LOW-ENERGY ELECTRON-DIFFRACTION INTENSITY CALCULATIONS WITH A REALISTIC CRYSTAL POTENTIAL*

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The band-matching approach has been used to calculate low-energy electron-diffraction intensity curves for the basal cleavage plane of beryllium. An approximation to the exact theory, made possible by the presence of strong inelastic scattering, has enabled these curves to be calculated very rapidly for general angles of incidence and with a detailed, nonlocal potential with no adjustable parameters. There is striking similarity between the calculated intensities and the detailed experimental work of Baker.

The potential applicability of low-energy electron diffraction in determining the structure and electronic properties of crystal surfaces has stimulated the recent development of a number of theoretical approaches to the problem.[1-7] In general, the scattering by the atoms in the crystal is expressed in terms of a potential or phase shifts and the scattered intensities are discussed as a function of both incident energy and angle. The major difficulties encountered in such calculations arise from the complexity of the computation, which has restricted the calculations either to fitting procedures with oversimplified potentials or to a single angle of incidence. In this Letter, we describe a band-matching method for the calculation of reflectivities using a detailed, nonlocal potential for beryllium. Inelastic effects, whose importance has been emphasized recently,[5,6] are included without adjustable parameters. Important advantages of the method are the speed of computation and its applicability to arbitrary angles of incidence. The calculated intensities show marked agreement with recent experimental data over a range of incident angles.

In the band-matching approach to low-energy electron-diffraction (LEED) intensity calculations, the wave function inside the crystal is expanded in terms of three-dimensional propagating and exponentially damped Bloch waves and the wave function and its slope are matched at the surface to the incident- and scattered-electron plane waves. For both sets of states the crystal momentum (up to a surface reciprocal lattice vector) and the energy are conserved.

The wave field outside the crystal is expanded:

$$\Psi^O = e^{i\vec{K}\cdot\vec{r}} + \sum_{j=0}^{N} A_j \exp[i(\vec{k}_j^{\perp} + \vec{K}^{\parallel} + \vec{g}_j^{\parallel})\cdot\vec{r}],$$

where

$$k_j^{\perp} = [E - (g_j^{\parallel} + K^{\parallel})^2]^{1/2}.$$

Inside the crystal,

$$\Psi^I = \sum_j C_j \Psi_j^B; \quad \Psi_j^B = e^{i(\vec{k}_j'^{\perp} + \vec{K}^{\parallel} + \vec{g}_j^{\parallel})\cdot\vec{r}}[1 + \sum_l B_j^l e^{i\vec{h}_l\cdot\vec{r}}],$$

where E is the energy of the incident beam, $\vec{g}_j^{\parallel}$ the surface component of the jth reciprocal lattice component, $\vec{K}^{\parallel}$ the parallel component of the incident beam, A_j the expansion coefficient of outside plane waves, and C_j the expansion coefficient of the Bloch functions. $|A_j|^2$ is proportional to the intensity of the jth reflected beam. If Ψ^I and Ψ^O, and their derivatives, are matched at the surface, we obtain

$$\vec{A} = (\vec{P} - \vec{Q})(\vec{P} + \vec{Q})^{-1}(100\cdots)^T, \quad \vec{C} = 2(\vec{P} + \vec{Q})^{-1}(100\cdots)^T,$$

where T indicates the corresponding column vector, and

$$P_{lj} = \delta_{lj} + \sum_i B_j^{(l-j)^{\parallel},i}; \quad Q_{lj} = [k_j'^{\perp}\delta_{lj} + \sum_i (k_j'^{\perp} + h_{(l-j),i}^{\perp})B_j^{(l-j),i}]/k_l^{\perp}.$$

The summation over i includes all Bloch-state expansion coefficients B_j^l along a reciprocal lattice rod

normal to the surface. If the term $(\vec{P}+\vec{Q})^{-1}$ is formally expanded and multiplied by $(\vec{P}-\vec{Q})$, the following exact expression for the reflection coefficients in the (00) specularly reflected beam is obtained:

$$A_1 = R_{11} - \sum_n R_{1n}L_{n1} + \sum_{np}R_{1n}L_{np}L_{p1} + \cdots, \quad L_{1j}\,(R_{1j}) = \frac{\sum_i [k_i^{\perp} \pm (k_j'^{\perp}+h_i^{\perp})]B_j^{(1-j),i}}{k_i^{\perp}+k_i'^{\perp}+\sum_i [k_i^{\perp}+(k_i'^{\perp}+h_i^{\perp})]B_i^{0,i}}, \tag{1}$$

where the plus sign is taken for L and the minus sign for R. A similar expression exists for the other beams. This expansion suggests a scattering interpretation which can be clarified by inspection of the terms L_{1j} and R_{1j}. In particular, in the limit of small elastic and zero inelastic scattering the values of R_{1n} (L_{1j}) are of the order of unity for a Bragg (Laue) excitation from beam j to l and zero otherwise. Although not strict selection rules, they indicate qualitatively the size of the terms. For example, if conditions are such that both R_{1n} and L_{n1} are large, i.e., there is an appreciable amplitude for both a Bragg and a Laue reflection in the same beam, there will be a large effect on the amplitude of the specularly reflected beam A_1.

If expansion (1) is truncated after the second term, we have the approximation adopted here for second-order scattering only (SOSO). Consistent with this second-order approximation to the infinite series, the coefficients in the term R_{11} are calculated to second order by perturbation theory and those in R_{1n}, L_{n1} to first order. The calculation proceeds very rapidly, and even with a complicated nonlocal potential an intensity curve of 100 points from 0 to 200 V requires only one minute on an IBM 360-67 computer. An important consideration is the presence of a large inelastic term which results in realistic values of the peak widths and reflectivities and which effectively removes the singularities in the perturbation matrix elements. The method is approximate, but the second-order calculations do not differ greatly from those to first order and the conditions for its applicability, namely, a weak elastic scattering potential and a strong inelastic scattering are, we believe, met in beryllium.

Beryllium has been chosen because (1) we have detailed experimental information collected at liquid-nitrogen temperatures.[8] (2) The $1s$ core wave function is localized near the nucleus and is well described by a simple analytic spherically symmetric function.[9] Resultant integrals can therefore be evaluated in closed form. (3) Recent Fermi-surface measurements and band-structure calculations are available.

The contributions to the potential seen by an incident electron are the following: (a) the core potential due to the nuclear charge plus the core electrons. This can be computed analytically or we may use tabulated values.[10] The differences are negligible. (b) Core–plane-wave exchange. Here we have adopted a modification of the Slater approximation which takes into account the nonorthogonality of the core states and plane waves.[11] This term is $\vec{k}$ dependent and vanishes at high energies as it should. It is comparable in magnitude with Slater exchange at low energies.
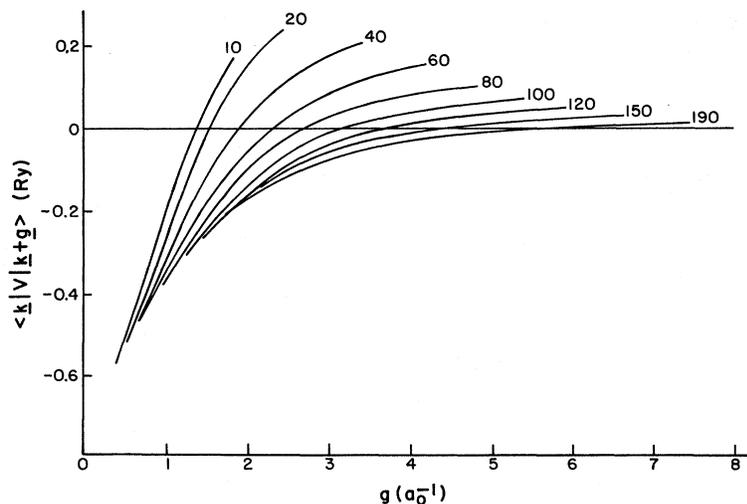
FIG. 1. Each curve is labeled by an energy E in electron volts. The ordinate is the matrix element $\langle\vec{k}|V|\vec{k}+\vec{g}\rangle$ (form factor) for which the abscissa $\vec{g}$ is chosen so that both $\vec{k}$ and $\vec{k}+\vec{g}$ lie on the constant-energy surface E.
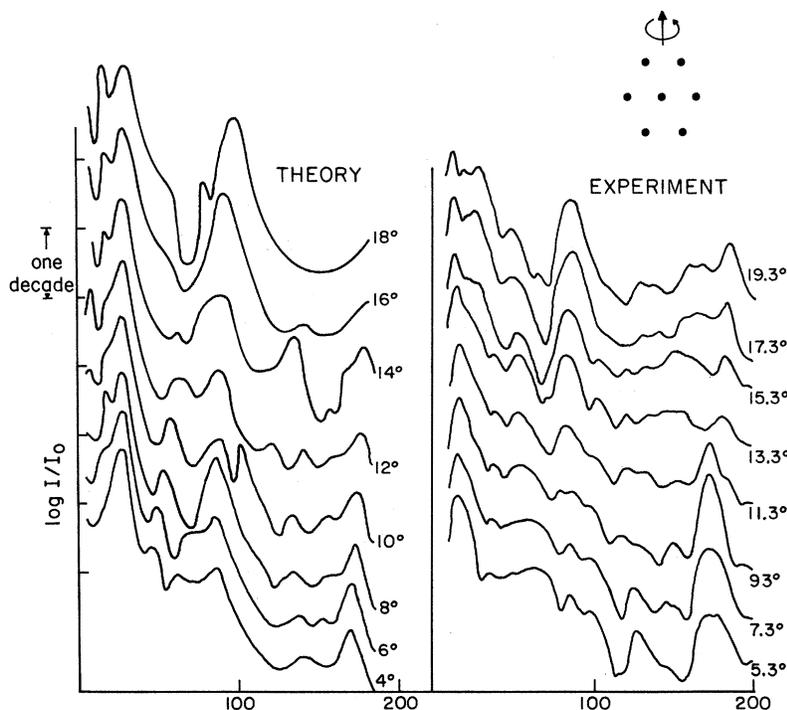
FIG. 2. Theoretical and experimental intensity-voltage curves for the (0001) face of beryllium with rotation about (11$\bar{2}$0). Experimental results due to Baker, Ref. 8. Angles of incidence are as marked, incident energies are in electron volts, and intensities are log normalized. One decade in intensity is shown at the left.

(c) From the calculations of Loucks and Cutler,[12] the conduction electrons in beryllium are well approximated by a uniform charge distribution and will mainly affect the diagonal terms. The conduction electrons give rise, however, to the screening of the final off-diagonal elements. We include this effect by using the Hartree dielectric function. (d) The orthogonalization term, which converts the potential to a pseudopotential, is taken in the form discussed in detail by Pendry[13] with resultant pseudopotential

$$V_{ps} = V - E_{1s} |1s\rangle\langle 1s|.$$

For E_{1s} we could take the free-atom $1s$ level, but we have adopted E_{1s} as a disposable parameter and have least-squares fitted our matrix elements at the Fermi energy to those obtained by Tripp, Everett, Gordon, and Stark[14] from Fermi-surface measurements. In fact, the fitted E_{1s} (8.953 Ry) is close to the free-atom value (8.698 Ry). The form factors of the above potential are shown in Fig. 1.

For the diagonal terms we average terms (a) and (b) over the atomic volume and find that the result is very close to the average potential energy of a uniform distribution over that volume of positive charge equal to the valence. Since

the conduction electrons are to a good approximation uniform, the result is a system which closely approximates the jellium model used in the random-phase-approximation self-energy calculations of Lundqvist.[15] We have adopted his calculated values.

Calculations have been carried out using the potential described above. The matching plane is taken midway between two atomic planes and the real part of the self-energy is set equal to zero. The latter can be justified by noting that a sharp discontinuity in the inner potential at the surface produces in the calculation a back reflection which interferes with the reflected beams. Although the overall reflectivities are not significantly changed by this step, the details of the calculated curves are. The real situation is somewhat different. In particular, the potential near the surface falls off to zero rather smoothly over a distance of a few angstroms. This will result in a decreased step reflection and hence a reduced perturbation in the reflected beams. Setting the real part of the diagonal matrix element to zero effectively eliminates this spurious reflection, the shift in the electron energy due to the inner potential being taken into account by shifting the energy scale by an amount
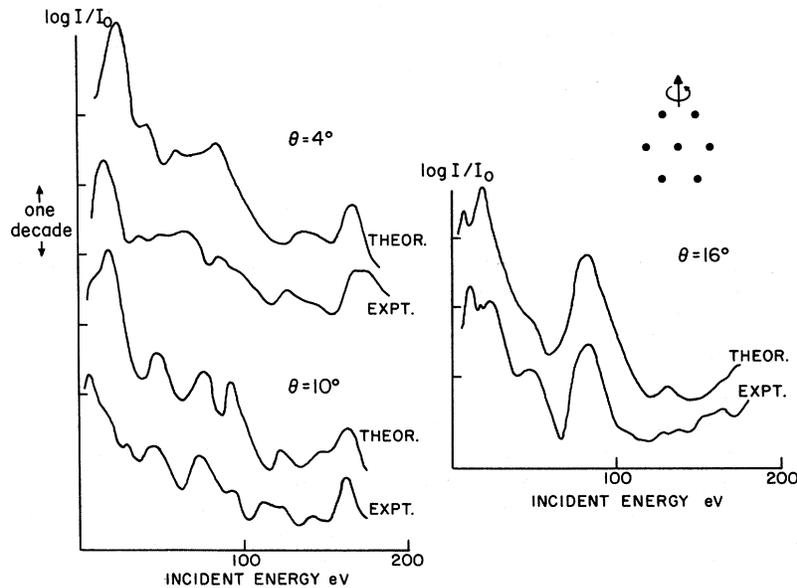
FIG. 3. Direct comparison of theory and experiment for $\theta = 4°$, 10°, and 16°. Experimental results due to Baker, Ref. 8.

equal to the average of the inner potential. A more rigorous solution would be to describe the space as three regions—bulk, surface, and vacuum—and perform the matching calculation at the two interfaces. Such a calculation, in which the potential in the bulk is continued smoothly to zero through the surface region, is presently being carried out.

In Figs. 2 and 3 the results of our calculation, in which each Bloch wave is expanded in terms of 90 plane waves by perturbation theory, are compared with the experimental results of Baker.[8] We note several marked similarities. A Bragg peak at 180 eV becomes less intense as θ increases, a very prominent peak at approximately 90 eV appears near $\theta = 12°$, a weak peak appears at low energies (~30 eV), and the splitting of both the first Bragg peak and the peak near 150 eV as θ increases.

The speed of computation has enabled us to examine in some detail the effect of changes in the crystal potential on the calculated intensities. We may discuss, for example, different approximations for core–plane-wave exchange, the use of the free-atom value for E_{1s}, and the results of changing the absorptive term in the potential. In general, the features such as peak position and width do not change greatly, though the absolute intensities are rather sensitive to the details of the potential. An extended discussion of this and other aspects of the theory will be given elsewhere.

The experimental results and the interest of Dr. J. M. Baker have made an important contribution to this work. We thank him, and also Dr. N. W. Ashcroft, Dr. J. M. Blakely, Dr. F. Jona, Dr. C. Y. Li, Dr. T. N. Rhodin, and Dr. J. W. Wilkins for helpful discussions, and Dr. E. G. McRae for comments on the manuscript.

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LOCALIZATION IN DISORDERED MATERIALS: BINARY ALLOYS*

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A criterion for localization of electron states in disordered materials is presented.
Applications to binary alloys, made using the self-energy calculated in the coherent-
potential approximation, confirm the Mott-Cohen-Fritzsche-Ovshinsky model in detail.
Mobility edges occur inside the band edges. A mobility gap can appear within the band.
The band can split into sub-bands, each with mobility edges. Below a critical concen-
tration, an Anderson transition, where the minority sub-band becomes entirely local-
ized, can occur.

Considerable effort has recently been devoted
to calculation of the densities of states in differ-
ent disordered materials.[1-3] In particular, the
case of substitutional disorder has been brought
to a quantitative level of understanding of the den-
sity of states through the application of the co-
herent-potential approximation (CPA)[4] to binary
alloys.[5] Nevertheless, understanding of the
nature of the wave functions in disordered mate-
rials has remained at the qualitative level ex-
emplified by the Mott-Cohen-Fritzsche-Ovshin-
sky (MCFO) model.[6,7] That model assumes the
existence of regions of exclusively localized
states separated by critical energies,[6] termed
mobility edges,[7] from regions of exclusively ex-
tended states.

In a recent paper[8] based on Anderson's statis-
tical approach,[9] the formal theory[9-12] supporting
the MCFO model has been reviewed and extended
to the point where it has been demonstrated that
a function $F(E)$ exists such that $F < 1$ in the re-
gions of localized states, $F > 1$ in the region of
extended states, and $F(E_c) = 1$ at the mobility
edges E_c. Moreover, a significant step towards
a quantitative determination of $F(E)$ has been
taken by relating $F(E)$ to properties of the aver-
age Green's function. Using this relation one
can easily prove that when the average Green's
function is translationally invariant with a k-in-
dependent self-energy, $\Sigma(E)$, $F(E)$ is then given
by

$$F(E) = \{\max_k |E(\vec{k})|\}/|E - \Sigma(E)|, \qquad (1)$$

where $E(\vec{k})$ is the band structure corresponding

to the average Hamiltonian. Formula (1) has
already been applied[8] to the specific case of a
Lorentzian distribution of single-site energies,
and exact quantitative results have been obtained
for E_c.

The first purpose of this paper is to present
as a conjecture the generalization of criterion
(1) to all disordered systems which are transla-
tionally invariant when averaged [so that the self-
energy becomes diagonal in $\vec{k}$, $\Sigma = \Sigma(\vec{k}, E)$]:

$$F(E) = \{\max_k |E(\vec{k})|/|E - \Sigma(\vec{k}, E)|\}. \qquad (2)$$

Second, we combine this criterion (1) with the
approximate self-energies available through the
CPA[13] to obtain quantitative predictions of the
character of the eigenstates in binary alloys.
The self-energy is k independent in the CPA. We
may therefore use (1), and errors will arise only
from inaccuracies in the CPA values for Σ. Such
errors in Σ, on entering $F(E)$, have the effect
only of shifting the values of E_c found; corre-
sponding errors in a mobility calculation lead
to finite mobilities within a region of states
which are actually localized.

For the calculations reported in this Letter,
we consider a binary substitutional alloy $A_x B_{1-x}$
in which there is a single Wannier function as-
sociated with each site. In the Hamiltonian,

$$H = \sum_i |i\rangle \epsilon_i \langle i| + \sum_{i \neq j} |i\rangle V_{ij} \langle j|, \qquad (3)$$

the diagonal elements, ϵ_i, take on two values
ϵ^A and ϵ^B, on A and B sites, respectively, while
the off-diagonal elements are translationally in-
variant. We shall define a scattering strength,