ever, the McWhan data are in excellent agreement with the orthorhombic structure for α'-Ce described above.

The metallic radii (as defined in terms of the experimental atomic volumes[7]) of the various forms of cerium metal adjusted to room pressure and temperature are 1.824 Å for γ-Ce, 1.719 Å for α-Ce, and 1.675 Å for α'-Ce. However, at the transition pressure of 56 kbar the difference in size is much smaller, with an effective metallic radius of 1.636 Å for α-Ce and 1.627 Å for α'-Ce. We find that the atomic volume is the same (within experimental error) for the α' and α'' phases.

The experimental value of the cerium radius in α'-Ce is nearly identical with the value obtained for tetravalent cerium metal by extrapolation from the $3d$ and $4d$ series[7] and suggests the complete absence of localized $4f$ electrons in α'-Ce.

As far as we can tell from the diffraction intensities, the single positional parameter in the α'-Ce structure has the same value as the α-U structure. Thus each metal atom forms four short bonds, all directed within one hemisphere. However, the metallic radius of uranium in α-U is much smaller than of cerium in α'-Ce because uranium is hexavalent[7] and cerium tetravalent in these metal structures.

The occurrence of the unusual metal structures for the low-temperature forms of uranium, neptunium, and plutonium, and now for α'-Ce, suggests a correlation with admixture of f character in the valence-electron band structure. However, we can offer no reasonable explanation why α'-Ce with four valence electrons and α-U with six valence electrons are isostructural.

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[1] R. A. Stager and H. G. Drickamer, Phys. Rev. 133, A830 (1964).

[2] J. Wittig, Phys. Rev. Lett. 21, 1250 (1968).

[3] E. King, J. A. Lee, I. R. Harris, and T. F. Smith, Phys. Rev. B 1, 1380 (1970).

[4] W. A. Bassett, T. Takahashi, and P. W. Stook, Rev. Sci. Instrum. 38, 37 (1967).

[5] E. Franceschi and G. L. Olcese, Phys. Rev. Lett. 22, 1299 (1969).

[6] D. B. McWhan, Phys. Rev. B 1, 2826 (1970).

[7] W. H. Zachariasen, J. Inorg. Nucl. Chem. 35, 3487 (1973).

Surface Electronic Structure via Generalized Wannier Functions

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A method which represents surface electronic structure exactly in terms of local functions is tested by applying it to a one-dimensional surface potential. A single four-parameter variational calculation yields continuum and surface-state wave functions for an entire perturbed band. Comparison with exact solutions obtained independently indicates that the calculation is quite accurate.

There is ample experimental evidence that the effects of a surface on the electronic properties of a solid, while locally strong, are rapidly damped so that such observables as charge densities and local densities of states quickly revert to their bulk values.[1] This suggests an inherent advantage in a description of the electronic structure in terms of local functions as opposed to a description in terms of wave functions, since the local description may more easily exploit the local nature of the surface perturbation. The generalized-Wannier-function concept recently introduced by Kohn and Onffroy[2,3] describes the electronic structure exactly in terms of local functions *which may be calculated directly without first calculating wave functions.* We report here the first test of this new concept and method as a practical tool for calculating the electronic structure of solid surfaces.

Generalized Wannier functions (GWF's) are the counterparts for crystals with defects of the familiar Wannier functions of perfect crystals. They are atomiclike functions localized about the lattice sites of the system and represent an alternative basis for the description of the electronic structure of the defect problem. A single set of GWF's is sufficient to describe an entire perturbed band, and only those GWF's near the defect need be different from the Wannier functions of the perfect crystal.

We test the GWF formalism by applying it to a one-dimensional model of a crystal surface. We deal with a one-electron problem of the form

$$H\varphi_q(x) = E_q\varphi_q(x), \tag{1}$$

where

$$H = -\tfrac{1}{2}d^2/dx^2 + V(x). \tag{2}$$

The $\varphi_q(x)$ are the wave functions belonging to a single perturbed band and q is an intraband quantum number. In terms of the GWF's, $a_n(x)$, we have

$$\varphi_q(x) = \textstyle\sum_n c_{q,n} a_n(x), \tag{3}$$

where the n are site coordinates. The $a_n(x)$ may be calculated variationally[2] by a straightforward generalization of the techniques developed[4] for Wannier functions of periodic systems. Because the matrix $\{C_{q,n}\}$ is unitary, the total band energy per electron is

$$E = N^{-1}\textstyle\sum_n \langle a_n(x)|H|a_n(x)\rangle, \tag{4}$$

where N is the total number of electrons. One obtains the $a_n(x)$ variationally by minimizing E subject to the constraint

$$\langle a_n(x)|a_{n'}(x)\rangle = \delta_{n,n'}. \tag{5}$$

This constraint is included, following Kohn,[4] via Löwdin[5] symmetric orthogonalization:

$$a_n(x) = \textstyle\sum_{n'} G_{n',n}{}^{-1/2} g_{n'}(x), \tag{6}$$

where

$$G_{n',n} = \langle g_{n'}(x)|g_n(x)\rangle, \tag{7}$$

and $g_n(x)$ is a simple, highly localized, nonorthogonal[6] trial function.

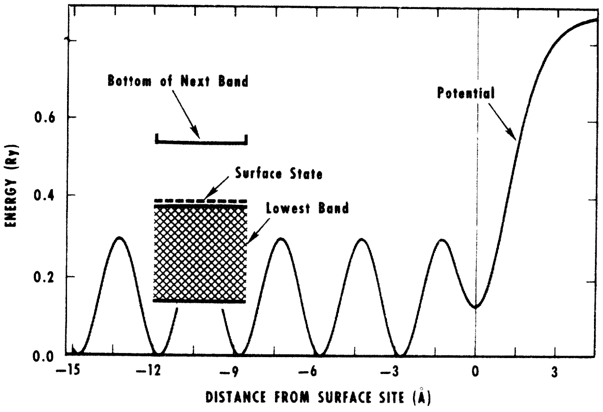

FIG. 1. Plot of the potential used in the calculation. The inset shows the relevant part of the energy spectrum of this potential.

Our crystal surface is characterized by the potential of Fig. 1. The potential was constructed by matching, at $x = -0.9$ Å, a Mathieu (sinusoidal) potential representing the bulk crystal to a soluble potential well,[7] reminiscent of a chemisorbed layer. The Mathieu potential is weak. That is, it is adjusted so that the Wannier functions of its lowest band are nearly free electron-like.[8,9] While we have solved this model for a wide range of lattice constants and surface-well characteristics, this nearly free-electron situation provides the most severe test of a local-orbital picture. Note finally that the surface well was made shallower than the bulk wells so that a surface state splits off from the top of the first band, as indicated in the inset of Fig. 1.

To calculate the GWF's of this lowest band we use as trial functions simple Gaussians,

$$g_n(x) = (\alpha_n{}^{1/2}/\pi^{1/4})\exp[-\alpha_n{}^2(x-n)^2/2]. \tag{8}$$

Because the potential is nonperiodic, the parameters α_n may vary from site to site. Combining Eqs. (4), (6), (7), and (8), we obtain E as a functional of the α_n, which is minimized by direct variation of the α_n. Starting with the surface site, the α_n which minimize E are $\alpha_1 = 0.75\pi/d$; $\alpha_2 = 0.72\pi/d$; $\alpha_3 = 0.70\pi/d$; and $\alpha_n = 0.69\pi/d$, $n \geq 4$, where d is the bulk lattice constant. Note that the α's for only the first three planes differ from the bulk value. Thus the calculation is very simple. The transition from surface to bulk behavior of the GWF is illustrated in Fig. 2. The GWF at the surface site has a smoothly decaying tail on its right-hand or vacuum side, but has the characteristic Wannier-function oscillations on its left-hand or crystal side. On moving into the crystal this asymmetry very rapidly disappears so that by the third site the GWF is essentially equal to the bulk Wannier function.

On any scale, the surface is a massive perturbation of the bulk potential. Yet we see that its effect on the GWF's is remarkably short ranged. This is true even though the bulk potential is weak, so that the bulk wave functions are closer to plane waves than atomic orbitals. This suggests that, in general, only a small number of GWF's in the vicinity of a defect need be changed from their bulk values. This is essential if the formalism is to be useful for chemisorption and other low-symmetry calculations on wide-band as well as tight-binding materials.

Once the approximate GWF's are known, one

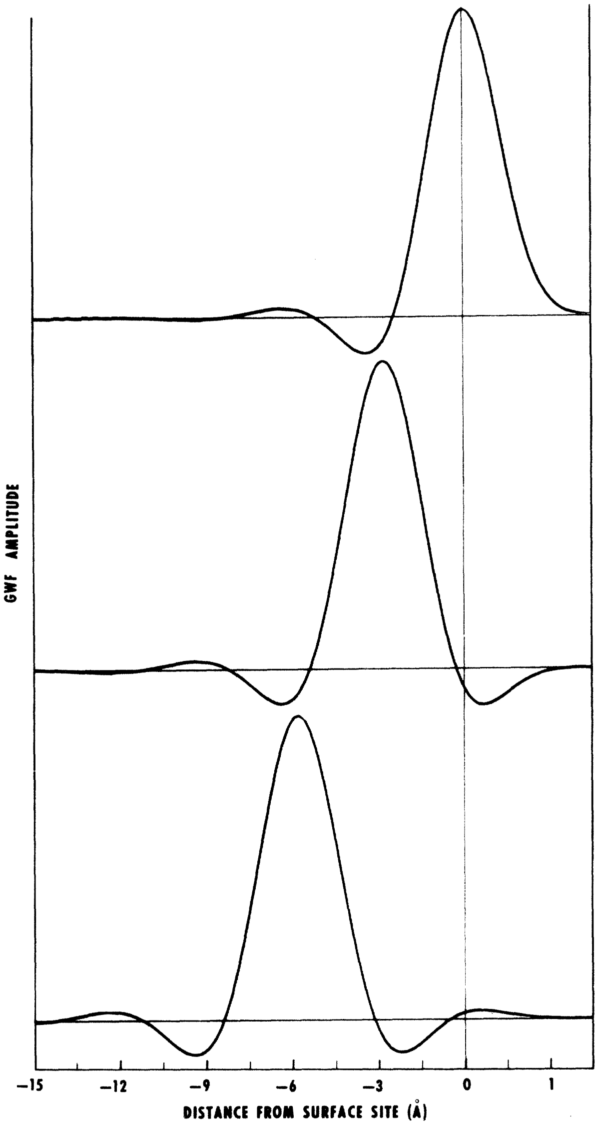

FIG. 2. Generalized Wannier functions belonging to the first three lattice sites. The maxima of the GWF's lie very close to the minima of the successive potential wells shown in Fig. 1. By the third site the local function is essentially the bulk Wannier function.

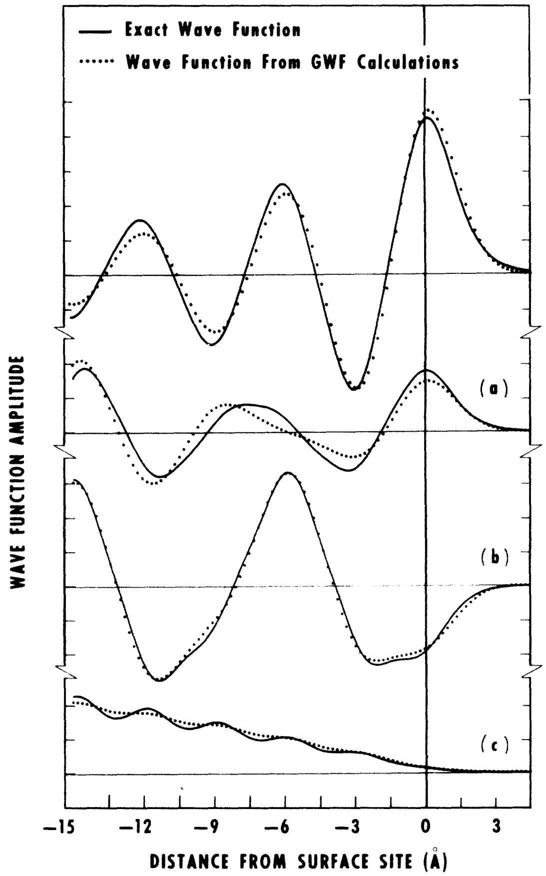

FIG. 3. Top curves, surface-state wave function, followed by examples of continuum states near to (a) top, (b) middle, and (c) bottom of the lowest band.

can determine[2,3] total energies, charge densities, and local densities of states without prior knowledge of the wave functions $\varphi_q(x)$. However, as a very difficult test of the GWF accuracy we calculate approximate $\varphi_q(x)$ via Eq. (3) (the $C_{q,n}$ are obtained from a matrix eigenvalue equation), and compare them to the exact $\varphi_q(x)$. Because the model problem is one-dimensional the $\varphi_q(x)$ can be obtained exactly by numerical integration or by matching the known series solutions of the two parts of the potential. The topmost plot of Fig. 3 compares surface-state wave functions, while subsequent plots compare representative continuum wave functions near the top, middle, and bottom of the lowest band. These are typical of the agreement found throughout the band. The overall agreement is quite good. In light of the simplicity of the GWF calculation (a single, four-parameter variational calculation), the results of this most stringent test of an approximate quantum-mechanical calculation are remarkable.

To summarize, we regard the following as the most important characteristics of the test calculation:

(1) The calculation is accurate, i.e., wave functions determined from the GWF's agree well with the exact wave functions. Thus all other quantities of interest such as expectation values and local densities of states will be similarly accurate.

(2) The calculation is efficient. The accurate results were obtained from a single variational

calculation with simple trial functions and only four parameters.

(3) The potential used in the calculation is weak, providing an extreme test for a local-orbital picture.

We feel these are encouraging results. They imply that the GWF formalism will provide a practical, efficient calculational technique for solid surfaces. We believe this to be especially important for transition metals and their oxides. For these, one must deal with a mixture of contracted and diffuse orbitals immersed in the inhomogeneous medium of the surface. A method which represents surface observables precisely in terms of local functions is ideally suited to this problem.

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[1] The evidence is especially apparent in recent experiments on the elemental semiconductors. Ion-neutralization spectroscopy, which probes essentially only the surface layer of atoms, gives electron energy distributions which are qualitatively different from the bulk density of states [H. B. Hagstrum and G. E. Becker, Phys. Rev. B 8, 1580 (1973)], whereas in ultraviolet photoemission spectroscopy, the electron energy distributions are dominated by the bulk density of states even under conditions in which the experiment probes only about four atom layers [D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 28, 1378 (1972)].

[2] W. Kohn and J. Onffroy, Phys. Rev. B 8, 2485 (1973).

[3] J. G. Gay and J. R. Smith, Phys. Rev. B (to be published).

[4] W. Kohn, Phys. Rev. B 1, 4388 (1973).

[5] P. O. Löwdin, J. Chem. Phys. 18, 365 (1950).

[6] J. D. Weeks, P. W. Anderson, and A. G. H. Davidson, J. Chem. Phys. 58, 1388 (1973).

[7] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Pt. II, p. 1650.

[8] J. C. Slater, *Symmetry and Energy Bands in Crystals* (Dover, New York, 1972), Chap. 6. The Mathieu potential used corresponds to a value of 1 for Slater's parameter *s*.

[9] J. C. Slater, Phys. Rev. 87, 807 (1952).

Angular Distributions of Electron-Stimulated–Desorption Ions: Oxygen on W(100)

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Ions liberated from an adsorbed layer by electron-stimulated desorption are shown to have sharply peaked, symmetric angular distributions which are in registry with the substrate. We propose a new method for investigation of the symmetry of binding sites for adsorbed species.

Low-energy electron (~ 100 eV) bombardment of a surface containing an adsorbed layer can produce a number of irreversible changes in the adsorbed layer. The electron-induced desorption of atomic and molecular ions, neutrals, and metastable species from monolayer and submonolayer quantities of simple gases adsorbed on metal and semiconductor surfaces has been observed. These processes are all classified as electron-stimulated desorption (ESD) phenomena.[1] In a recent ESD study of oxygen adsorbed on a single-crystal tungsten (100) surface, evidence was found that O^+ ions liberated from the surface had an angular distribution which was sharply peaked in the direction normal to the surface.[2]

In the present report, we have employed a display-type apparatus to examine the details of the angular distribution of O^+ ions in an ESD study of oxygen on W(100). Surprisingly, the angular distributions of ESD ions reveal complex symmetrical patterns in registry with the substrate lattice which change as a function of the oxygen coverage and heat treatment of the surface. We propose that the symmetry observed in the patterns for the angular distributions of ESD ions provides new insights into the details of bonding of atoms and molecules at surfaces.

In the experimental ultrahigh-vacuum apparatus, an electron gun was used to bombard a W(100) crystal with a focused electron beam at a 45° angle of incidence. Ions liberated from the crystal passed through a hemispherical grid system and were accelerated to a planar microchannel plate assembly.[3] The secondary-electron signal