FIG. 3. Spherical average of components of the self-consistent vacancy potential and the total potential of Ref. 3 (dashed line). Angular anisotropy of the potentials is generally smaller than $\pm 10\%$.

than the potential.

In Fig. 3, we present the spherical average of various components of the defect potential. The total potential of Ref. 3 (dashed line) was evaluated using a relatively low cutoff of Fourier components which introduced spurious oscillations into the "supercell" ionic potential. We believe that this accounts for the difference between the two calculated defect potentials.

In summary, this Green's-function technique

yields self-consistent *densities* and *potentials* which agree with those calculated self-consistently via a bulk–band-structure calculation of a periodic vacancy array. Its real strength, however, is that it produces bound-state energies, resonance energies, and resonance widths that are more reliable than, or inaccessible to, the periodic-array technique and at less cost. The type of information and the degree of accuracy made available by this new technique will be needed to study the effects of lattice distortions and their coupling to the electronic system.

[1]G. F. Koster and J. C. Slater, Phys. Rev. 95, 1167 (1954).

[2]An excellent review has been prepared by S. T. Pantelides, to be published.

[3]S. G. Louie, M. Schlüter, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 13, 1654 (1976).

[4]M. Jaros and S. Brand, Phys. Rev. B 14, 4494 (1976).

[5]E. Kauffer, P. Pecheur, and M. Gerl, Phys. Rev. B 15, 4107 (1977).

[6]J. Callaway, J. Math. Phys. (N. Y.) 5, 783 (1964).

[7]W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954).

[8]W. Kohn and C. Majumdar, Phys. Rev. 138, A1617 (1965).

[9]E. O. Kane, Phys. Rev. B 13, 3478 (1976).

[10]G. D. Watkins, in Lattice Defects in Semiconductors, edited by F. A. Huntley, The Institute of Physics Conference Series No. 23 (Institute of Physics, London, 1975), p. 1.

Self-Consistent Method for Point Defects in Semiconductors: Application to the Vacancy in Silicon

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We report the development of a method to calculate self-consistently the electronic structure of neutral point defects in semiconductors. The method is an adaptation of the original Koster-Slater idea. Calculations become feasible, practical, and accurate at the level of current band-structure and surface calculations when an LCAO basis set is used instead of Wannier functions. A detailed study of the isolated vacancy is Si is used to illustrate the method.

Point defects (vacancies, interstitials, etc.) and impurities in semiconductors are known to introduce localized states with energy levels in the fundamental gap. While shallow levels and some moderately deep levels are adequately described by effective-mass theory,[1] the theoretical de-

scription of most deep levels, which play a dominant role in determining many properties of electronic devices, has been one of the major outstanding problems of semiconductor physics. A large number of methods have been introduced and used for a variety of defects and impurities.[2]

The results have provided substantial qualitative understanding of the nature of binding at deep levels, but no approach has established itself as capable of providing accurate and unambiguous solutions, comparable in accuracy and reliability to the calculations that are currently possible for perfect bulk solids (band theory), surfaces, and interfaces. In this Letter, we report the development of a method which is capable of producing results of precisely such accuracy and reliability and illustrate its power with a detailed description of an isolated neutral unreconstructed vacancy in silicon.

The problem at hand has two distinct aspects: the choice of *Hamiltonian* and that of a *method* to seek the corresponding eigensolutions. Even though a variety of Hamiltonian choices (semiempirical, superposition of atomic potentials, etc.) can provide useful information, we have elected to use our method in the context of a self-consistent local-density theory of electronic structure. This choice frees our results from any dependence on the assumed similarity of interactions in the perturbed system to those in the unperturbed bulk crystal. We show below that some of the results we obtained previously using a semiempirical tight-binding Hamiltonian in fact survive the iteration to self-consistency, but others do not.

Given the Hamiltonian, we now turn to the choice of method. The most common method, namely the cluster method, has recently[3] been used with self-consistent Hamiltonians. The conclusion from these studies was that even 54-atom clusters, the largest that could be handled, are not adequate to contain the bound-state wave functions and produce a large uncertainty.[3] More recently, two of us[4] demonstrated that, when a semiempirical Hamiltonian is used, the most powerful and accurate method available to solve the problem of neutral point defects is an adaptation of the Koster-Slater[5] method, first introduced in 1954 and subsequently used in several studies of point defects[6,7] and surfaces.[8] Our method has three clear-cut advantages over the cluster approach. First, our approach permits us to focus directly on *changes* in the electronic structure caused by the defect; related to this point is the fact that properties of the bulk, such as the band gap, are accurately built in to our calculations and are not affected by introduction of the defect. This is not true of even the largest clusters (54 atoms[3]) which have been studied self-consistently. Second, our formalism fully exploits the translation-

al symmetry of the host material. The third important advantage of this approach is that the magnitude of the required numerical problem is governed by the spatial range of the *perturbation potential* rather than the very much greater range over which the electronic *wave function* is altered. In the particular application discussed below, for example, a full 30% of the charge associated with the localized state in the band gap lies outside of the region in which the perturbation potential is localized.

A description of the Koster-Slater method is available in the original paper and in a series of papers by Callaway and Hughes[6] and Callaway.[9] The most convenient formulation of the method is in terms of Green's functions. If $G^0(E)$ is the Green's-function operator for the perfect crystal, bound states in the gap introduced by a given perturbation U are given by the zeros of the determinant

$$D(E) = \det \| 1 - G^0(E)U \|. \tag{1}$$

The change in the density of states in the band continua is also given by an expression involving only $D(E)$. More importantly, the change in the charge density, which is needed for self-consistency, is given by

$$\Delta\rho = \frac{2}{\pi} \int_{occ} dE \{ 1 - [1 - G^0(E)U]^{-1} \} G^0(E). \tag{2}$$

For analytical as well as numerical work, the operators appearing in the above formulas must be represented in a convenient basis set. Traditionally, operators have been expressed in terms of Wannier functions as the natural basis set of localized functions. The first applications of the Koster-Slater approach,[6] however, proved extremely cumbersome, not for reasons related to the method *per se*, but for reasons related to the construction of the Wannier functions. The final results had to be empirically adjusted even to obtain a bound state in the gap. We avoid these serious difficulties by starting with the linear-combination-of-atomic-orbitals (LCAO) method for a self-consistent pseudopotential band-structure calculation.[10] We then use the same set of LCAO orbitals as basis states for all the operators of the Koster-Slater–Green's-function formalism.[11] While simple LCAO orbitals are not conveniently orthonormal, they are enormously easier to generate and the relatively small number of functions actually required to describe the defect-induced *change* in the electron density can be easily orthonormalized. Physically, the

implicit assumption is made that as long as the chosen set of LCAO orbitals on each atom of the perfect crystal is adequate to give an accurate band structure, then the same set of orbitals at all sites is also adequate to describe the infinite crystal containing a single vacancy.[11] Having chosen a set of LCAO orbitals on each atom,[10] we exploit symmetry and form symmetrized orbitals on each shell of atoms surrounding the defect site (shell orbitals). Finally, because shell orbitals are not orthogonal, we construct orthogonalized shell orbitals (OSO's) by orthogonalizing each shell orbital to the orbitals on all the shells closer to the defect site.

The Green's-function matrix elements between pairs of OSO's are then calculated using standard techniques of Brillouin-zone integration for the imaginary part and a Hilbert transform for the real part. Since the number of LCAO orbitals on each atom is finite, the Hilbert transform is uniquely defined in this case.[11] These quantities are calculated once for a given host crystal and stored. For a given U, one has simply to calculate its matrix elements between pairs of OSO's and construct the quantity $D(E)$ of Eq. (1), which now becomes

$$D(E) = \det \| \delta_{\alpha\beta} - \sum_\gamma G_{\alpha\gamma}{}^0(E)U_{\gamma\beta} \|, \qquad (3)$$

where α, β, and γ label the OSO's. The self-consistent-field iteration is initiated with an arbitrary estimate of U. The change in the charge density $\Delta\rho(r)$ is then obtained by expressing (2) in the OSO representation. From this quantity, a new perturbation potential is constructed and so on. Details of the calculations will be given elsewhere.

We turn now to our results for the isolated vacancy in Si. The objectives of the calculations are to investigate the following: (a) bound-state energies and wave functions, (b) changes in the density of states within the band continua corresponding to resonances and antiresonances, and (c) the charge distribution in the vicinity of the vacancy.

The calculations were performed using LCAO's centered on the first three shells of neighbors surrounding the vacancy (total of 28 atoms) and on the vacancy site. From simple tight-binding arguments[4] for an unreconstructed vacancy, one expects bound states and the most important changes in the density of states to occur in the A_1 and T_2 symmetries. In Si, we find only one bound state within the fundamental gap; it has T_2 symmetry (threefold degenerate) and lies at

0.8 eV above valence bands, which is our reference energy. Since the crystal is neutral, this state contains only two electrons. The changes in the density of states for A_1 and T_2 symmetries are shown in Fig. 1. From the analytic properties of $D(E)$ [Eq. (1)], it can easily be shown that the total change in the density of states in the valence bands, for each symmetry, must integrate to an integer. In the case of T_2 states, the change is mostly negative and the integral is -6, thereby compensating the T_2 bound state in the gap. In the case of A_1 states, a sharp resonance is present at -0.6 eV. This resonance lies in an energy region where the local density of states of A_1 symmetry is very small so that the resonance is effectively a bound state. A second resonance is present at -8.1 eV. Antiresonances compensate so that the total integral is zero.

The contour plot in Fig. 2(a) shows that the total change in the charge density (and therefore also the corresponding potential) is localized almost entirely within the cavity defined by the nearest neighbors. Correspondingly, in our basis (which includes LCAO on the first three shells) the total change in the charge density integrates to its full value -4.0 (as we have removed an atom with
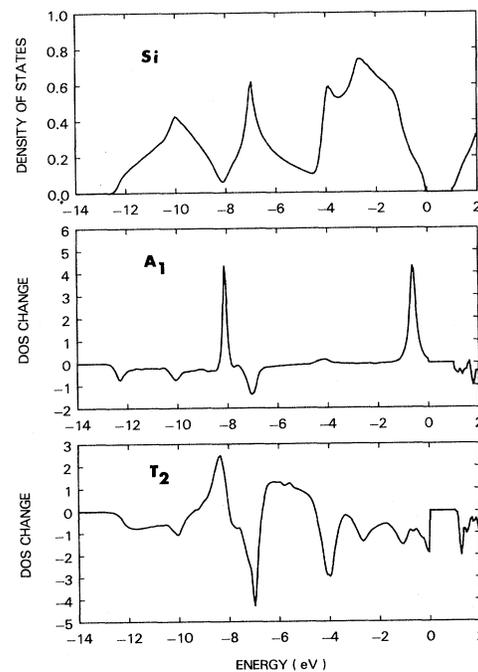
FIG. 1. The density of states and the change in the density of states of A_1 and T_2 symmetries. The curves are broadened by 0.2 eV and the reference energy is the top of the valence bands.
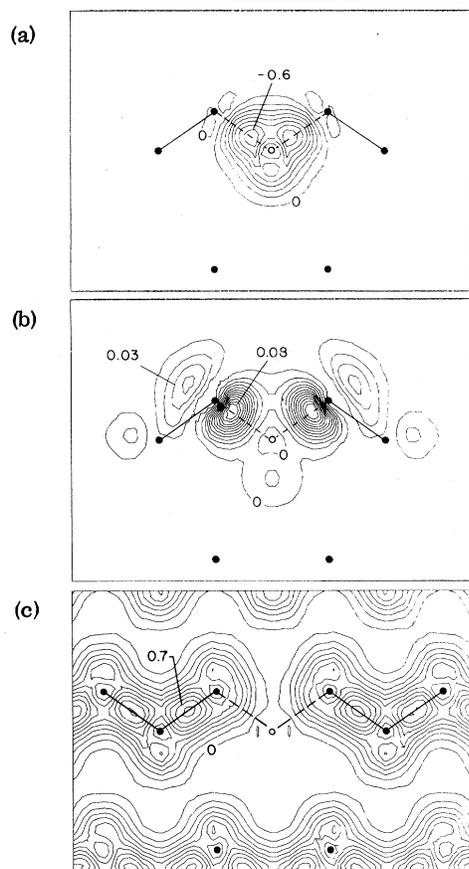
FIG. 2. Contours of constant electron density near the vacancy (in atomic units) for (a) the total change in the charge density (*negative* contours); (b) the T_2 bound state (see text); (c) the total charge density.

four valence electrons). Since the self-consistent procedure requires knowledge of the potential alone, this implies the adequacy of our basis for this purpose. It is interesting to note that the *individual states* of the vacancy are quite *extended*. In fact, our basis contains only 70% of the bound-state wave function (i.e., 1.4 electrons instead of 2). A contour plot of the contributions of the first three shells to the T_2 bound state is shown in Fig. 2(b). Similarly, the change in the density of states in the valence bands integrates to -5.2 electrons for the T_2 symmetry (instead of -6), and to -0.1 for A_1 symmetry (instead of 0). This indicates that the extented bound state, resonances, and antiresonances screen each other in a rather intriguing way, producing finally a very *localized* potential, which in turn can easily be expanded in a localized basis. It also clearly demonstrates the advantage of the present formalism. A cluster, which would adequately repre-

sent this infinite system, would need to contain fully these extended states individually.

The total charge density around the vacancy is shown in Fig. 2(c). We observe that all the bonds in the crystal remain virtually unchanged, and the dangling bonds remain pointing toward the missing atom. The contour plots reveal that the dangling bonds have a rather constant charge density near the atoms and extend appreciably into the vacant site. The bound-state orbital [Fig. 2(b)], although considerably delocalized, has a dangling-bond character.

Comparison of the present self-consistent results with those obtained earlier[4] using the semiempirical tight-binding method (SETBM) reveals the following: (1) The state-density changes are strikingly similar. (2) The position of the bound state in the gap (0.8 eV versus 0.3 eV found earlier[4]) is appreciably different and probably reflects not only self-consistency, but mainly the effect of the more realistically broad conduction bands of the present work. (3) The electron-density maps *provided* by the present work confirm the basic *assumption* of the SETBM study, namely that the Si-Si bonds near the vacancy are not significantly affected. The present work also indicates that the simple "removal" model used in Ref. 4 to describe the vacancy is fundamentally correct.

Comparison with experiment is not yet possible because the vacancy in Si is known[12] to induce a significant lattice reconstruction, an effect which has not been included in the present calculations. The situation is comparable to free surfaces, where the determination of reconstruction is still an unsolved problem. However, the bound state we find at 0.8 eV is consistent with experimental observation[12] according to which the level for the neutral vacancy is near the bottom of the gap after Jahn-Teller stabilization by about 1 eV.[12]

In conclusion, we feel that the present work goes a long way towards bringing the isolated-defect problem to the level of sophistication which characterizes contemporary studies of crystal surfaces; we hope that theory will soon play an important role in analyzing the wealth of experimental data which already exists in this context.

[1]W. Kohn, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York,

1957), Vol. 5, p. 257; S. T. Pantelides, Festkörperprobleme 15, 149 (1975).

[2]For a recent critical review of the field, see S. T. Pantelides, to be published.

[3]S. G. Louie, M. Schlüter, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 13, 1634 (1976). In this work, periodic boundary conditions were used (superlattice of defects). The bound state had a dispersion of 1 eV in the 1-eV gap of Si. Self-consistent calculations with even smaller clusters have been reported by B. Cartling, J. Phys. C 8, 3183 (1975) and by L. A. Hemstreet, Phys. Rev. B 15, 834 (1977).

[4]J. Bernholc and S. T. Pantelides, Phys. Rev. B 18, 1780 (1978).

[5]G. F. Koster and J. C. Slater, Phys. Rev. 95, 1167 (1954).

[6]J. Callaway and A. J. Hughes, Phys. Rev. 156, 860 (1967); and 164, 1043 (1967).

[7]M. Jaros and S. Brand, Phys. Rev. B 14, 4494 (1976). The method used in this work is a modification of the Koster-Slater approach introduced first by F. Bassani, G. Iadonisi, and B. Preziosi, Phys. Rev. 186, 735

(1969).

[8]J. Koutecky, Adv. Chem. Phys. 9, 85 (1965); J. Pollmann and S. T. Pantelides, Phys. Rev. B (to be published).

[9]J. Callaway, J. Math. Phys. (N. Y.) 5, 783 (1964).

[10]D. J. Chadi, Phys. Rev. B 16, 790 (1977).

[11]Ten orbitals per atom are used as in Ref. 10. The use of the same set of orbitals for the defect problem means that a total of twenty bands are used for the expansion of the defect wave functions. (It was established in Ref. 8 that ten bands are entirely adequate for convergence.) Our choice of orbitals for the defect problem also eliminates any ambiguities associated with Hilbert transforms which are necessary for the evaluation of Green's functions (see also Ref. 5). In the case of an impurity with an electronic structure significantly different from that of the host atoms, additional LCAO orbitals would have to be included on the impurity atom.

[12]G. D. Watkins, in Gallium Arsenide and Related Compounds—1974, Institute of Physics Conference Series No. 23, edited by J. Bok (American Institute of Physics, New York, 1975), p. 1.

Electronic Properties and the Lattice Instability of Laves-Phase ZrV$_2$

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Pure, perfect, single-crystal ZrV$_2$ does not undergo a structural phase transformation but all other sample modifications, including twinned single crystal, do transform (~100 K) from the cubic to a rhombohedral phase. All samples exhibit, in addition, an electronic instability (also ~100 K). An anomaly in the ultrasonic velocity occurs at higher temperatures (~150–180 K) for pure polycrystalline ZrV$_2$ samples.

Since the discovery of martensitic transformations[1] in the high-T_c superconductors V$_3$Si and Nb$_3$Sn, it has become increasingly clear that compounds whose lattice and electronic structures seem to favor superconductivity often exhibit lattice softening and/or structural transformations or, in extreme cases, exhibit a thermodynamic instability of the crystal structure itself.[1-3] In order to elicit the relationship, if any exists, between these instabilities and high-temperature superconductivity, the nature of the lattice transitions themselves has become the focus of much of the current research in this area. Among the most studied examples of materials in which the two phenomena coexist [A15, VRu, and MoRe alloys; and B1 compounds, e.g., Refs. 1–3] no common characteristics connecting lattice instability and high T_c have emerged, either because of the very different natures of the particular lattice transitions or because the role of sample micro-

structure in the observed properties has not been unraveled.

ZrV$_2$, HfV$_2$, and their pseudobinary alloys (Hf$_x$Zr$_{1-x}$V$_2$) have the highest superconducting transition temperatures[4] among the cubic Laves-phase compounds (C15) and have, in their arc-cast modification, been shown to undergo lattice transformations from the cubic structure to a low-temperature phase of lower symmetry[5,6]: ZrV$_2$ transforms to a rhombohedral symmetry[6]; HfV$_2$, to an orthorhombic crystal structure.[5] The similarities between these compounds and the high-T_c A15 alloys are striking in that, for those low-temperature transport properties found to be anomalous in the A15-structure group, there are analogous abnormalities[7-9] observed for both ZrV$_2$ and HfV$_2$. On the other hand, the origins of the structural transformation in the two different symmetry classes are clearly different since the C15 transitions are unambiguous first-order