$$D = 1.0\,e^{-11220/RT} + 0.05\,e^{-8890/RT}\,. \qquad (4)$$

Statistically this is not a better fit than a single-exponential fit, and confirmation of the curvature of the Arrhenius plot could probably be obtained only by extending the present measurements to lower temperatures. Unfortunately, the short half-life ^{42}K (12.4 h) and the minimum section thickness (~ 10 μ) set the present limit for the lowest temperature.

The curvature for potassium was compared with that for sodium,[2] using a normalized temperature scale (T/T_m, °K). A linear Arrhenius fit of the data above $0.75T_m$ was made for both the sodium and potassium data. At $0.65T_m$ (the lowest data point for potassium) the deviation of the diffusion coefficients of both potassium and sodium from their respective Arrhenius lines were approximately 20%. This again would suggest that the diffusion behaviors of potassium and sodium are similar, although the evidence for curvature is not as conclusive for potassium.

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Calculated Low-Energy Electron-Diffraction Intensities for (111) and (110) Surface of Al[†]

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Reflected low-energy electron-diffraction spectra are calculated for the (111) and (110) surfaces of Al using the band-structure-matching approach without taking into account inelastic effects. The main effort was put into the calculation of a realistic pseudopotential (no adjustable parameters). The results are compared with experiment and found to be in over-all agreement with respect to the widths and positions of the peaks, provided we identify a single experimental peak with a group of calculated ones.

I. METHOD OF CALCULATION

In a recent Letter[1] we reported the results of an elastic calculation of low-energy electron-diffraction (LEED) intensities for the (001) surface of Al using the band-structure-matching formalism.[2] We have now applied the same method to calculate the reflected LEED spectra as a function of energy for the (111) and (110) surfaces of Al.

The band structure of Al in the energy range between 0 and 10 Ry has already been extensively discussed elsewhere.[3] Let us only mention here that it was calculated using a pseudopotential based on the orthogonalized-plane-wave (OPW) approximation without any adjustable parameters.[4] Full nonlocality and $\vec{k}$ dependence of the pseudopotential was retained throughout all calculations. The crystal potential contained all of the usual contributions,[4] with the exception that instead of Slater's approximation in calculating the core-electron–conduction-electron exchange we employed an OPW approximation, where the conduction electron was described by a single OPW, and the core electron by a Hartree-Fock wave function taken from Frose-Fisher.[5]

The band structure along the Λ direction was

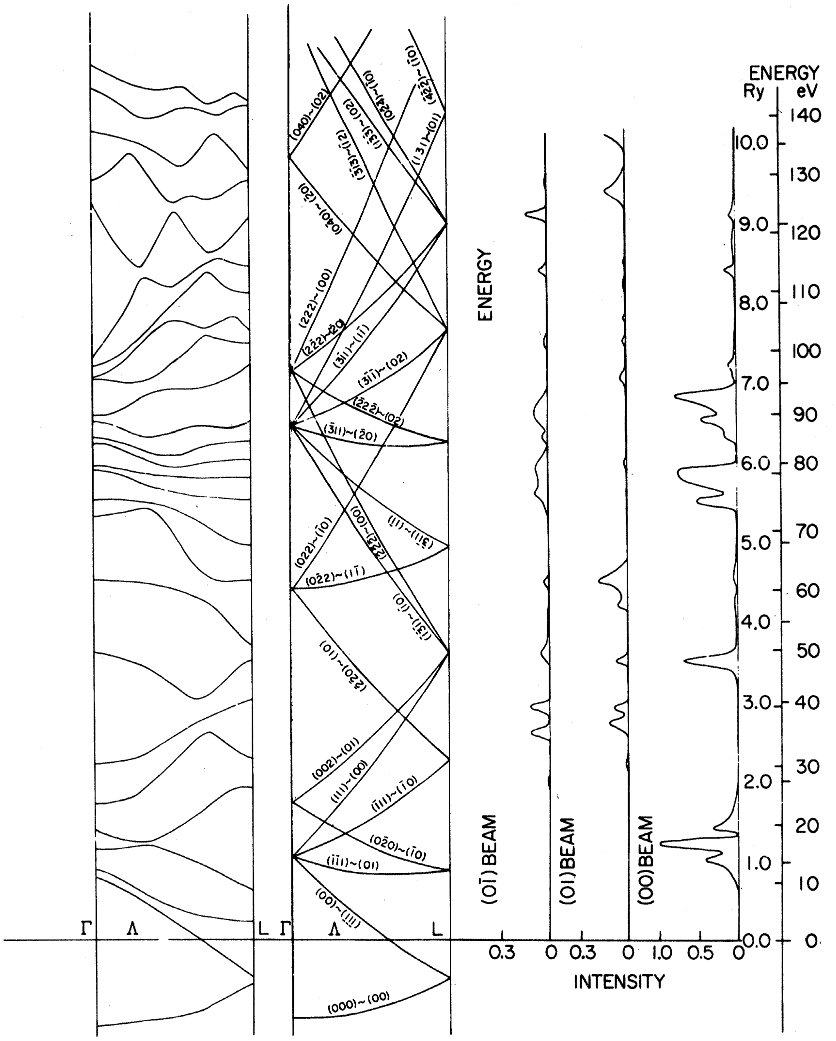

FIG. 1. Summary of the theoretical results for the (111) surface: left, calculated band structure (only Λ_1 bands are shown); center, free-electron band structure (each band is identified by a three-dimensional reciprocal-lattice vector in the cubic system together with its transform in a surface-connected system); right, intensities of the various diffracted beams vs energy.

calculated using 51 symmetrized plane waves in the expansion of the pseudo-wave-function, and the band structure along the Σ direction was calculated using 70 symmetrized plane waves. Depending on the energy, the rate of convergence varied between 0.02 and 0.2 Ry. This estimate was arrived at by the method described in Ref. 3. The calculated band structure at the lowest-energy end (i.e., below and around the Fermi level) was compared with the existing results (see the references given in Ref. 3) and found to be in satisfactory agreement.

Having obtained the real band structure, we calculated the complex band structure using the $\vec{k}\cdot\vec{p}$ approach,[6] where we treated the Bloch waves at the band edges as the zero-order states.

LEED intensities were obtained using the (by now standard) matching procedure[7,8] which consists essentially in equating the terms in the wave function outside and inside the crystal which have the same components of reciprocal-lattice vectors in the surface plane (which are precisely the beam indices).

II. DISCUSSION OF THEORETICAL RESULTS

Figure 1 shows the calculated band structure, free-electron band structure, and the reflected spectrum for the (111) surface of Al. Only the symmetric Λ_1 bands are shown, since at normal incidence only these bands couple to the incident field. We immediately notice a close correspondence between the reflected spectrum and the band structure—a fact which has been consistently emphasized in all matching calculations.[1,7,8] It must be pointed out, however, that the intensity also depends on the fraction of the total current carried into the solid, and this fact, together with the magnitude of the band gap, accounts for the width and position of the peaks. In addition, the variation of the peak positions within a band gap for various beams is due to the energy dependence of the expansion coefficients of the wave function

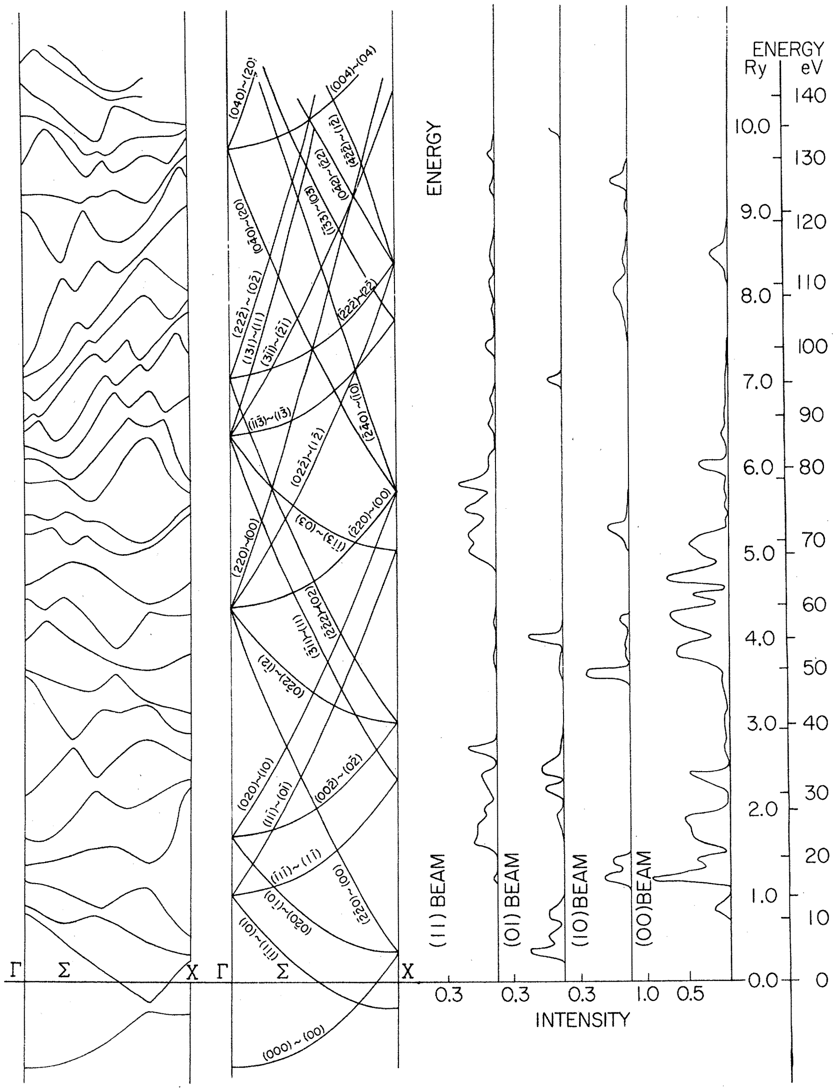

FIG. 2. Summary of the theoretical results for the (110) surface: left, calculated band structure (only Σ_1 bands are shown); center, free-electron band structure (same identification of the bands as in Fig. 1); right, intensities of the various diffracted beams vs energy.

inside the band gap.

As we have already mentioned in Ref. 1, the identification of each peak is rather difficult because of the strong multiple scattering which takes place in the energy range under consideration. Formally, this is manifested by the fact that the plane-wave expansion of the pseudo-wave-function contains many terms with comparable amplitudes. Consequently, it is not correct in general to associate a peak with a single reflection, except in some obvious cases such as the low-lying strong Bragg primaries which can be usually identified by examining the band structure and the corresponding wave functions. With this in mind, let us discuss the calculated spectra.

(111) *surface*. Consider the (00) beam. In the region between 10 and 30 eV there are three peaks. The largest one is most definitely the Bragg peak, as is also quite evident if we examine the associated band structure. The smaller peaks on the low- and high-energy shoulders of the Bragg peak cannot be identified by kinematical assignment. We note that on the high-energy shoulder we have a combination of (10) secondary as well as a (10) tertiary due to the interaction of two (10) waves. On the low-energy side of the Bragg peak we have a possible (01) secondary and a tertiary (peak) due to the interaction of (01) and (10) waves. Higher in energy we see a peak at 48 eV, which is presumably again a Bragg peak, combined perhaps with the interaction from (01) and (10) secondaries. In the region between 70 and 100 eV the situation becomes much more complicated, as we can see from the band structure. It would be presumptuous to identify each peak here using the above type of arguments. Examination of the wave function shows that many plane waves are strongly coupled, thus indicating that the peaks are dynamical in origin. The Bragg

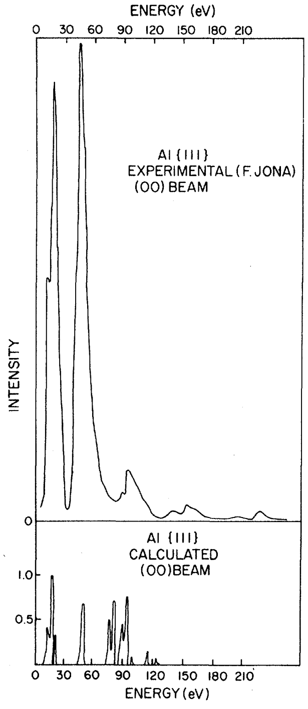

FIG. 3. Comparison between the experimental and theoretical spectra for the (00) beam from (111) surface.

peaks are not necessarily stronger than the secondaries. In fact, a peak at 78 eV is definitely due to (10) and (11) secondaries.

The spectra for the nonspecular beams are much weaker (because of the sharing of intensity between the equivalent beams) and show much less structure than the (00) beam [because the incident wave is usually strongly coupled to the specularly reflected one and thus any band gap affects the (00) spectrum]. In the (01) beam the two first peaks at 33 and 38 eV are believed to be the primary [due to the interaction of (00) and (01) waves] and secondary [due to the interaction of two (01) waves] peaks, respectively. The peak at 47 eV is a primary Bragg peak, as is evident from the band structure. Above 50 eV the situation is much more complicated and we cannot give a meaningful identification of the peaks due to the strong dynamical effects.

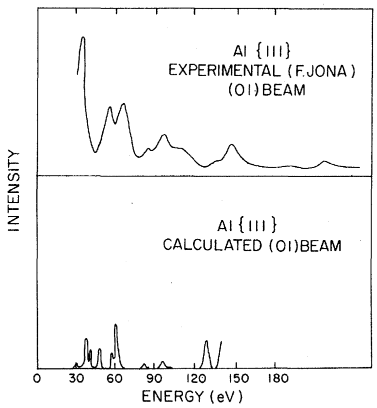

FIG. 4. Comparison between the experimental and theoretical spectra for the (01) beam from (111) surface.

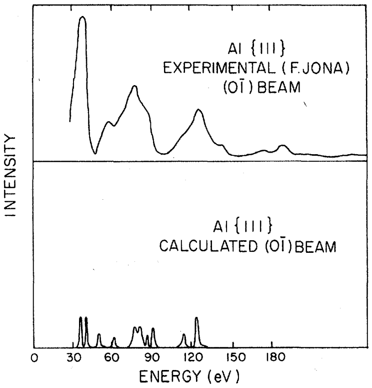

FIG. 5. Comparison between the experimental and theoretical spectra for the $(0\bar{1})$ beam from (111) surface.

(110) *surface*. A similar analysis carried out for the (111) surface (see Fig. 2) can also be applied here with a few more reservations because the band structure is much more complicated, since the symmetry is lower. In the energy range 10–35 eV we see a series of peaks in the (00) beam. Examination of the wave function shows that they are caused by strong multiple scattering and thus it would be a mistake to identify them as primaries, secondaries, etc. Instead, we can only say that this series of peaks is caused by the interaction of a (00) wave with (00), (10), (11), (02) waves, and an additonal effect due to the appearance of (01) and (11) beams propagating parallel to the surface.

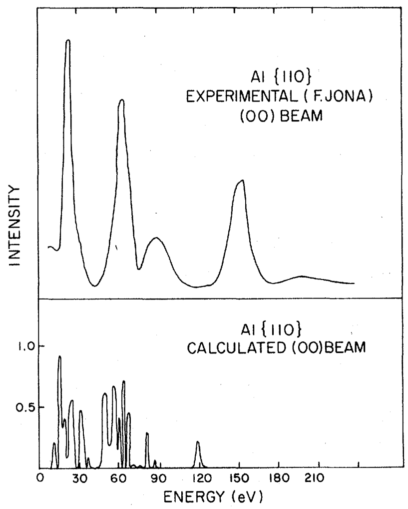

FIG. 6. Comparison between the experimental and theoretical spectra for the (00) beam from (110) surface.

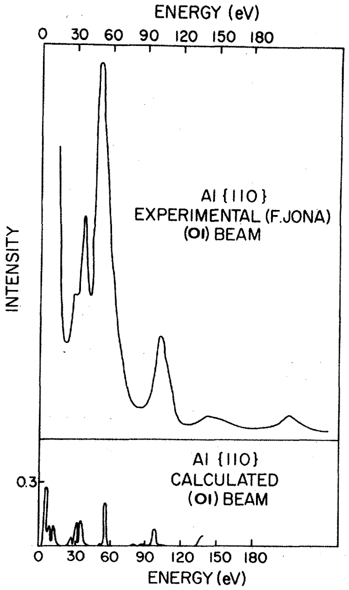

FIG. 7. Comparison between the experimental and theoretical spectra for the (01) beam from (110) surface.

In the energy range 45–72 eV the situation is even more complicated. Here we have a primary peak, a (12) secondary, and an effect of an emerging (02) beam propagating parallel to the surface. Let us note that we also have various tertiary peaks in the (00) beam, corresponding to the fact that the normal component of momentum need not be conserved across the surface.

III. COMPARISON WITH EXPERIMENT

Figures 3–9 show the comparison of our calculated results with the experimental curves obtained by Jona.[9] More refined measurements in the low-energy range (0–50 eV) with a new goniometer apparatus are now under way in this laboratory.[10]

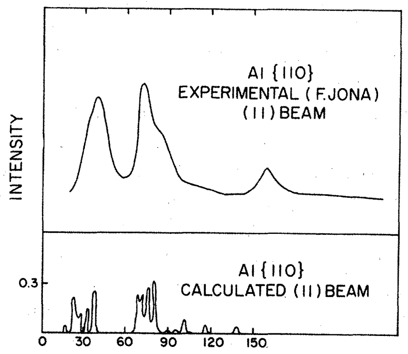

FIG. 8. Comparison between the experimental and theoretical spectra for the (11) beam from (110) surface.

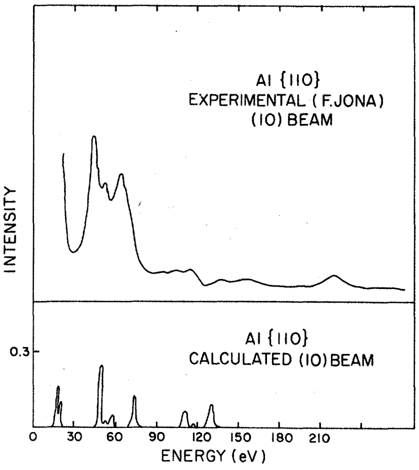

FIG. 9. Comparison between the experimental and theoretical spectra for the (10) beam from (110) surface.

We shall discuss the comparison between experimental and theoretical curves with respect to the three parameters: position of the peaks, their widths, and their relative intensities. In all of the figures we note striking correspondence between an experimental peak and a group of the calculated ones. It is possible that the experimental resolution is not sufficient to resolve the peaks (experimental peaks usually exhibit a lot of structure), but it is more probable that inelastic effects are responsible for removing the sharp features and thus broadening the peaks. Consequently, we may compare the groups of calculated peaks with a single experimental one, noting then a close agreement in the widths. One marked discrepancy occurs in the (00) beam for the (111) surface where we have a peak at about 75 eV which is not observed experimentally. One can also talk about the mean position of a group of closely spaced peaks and compare it with the position of an experimental peak. Again we note a marked agreement. Let us emphasize that the pseudopotential contained no adjustable parameters and we have been very careful in evaluating its diagonal matrix elements. The agreement in positions provides a direct test of the correctness of our calculation of the inner potential. As far as the relative intensities are concerned, there are some differences between the theoretical and the experimental curves. The most pronounced disagreement is for the (00) beam for the (111) surface. We must not forget, however, that a purely elastic calculation for an ideal surface cannot be expected to reproduce quantitatively the results of experiments carried out on the real crystals. It suffices to mention that there are even disagreements between different experiments carried out on the same surface.[1]

IV. CONCLUSIONS

We have presented the results of an extensive LEED study from the various surfaces of Al using the band-structure-matching approach. We have seen explicitly the importance of multiple scattering in interpreting the LEED spectra. It was demonstrated that this method can be successfully used to explain more than qualitatively the nature of the observed spectra. Its advantages are a clear physical meaning and manageable volume of computer calculations. The effects of inelastic scattering may be included phenomenologically in much the same way as in the treatments of McRae, Kambe, and Marcus and Jepsen (see references given in Ref. 1). Its main disadvantage lies in the fact that in its present form it assumes that the penetration depth of an incident electron is large enough to see the three-dimensional band structure. But our pseudo-wave-functions are still a good set of functions with which to carry out the expansion. In addition, it is less suitable for the study of surface layers than, e.g., other methods based on the layer-by-layer calculations.

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Model Calculations in the Theory of Photoemission[*]

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Photoemission from several simple models describing the electronic structure of a solid in the presence of a surface is studied. Both nearly free-electron and tight-binding situations are treated, and the yield from the surface states of the latter can be calculated. For a reasonable choice of escape depth, the surface-state yield is roughly of the same magnitude as that from bulk states. With the abundance of different effects, the accent here is placed on understanding the physics involved in the photoemission process rather than on a detailed comparison with experiment. However, several approximate evaluation schemes are also presented and discussed.

I. INTRODUCTION

Photoemission from solids has long been a source of interesting physics,[1] but only recently has its potential as a probe of their electronic structure been pursued.[2-5] Experimental resolution has now improved to the point where rather detailed calculations are necessary for proper analysis of the data. In the last year, two formalisms have appeared which permit a general treatment of the problem.[6,7] One of them, the quadratic-response formalism, is presented along with its independent-particle reduction in Sec. II. The other, a scattering-theory formalism due to Mahan[7] is shown to be equivalent.

Our major purpose in this paper is to examine in detail some computationally simple models of electronic structure in solids and surfaces in order to develop an appreciation for the relevant physics involved in understanding photoemission. In some respects, the models may be too unrealistic for comparison with experiments, but they perform the valuable service of permitting us to identify many basic and important characteristics. We begin in Sec. III with the Sommerfeld model whose photoemissive properties were first properly an-