the phys-
174 icist the problem is simply one of knowing the geometry and applying the tech-
175 niques. Therefore, the more powerful the computer, the easier it is for one to treat
176 a complex defect. For the near term, the optimum approach will likely be to combine
177 the two, with accurate semi-empirical approaches obtained from first-principles
178 methods giving the minimum energy geometry for the final, more correct first-prin-
179 ciples calculations.

180 The rapid advance in computer technology is also likely to continue for at least
181 the foreseeable future. Such advances will, in the near future, affect these compu-
182 tations in two ways. Within a year, it is expected that desk top systems will be avail-

Ed: desk-top ?

183 able with the computational power of a vector super computer of a few years past.
 184 When this happens, it will in many cases radically increase the productivity of work-
 185 ers performing these types of calculations. In many super computer installations,
 186 the actual CPU time used by a program is a very small fraction of the program's
 187 "turn around time" — many hours or even days may be lost while a program waits
 188 in the queue for time on a heavily-used super computer. With the advent of pow-
 189 erful, inexpensive desk-top systems, shared by one or two workers, this part of the
 190 turn around time is effectively eliminated; furthermore, the performance/price ratio
 191 of these systems is becoming extremely attractive, making it practical to provide dis-
 192 persed super computer-equivalent power to workers performing atomistic simula-
 193 tions.

194 In addition, it is becoming increasingly apparent that the best way to perform
 195 these calculations is through the use of massively-parallel machines. In many in-
 196 stances, an atomistic simulation "maps onto" a massively parallel machine in a nat-
 197 ural and intuitive way, and the performance obtained from such systems is already
 198 starting to exceed that of more conventional vector super computers. These mas-
 199 sively parallel machines are at an early stage of development, and it is not clear
 200 which of the several proposed architectures will prevail. Still, enough work has been
 201 done using these systems to begin to point out their promise (Ref. 4).
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203 SUMMARY

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In any event, when increased computational power becomes available, it will be possible to more accurately simulate large defect complexes, and also defect dynamics. It will also be possible to perform first-principles calculations for larger systems than is currently practicable, again permitting a more complete understanding of larger defects and complexes. As these expectations are realized, a new era in material science will develop which will include design of new materials with special properties, e.g., high modulus super-lattices (Ref. 9) and an understanding of, and greater accuracy in, "rules of thumb" presently used in design.

214 APPENDIX

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216 First-Principles Equations

The first-principles calculations involve solving the Kohn-Sham Equations usually within the local density approximation (LDA) (Ref. 11). The Kohn-Sham equations are

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$$(-1/2) \nabla^2 + V(r) \Psi_i(k, r) = \epsilon_i \Psi_i(k, r) \quad (1)$$

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where Ψ_i and ϵ_i are the one-electron wave function and energy, respectively and

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$$V(r) = \Phi(r) + V_x(\rho(r)) \quad (2)$$

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233 $V_{xc}(\rho(r))$ is the exchange and correlation energy, and $\Phi(r)$ is the electrostatic energy
234 given by

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$$\Phi(r) = \int dr' \frac{\rho(r')}{(|r - r'|)} - \sum_j \frac{Z_j}{(|r - R_j|)} \quad (3)$$

249 The first term is the electron-electron interaction and the second term is the electron-
250 ion interaction, r is the electron coordinate and R is the ion coordinate, z_j is the ion
charge. The electron number density is given by

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$$\rho(r) = \sum_{occ} |\Psi(k, r)|^2 \quad (4)$$

258 occ refers to the sum over k -space occupied states. With the geometry and an ap-
259 proximation for the wave functions, these equations are solved self-consistently, i.e.,
260 one iterates until the output density or potential agree. The total energy is then ob-
tained from the LDA as

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$$E(\rho) = E_{KE}(\rho) + E_{ES}(\rho) + E_{XC}(\rho) \quad (5)$$

267 where KE refers to the kinetic energy, ES to the electrostatic energy, XC refers to the
268 exchange and correlation energy and the brackets refer to the energy being a function
269 of the electron number density (atomic units are used throughout).

270 Embedded Atom Method

271 The energy for the i^{th} particles is given by
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$$E_i = F(\rho_i) + (1/2) \sum_j Z_i(R_{ij}) Z_j(R_{ij})/R_{ij} \quad (6)$$

279 where $F(\rho)$ is called the embedding energy, the second term gives the ion-core re-
280 pulsion, R_{ij} distance, ρ_i is the electron density contributed by all of the atoms except
the one at the i^{th} site and $Z(R)$ is the ionic charge given by

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$$Z(R) = Z_0 (1 + \beta R^\alpha) \exp(-\gamma R) \quad (7)$$

288 $Z(R)$ is determined by overlapping atomic electron densities, requiring that this
expression agree with the UBER given by

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$$E(R) = -\Delta E (1 + a^*) \exp(-a^*) \quad (8)$$

294 where ΔE is the cohesive energy, $a^* = (R - R_{eq})/d$ is the equilibrium distance and d
295 is a scaling length. The other parameters are obtained by fitting to other physical
296 properties, such as the vacancy formation energy or elastic constants. Once the
297 embedding energy for metal is determined and the geometry specified, the energy
for a defect can be easily calculated.

Equivalent Crystal Theory

This technique also uses the UBER. The energy of a solid with a defect is written as

$$E_{\text{solid}} = E_{\text{crystal}}(a) + \delta E(a) \quad (9)$$

here $E_{\text{crystal}}(a)$ is the energy of a crystal of the same material and with the same crystal structure as the ground state crystal which is represented as a point on the UBER. The energy difference $\delta E(a)$ between the real crystal and the equivalent crystal can be expressed as perturbation series. A simple procedure is specified which finds the value of, a , for which $\delta E = 0$, thus one is left with the simple result of evaluating ($E_{\text{crystal}}(a)$ for an atom in the defect from the UBER, (Eq. 8). ECT at this stage requires only one fitting parameter which is contained in the expression for δE .

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