tating frame of reference, the cross-effect terms in the rate equation for the polarization $p(x)$ of spin-$\frac{1}{2}$ nuclei, of the form $p(x)[1-P(x)P(x\pm\omega_I)]\pm[P(x)-P(x\pm\omega_I)]$, both became proportional to $p(x)-\tanh(\hbar\omega_I/2kT_S)$. This means that spin-$\frac{1}{2}$ nuclei tend to acquire a polarization just equal to that predicted by dynamic orientation of nuclei by cooling of electron interactions. This conclusion may be shown to be true for spin-1 nuclei as well; the cross effect thus reduces to an electron-interaction cooling effect. This explains why the corresponding curve on Fig. 1 is not very different from the unique spin-temperature prediction.

[15] Applying this model to other nuclei, one would predict, for example, a polarization of 26% for ^{13}C nuclei in perdeuterated 1-butanol doped with porphyrexide, at 0.5°K and 25 kG.

Accurate Calculation of the Low-Energy Electron-Diffraction Spectra of Al by the Layer–Korringa-Kohn-Rostoker Method

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Low-energy electron-diffraction spectra for three beams of Al {001} have been calculated from a complex static potential by a method of an accuracy comparable to modern band calculations. Despite the presence of strong attenuation, the spectra still show considerable structure which arises from the potential and which corresponds closely to experiment.

Several recent calculations[1-4] of low-energy electron-diffraction (LEED) spectra (i.e., the intensity of coherent elastically reflected electron flux from a crystal surface versus incident energy) for Al have given results which show encouraging agreement with the measured spectra. We find that a more precise calculation with a given potential provides a closer correspondence with experiment. Thus a more quantitative theory of LEED seems possible which links the scattering potential of the crystal to details of the spectrum. The present work will show the surprising extent to which this linking can be accomplished in Al with a static, complex, truncated bulk periodic scattering potential in the energy range 25 to 150 eV, despite the neglect of various surface and many-body effects.

In the work of Hoffstein and Boudreaux[1] (HB) who used the Fourier expansion (Bethe) method and a pseudopotential, the calculated spectra consist of groups of narrow lines which correspond suggestively to the broad measured lines out to 140 eV. However, detailed comparison of the HB theory with experiment is prevented by the restriction of the calculation to zero absorption and normal incidence of the electrons. In the work of Duke and Tucker,[2] by the inelastic-multiple-scattering method, it is shown that the main features of the spectrum can be obtained by simple selection of an s-wave–scattering phase shift and electron absorption.[3] However, the correspondence of theory and experiment is rough: The calculated secondary peaks are too small, and the calculated lines show little structure.[4]

In the present work, the spectra of a given complex static potential are calculated by a method of high accuracy (comparable to the accuracy achieved in band calculations). By means of a potential for Al whose real part is a self-consistent potential due to Snow[5] and whose imaginary part is taken from uniform-electron-gas theory,[6] this method is able to calculate the detailed structure of LEED peaks which show noteworthy correspondence with experiment. Not only do the spacings and widths of the peaks on three beams correspond closely, but structural details such as splittings, shoulders, and shapes appear to be significant. We note further the useful conclusion from comparison of the absorption-free (zero imaginary part) and full-absorption curves that the substantial experimental linewidths arise from the merging of whole clumps of elastic lines when absorption is introduced, and that the widths are rather greater than the broadening given by a simple (two-beam) theory of the effect of absorption.[7] The present calculations omit such complications as the effects of thermal motion, special surface layers and relaxed or otherwise disturbed surface transition layers, surface plasmons, etc., so that we can fix precisely the effects of the static potential. This potential by itself provides a model that gives significant structure in the spectrum and whose features must be known precisely before the contribution of additional complications of the model can be determined. The agreement with experiment is close enough to estimate and perhaps set limits on the influence of these complications.

The layer-Korringa-Kohn-Rostoker (KKR) method employed here arose out of necessary modifications of our previous work with the propagation- (P-) matrix method[8] which relied on a Fourier expansion of the wave field in x and y over the entire scattering volume (the z direction is normal to the surface). Such an expansion is not adequate in the core of the strong scattering potential of a realistic model for Al, although it was adequate for the weak-potential model to which it was previously applied. Thus the direct integration of a matrix differential equation through one period in z to find the propagation matrix P is not sufficiently accurate, and has been replaced by a procedure which finds the P matrix of a layer by multiple-scattering theory for a single layer; the procedure is the one developed by Kambe[9] from the KKR method in band theory, but extended here to include a uniform imaginary part to the potential. However, the solution of the matching problem between vacuum and crystal, and, in particular, the imposition of the outward radiation condition for Bloch waves at infinity in the semi-infinite solid, is carried out just as in the previous formulation[8, 10]; the essential point is the need to find the eigenvectors of the P matrix, in particular those eigenvectors which propagate or attenuate going into the solid. The Fourier expansion on x and y need be valid only on an interstitial plane between layers where it is a highly accurate representation. The combined treatment of the layer and boundary conditions is equivalent to that of Jennings and McRae,[11] but it is extended to include a uniform imaginary part in the potential, and the matrix transformations are treated somewhat differently.[10] The calculations on Al employed Snow's[5] self-consistent (Hartree-Fock-Slater) potential in the crystal in "muffin-tin" form (required by the present procedure), which fits Fermi-surface measurements rather well and has been employed by Connolly[12] in density-of-states calculations up to 50 V. A uniform imaginary part to the potential of $\beta = 0.3$ Ry was taken from the calculations of Lundqvist[6] on the uniform electron gas with three electrons per atomic volume (the variation with energy over the range 20 to 150 V is small); the imaginary part ends abruptly at the surface plane [halfway between adjacent (001) atomic layers]; the reference level of the real part of the potential between atomic spheres was taken at the vacuum level to reduce the artificially strong scattering at an abrupt change of potential at the surface; the spectrum was later shifted along the energy axis for best alignment with the measured spectrum.[13] There are no other parameters in the calculation to be adjusted. The convergence of

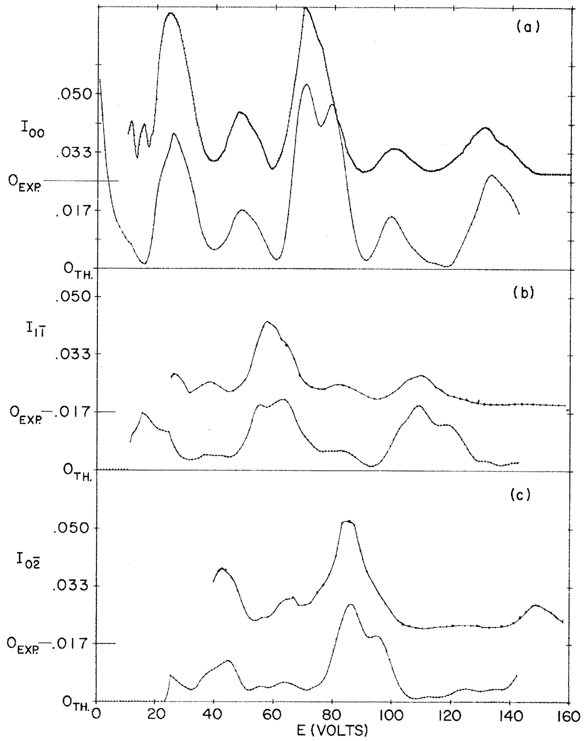

FIG. 1. Comparison between theoretical LEED spectra (lower curves in each box) and experimental spectra (upper curves) for Al {100} for three beams up to 150 V. (a) 00 (specular) beams, (b) $1\bar{1}$ beams, and (c) $0\bar{2}$ beams. In all cases, $\theta = 6°$, $\varphi = 45°$ (for identification of beams and definitions of parameters, see Ref. 14). The intensities of the three experimental curves are plotted on convenient arbitrary scales. The scales of diffracted beam intensities I_{00}, $I_{1\bar{1}}$, $I_{0\bar{2}}$ (relative to the incident intensity) of the three theoretical curves are given at the left. The theoretical spectra, calculated with zero real potential between atomic scatterers, but a constant imaginary potential of 0.3 Ry, are shifted by −7.5 V to align the peaks.

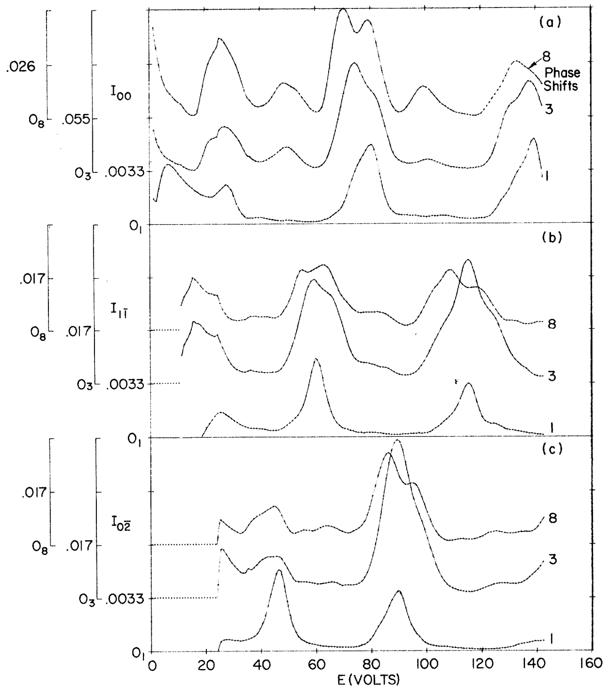

FIG. 2. Effect on the LEED spectra of Al {001} of using different numbers of phase shifts from the Snow potential for Al in the theoretical calculation. The three curves in each box were calculated with one, three, and eight phase shifts as indicated. (a) 00 beam, (b) $1\bar{1}$ beam, and (c) $0\bar{2}$ beam. For all spectra $\theta=6°$, $\varphi=45°$ (same as Fig. 1), and $\beta=0.3$ Ry. Note that 0_1, 0_3, 0_8 on the left refer to the origins of the three scales of intensities for the three curves in each box.

the calculation indicates an inaccuracy of at most 2%; attainment of this level of accuracy required up to 8 phase shifts and 29 Fourier components in x and y (i.e., 29 beams) at the higher energies. The band structure found without absorption agreed well with Connolly's results but differs in various details from HB[1] (who used a different potential).

The agreement obtained between theory and experiment[14] from 20 to 150 V is shown in Fig. 1 for three beams of Al {001} at $\theta=6°$, $\varphi=45°$. Note that in all three beams considerable corresponding structure appears in both the theoretical and experimental spectra. Thus the middle peak of the 00 beam between 60 and 90 V is clearly double, but the theoretical splitting is more pronounced.[15] However, more recent calculations which include the effects of thermal motion show a much reduced splitting. Similar remarks apply to the secondary peak at 50 V. Thermal motion effects also reduce the peak intensities at higher energies toward the somewhat lower experimental values (e.g., the Debye-Waller factors at $\varphi_D=428°$K for the peaks at 25, 70, and 130 V are 0.8, 0.5, and 0.3, respectively).

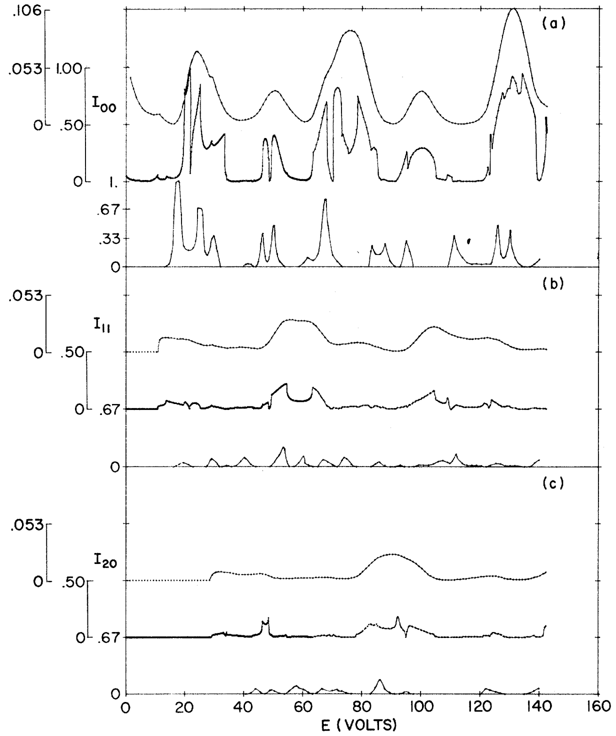

FIG. 3. Theoretical Al {001} LEED spectra with and without absorption. In each box, the top curve was calculated with $\beta=0.3$ Ry and eight phase shifts from the Snow potential; the middle curve was calculated with $\beta=0.0$ and the same phase shifts; the lower curve was obtained by HB with $\beta=0.0$ and their pseudopotential. For all spectra, $\theta=0°$. (a) 00 beam, (b) 11 beam, and (c) 20 beam. The top two curves are shifted −7.5 V as in Figs. 1 and 2. The same scale is used for the three beams of a given calculation.

In order to exhibit the dependence of features of the spectra upon the choice of the potential, similar calculations were performed using first only the $l=0$ phase shift and then the $l=0$, 1, 2 phase shifts of the Snow potential in the LEED calculation. Figure 2 shows that with only one phase shift the secondary peaks are too small and the overall scattering is weak but that with three phase shifts closer correspondence with experiment appears. The full complement of non-negligible phase shifts (i.e., eight phase shifts) gives a better fit than only three phase shifts (the secondary peaks grow), showing that the actual shape of the Snow potential is necessary to obtain the sort of agreement seen in Fig. 1. In fact, the phase shift δ_0 remains near $\frac{3}{2}\pi$, and δ_2 near $\frac{1}{2}\pi$, through most of the energy range while the other phase shifts are all relatively small, hence it is understandable that the spectrum in Fig. 2 calculated with three phase shifts gives a reasonable representation of the experiments; nevertheless, the combined effect of the other is not negligible.[16]

The calculated spectra at normal incidence are shown in Fig. 3 in order to exhibit the relationship between the spectra with attenuation (top curves in each box) and without attenuation (middle curves in each box) on the one hand, and the comparison with the HB spectra without attenuation (bottom curves in each box) on the other hand. Attenuation dramatically reduces and smooths the clumps of elastic lines leaving only a few broad observable features of structure, but does not alter the positions of the clumps. The two spectra without attenuation show a general but not a detailed correspondence. In particular, the HB peak in the 00 spectrum at 60-70 V is considerably narrower than its counterpart in our calculation (and narrower than the experimental peak at $\theta = 6^\circ$ in Fig. 1), and the peaks at 80-100 V and at 110-130 V are shifted to lower energies. Further study of the potential would be useful in deciding on the most satisfactory form for the energy range of interest, but the Snow potential appears to have a clear advantage. However, the Pendry-Capart potential[4] appears to give satisfactory widths and positions of 00-beam peaks.

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[15] The three large peaks of the 00 spectrum are readily identified as deriving from primary Bragg peaks by examining the band structure which shows they arise from intersections of the 00 band with the edges of the Brillouin zone (i.e., with itself). Similarly, the two smaller intermediate peaks are derived from secondary Bragg peaks and may be traced to intersections of the 00 band with other bands. The interpretation of energy diagrams in this way in terms of Bragg peaks is discussed at length in P. M. Marcus, F. P. Jona, and D. W. Jepsen, IBM J. Res. Develop. 13, 646 (1969).

[16] A further test that the LEED spectrum really shows features characteristic of the individual scattering potential is provided by theory and experiment for Cu which also agree well. Although Cu, like Al, is fcc with a lattice spacing only 11% smaller, the spectra are strikingly different from Al in shapes and positions of secondary peaks.