CALCULATED LOW-ENERGY ELECTRON-DIFFRACTION INTENSITIES FOR THE (001) SURFACE OF Al*

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The band-structure–matching formalism has been used to calculate the elastic intensities of (00), (01), (11), and (02) beams for normal incidence on the (001) surface of Al within an energy range between 0 and 10 Ry. The band structure was calculated using an orthogonalized plane-wave–based pseudopotential which contained no adjustable parameters. Symmetry was used to its fullest extent in expanding the crystal Bloch functions in order to obtain very accurate numerical results. Comparison with experiment shows good agreement with regard to the positions and relative intensities of the peaks.

In the last few years there have been several theories[1-10] explaining the origin of the intensity peaks in low-energy electron-diffraction (LEED) spectra. Calculations performed according to these theories all involved either a model potential or a number of parameters which had to be fitted to the experimental data.

In this Letter we would like to report the results of a realistic elastic calculation with no adjustable parameters, performed according to the band-structure–matching formalism disdussed in Ref. 3. Briefly, in this formulation, the intensity peaks in the LEED spectra are directly related to the forbidden energy gaps in the band structure. The intensities of various diffracted beams are obtained by matching the wave functions and their derivatives outside and inside the crystal at the surface; the wave function outside the crystal consists of an incident plus various diffracted beams, while the wave functions inside the crystal at any energy are a superposition of all Bloch waves (propagating and decaying ones) at that energy. Thus, we see that in order to calculate the LEED intensities we must first obtain the band structure for both the real and complex $\vec{k}$'s in the energy range of interest.

It is most convenient in matching to consider an expansion of the inside and outside wave functions in plane waves, although one could use a different type of expansion in an intermediate step; thus the accuracy of the calculation depends on the number of plane waves used, a fact which is particularly important in determining the Bloch functions inside the crystal. The accuracy is estimated from the degree of convergence of numerical results as the number of plane waves is increased.[11] The number of plane waves required for a highly accurate calculation was kept small by (a) using a pseudopotential to eliminate the oscillations of the wave functions in the core region which are important in the match, and (b) making sophisticated use of symmetry.[12]

We have calculated the band structure of Al along various symmetry directions using an orthogonalized plane-wave–based pseudopotential described by Harrison[13] with several modifications, the most important of which is a different treatment of the conduction-electron–core-electron exchange. We found it absolutely essential to keep the full nonlocality of the pseudopotential in all calculations although, of course, we could recover the structure near the Fermi energy with a local pseudopotential. We have calculated the band structure up to 10.5 Ry with this pseudopotential using 259 plane waves (53 symmetrized plane waves), or 45 beams. Our results at low energies (near the Fermi level) compare well with the previously published data. Since we were careful in calculating the diagonal term of the pseudopotential and kept it throughout all calculations, the energy of the lowest lying Γ_1 point correlates well with the known values of the Fermi energy and the work function; an additional advantage of this was that no inner potential corrections were required to compare our data with experiment. The accuracy of the band-structure calculation varies from 0.02 Ry for the lowest levels to 0.2 Ry for the energy states near 10 Ry. A detailed analysis of all of the points discussed in this paragraph as well as numerical results for the additional bands not shown in this paper is to be published.[11]

Using the results of real band-structure calculation we have also calculated the complex bands on the basis of an approach described elsewhere.[14] It is a modification of the $\vec{k}\cdot\vec{p}$ approach which is adaptable to include many nearly degenerate bands and which is more accurate and easier to use than methods previously discussed.

Having obtained the real and complex structure, we performed the matching to get the intensities

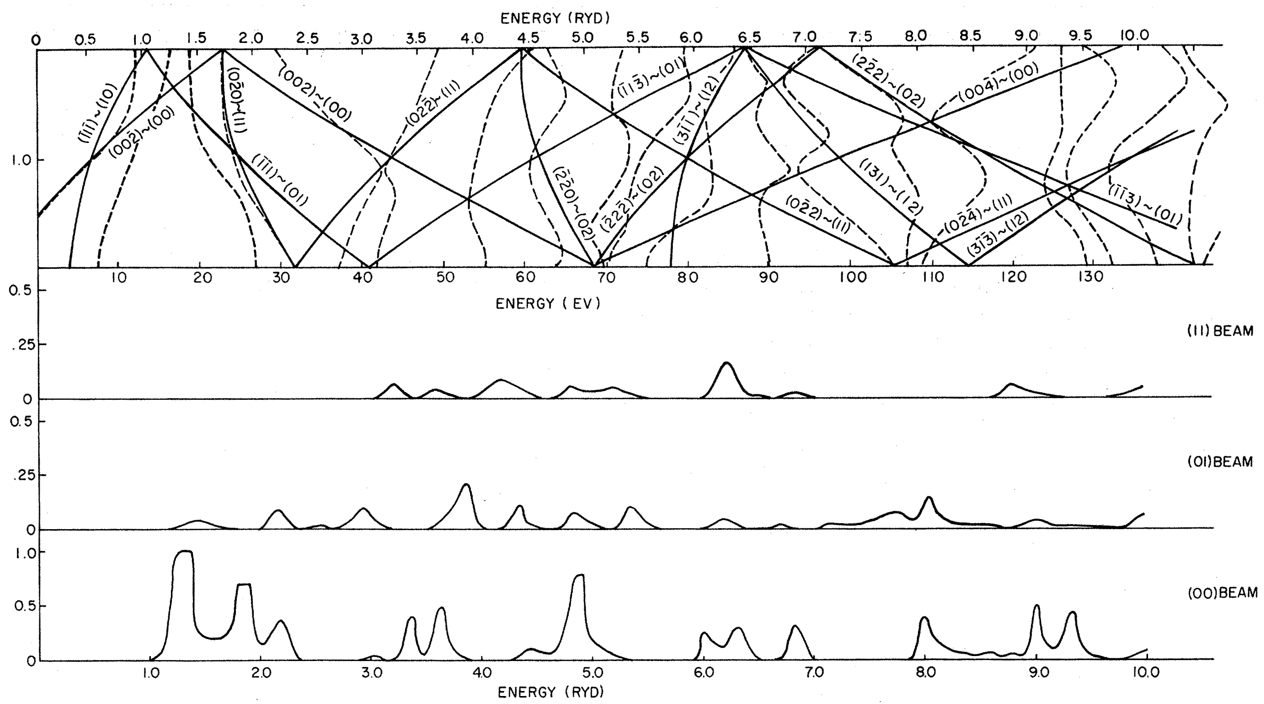

FIG. 1. Intensities of (00), (01), and (11) beams reflected from the (100) surface of Al. Upper diagram shows the electronic band structure along the Δ direction: solid lines, free-electron bands; dashed lines, calculated symmetric Δ_1 bands.

of the (00), (01), (11), and (02) beams. The corresponding results are given in Fig. 1, where we also show the band structure. Only the Δ_1 bands are shown for simplicity; the other bands in the Δ direction do not couple to a normally incident beam. It is apparent that the reflectivity curves are dominated by the secondaries whose magnitudes are sometimes comparable with the primary Bragg peaks, a result which indicates strong dynamical effects.

Proper identification of each peak is a rather complicated procedure due to the fact that multiple-scattering effects take place which strongly mix more than one plane wave in the expansion of the Bloch wave function; however, examination of the free-electron band structure in conjunction with the calculated band structure enables us to make the following identifications, which are useful in determining the physical origin of the various features and the correspondence of features in several beams. Consider the specularly reflected (00) beam. The first three peaks occur at 1.3, 1.82, and 2.2 Ry. From the band structure we see that the first peak is a primary Bragg peak; we expect unit reflectivity into this peak because (1) it corresponds to an absolute band gap, and (2) the energy at which it occurs is below the excitation energy threshold for any other beams in vacuum. It is interesting to note that the intensity of the beam does not become noticeable at 0.9 Ry where there is a band-edge feature; the reason is the nonsimple nature of the multibeam situation. In matching we find very strong coupling to the Bloch state corresponding to the second band whose current is directed into the crystal; the coupling with the second band begins to diminish at about 1.0 Ry and the reflected beam intensity grows. The peak at 1.82 Ry is connected to the surface resonance phenomena. It is seen particularly well here because all of the current must go into the (00) beam since the $(1\bar{1})$ beam cannot get out of the crystal due to a potential step. A small peak at 2.2 Ry is believed to be tertiary. In the free-electron language, at this energy, bands (01) and (11) intersect (thus causing a band gap when nonzero potential is switched on) and at the same time we have an exponentially decaying Bloch wave at that energy with a strong (00) character; consequently, we have a reflection into the (00) beam. Note that the normal component of $\vec{k}$ need not be conserved upon reflection as the above peak illustrates. Going toward higher energies we see a small peak at 3.0 Ry which again can be identified as a tertiary corresponding to the interaction of two (01) bands. The strong secondary peaks are present at 3.32 and 3.62 Ry and again their origin may be clearly related to the band structure. These two peaks may be identified as (11) and (01) secondaries, respectively. A small peak at 4.4 Ry cannot be unambiguously identified; presumably, it is due to the scattering into (11) and (01) beams as well as to the emergence of a new (02) band which satisfies the surface resonance condition. A strong primary Bragg peak is seen at about 4.85 Ry. At these energies it becomes increasingly difficult to assign the corresponding reflection indices because the band structure is rather complicated, many band gaps occur, and more Bloch waves enter into the wave function inside the solid. The above three secondaries might possibly be identified as (12), (11), and (12), respectively.

Similar analysis can be carried out for the nonspecular (01) beam. Although there may be a (01) beam excited inside the crystal at an energy as low as 0.7 Ry, total internal reflection by the surface step does not permit it to escape. There are no observable consequences of the surface-wave resonance here because there are no reflected beams at this energy (note the parabolic nature of the lowest band at resonance, indicating that the incident beam is simply transmitted). A small peak at about 1.4 Ry corresponds to the vacuum excitation threshold of the (01) beam. It occurs on the high-energy shoulder of the primary Bragg peak in the (00) beam. A peak at 2.1 Ry may be attributed to an interaction between the (01) and (11) bands, and thus it is a secondary peak. Two small peaks at 2.5 and 2.9 Ry are the secondaries corresponding to an interaction with (11) and (01) bands, respectively. A large peak seen at 3.85 Ry is undoubtedly a primary Bragg peak due to an interaction between (00) and (01) bands at 3.9 Ry in the free-electron picture. A corresponding secondary Bragg peak in the (00) beam may be seen at approximately the same energy. Three peaks at 4.3, 4.85, and 5.3 Ry are all secondaries. A rather strong peak at 8 Ry is a primary Bragg peak.

An analysis such as this, using nearly-free-electron labels to discuss LEED data, can lead to fruitful insights even when the actual band structure is not available; but it breaks down at the higher energies.

Finally, let us discuss the relationship between the theoretical and the experimental results. Figures 2 and 3 compare the experimentally obtained data for Al[15, 16] and our calculated results of Fig. 1, replotted here on a different scale. The most striking difference is the presence of

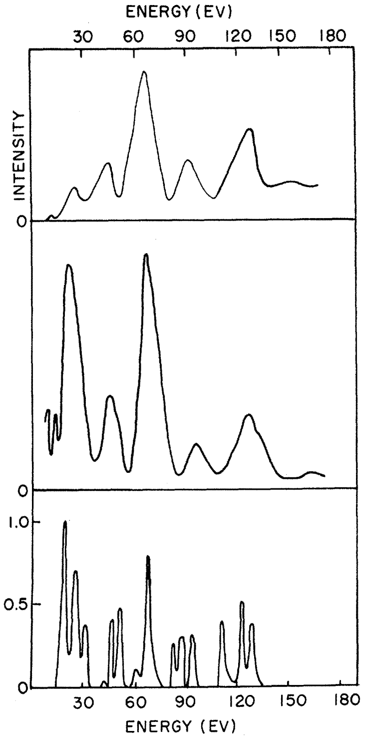

FIG. 2. Comparison between theoretical and experimental intensities for the (00) beam, Al(100). Upper curve (not normalized) from Ref. 16; middle curve (normalized) from Ref. 15; lower curve, calculated.

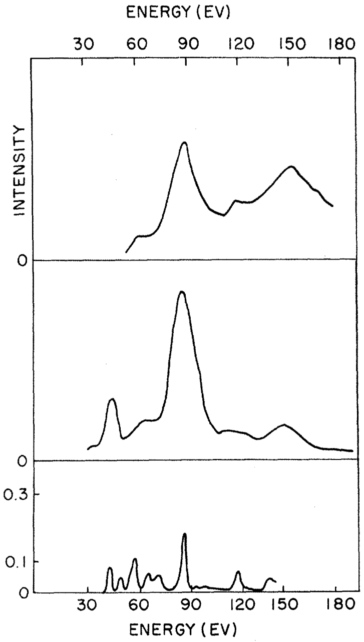

FIG. 3. Comparison between theoretical and experimental intensities for the (11) beam, Al(100). Upper curve (not normalized) from Ref. 16; middle curve (normalized) from Ref. 15; lower curve, calculated.

structure in the theoretical curve and narrow widths of the peaks. Experimentally, peaks which are 9-12 eV wide are observed, while the theoretical widths are at the most 2.5-3 eV. However if we note that experimentally one does not observe such fine splitting (either due to the experimental resolution or perhaps due to the fact that fine structure is lost when the inelastic scattering is taken into account), then we notice a great similarity between the positions of the experimental peaks and the groups of calculated peaks. As far as comparison of the intensities between the theoretical and experimental spectra is concerned, let us note that all experimental intensities are given in arbitrary units and thus the only meaningful experimental quantity is the relative height of the peaks in each beam. If we again identify the group of theoretical peaks with a single experimental peak, we find that the relative intensities are roughly in accordance with experimental results, the disagreement being sometimes perhaps as much as 10-20%. As for the absolute intensities, the disagreement between theory and experiment is quite strong. Theoretically, one obtains reflectivities between 100 and 10% in the (00) beam, while experimentally one sees only a small fraction (~10%) in the reflected intensities. This is a result of inelastic scattering which takes the current out of the incident beam. In fact it is apparent from Figs. 2 and 3 that if we try to include even the smallest amount of absorption, which increases the widths of the peaks and reduces the intensities, we can bring our results to even better agreement with experiment. At the present time we are planning to examine the effect of absorption (included in the phenomenological way) on the elastic intensities for (001) surface of Al, as well as calculate the spectra for other surfaces using the already obtained band-structure data.

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[1] E. G. McRae, J. Chem. Phys. 45, 3258 (1966).

[2] K. Hirabayashi and Y. Takeishi, Surface Sci. 4, 150 (1966).

[3] D. S. Boudreaux and V. Heine, Surface Sci. 8, 426 (1967).

[4] F. Hofmann and H. P. Smith, Jr., Phys. Rev. Lett. 19, 1472 (1967).

[5] P. M. Marcus and D. W. Jepsen, Phys. Rev. Lett. 20, 925 (1967).

[6] J. L. Beeby, J. Phys. C: Proc. Phys. Soc., London 2, 82 (1968).

[7] A. P. Shen and J. B. Krieger, Phys. Rev. B, 1, 2500 (1970).

[8] K. Kambe, Z. Naturforsch. A 22, 322, 422 (1967).

[9] Y. H. Ohtsuki, J. Phys. Soc. Jap. 24, 1116 (1968).

[10] C. B. Duke and C. W. Tucker, Jr., Surface Sci. 15, 23 (1969).

[11] V. Hoffstein and D. S. Boudreaux, Phys. Rev. B (to be published).

[12] V. Hoffstein and O. Moller, to be published.

[13] W. H. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

[14] V. Hoffstein and D. S. Boudreaux, to be published.

[15] F. Jona, IBM J. Res. Develop. 14, 444 (1970).

[16] H. H. Farrell and G. A. Somorjai, Phys. Rev. 182, 751 (1969).