Measurement of Surface-Plasmon Dispersion in Aluminum by Inelastic Low-Energy Electron Diffraction*

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Analysis of the inelastic differential cross section for low-energy ($10 \lesssim E \lesssim 10^3$ eV) electron scattering from single-crystal solid surfaces permits the determination of the dispersion relation of the excitations created by the electron. With energies measured in eV and momenta parallel to the surface, $p_\parallel$, in Å^{-1}, the surface-plasmon dispersion for Al(111) is $\hbar\omega_s(p_\parallel) = 10.1 - 0.7p_\parallel + 10p_\parallel^2$ and its damping is $\Gamma_s(p_\parallel) = 0.9 + 0.7p_\parallel$.

Despite many years of measuring surface-plasmon losses by keV electron transmission,[1,2] optical techniques,[2,3] and low-energy-electron reflection,[4] only one quantitative measurement of surface-plasmon dispersion for values of momenta large relative to 10^{-3} Å^{-1} has been reported (for Mg).[5] In this Letter we provide such a measurement for Al(111) by applying a quantum field theory of electron-solid scattering[6-8] to analyze observations of inelastic low-energy-electron diffraction (ILEED). We find for our "best-fit" values

$$\hbar\omega_s(p_\parallel) = 10.1 - 0.7p_\parallel + 10p_\parallel^2 \tag{1}$$

$$\Gamma_s(p_\parallel) = 0.9 + 0.7p_\parallel; \quad p_\parallel \lesssim 1 \text{ Å}^{-1} \tag{2}$$

for the dispersion and damping, respectively, of the surface plasmons, when energies are measured in eV and momenta parallel to the surface ($p_\parallel$) in Å^{-1}.

The use of ILEED to measure these quantities is interesting both because it is the first application of the technique to achieve a quantitative characterization of the excitation spectrum of a solid, and because the technique probes this spectrum for much larger values of $p_\parallel$ ($p_\parallel \approx 1$ Å^{-1}) than optical methods.[2,3] In principle, ILEED is comparable to keV transmission measurements in the range of values of $p_\parallel$ sampled, although in this Letter we report a wider range than Kunz.[5] The results are of interest because they indicate that the coefficient of the linear term in the dispersion relation, Eq. (1), is an order of magnitude smaller and probably of the opposite sign than that predicted by microscopic theories of surface plasmons.[9-11]

Our analysis applies the quantum field theory developed by Duke and co-workers[6-8,12,13] to the ILEED data taken by Porteus and Faith.[14,15] The measurements were made on epitaxially grown Al films in a scanning ultrahigh-vacuum LEED spectrometer, whose unique features include 2° angular resolution, 10^{-15}-A current sensitivity, and semiautomated digital recording of data. Further details and experimental results in addition to those reproduced here have been reported elsewhere.[14,15] Here, we simply quote selected data. The dispersion and damping of surface and bulk plasmons are written (for $p, p_\parallel \lesssim 1$ Å^{-1}) as[9-11]

$$\hbar\omega_s(p_\parallel) = \hbar\omega_s + C_1 p_\parallel + C_2 p_\parallel^2, \tag{3}$$

$$\Gamma_s(p_\parallel) = \Gamma_s + D_1 p_\parallel + D_2 p_\parallel^2, \tag{4}$$

$$\hbar\omega_b(p) = \hbar\omega_b + Ap^2, \tag{5}$$

$$\Gamma_b(p) = \Gamma_b + B_1 p^2 + B_2 p^4. \tag{6}$$

The subscripts s and b refer to surface and bulk plasmons, respectively. The various coefficients are the parameters to be obtained for the data analysis.

The parameters describing the bulk-plasmon dispersion and damping are, insofar as possible, taken from keV-electron-transmission data.[16,17] We use $A = 3.048$ eV Å^2, $\Gamma_b = 0.53$ eV, $B_1 = 0.103$ eV Å^2, and $B_2 = 1.052$ eV Å^4. However, the ILEED data require the use of $\hbar\omega_b = 14.2 \pm 0.2$ eV in contrast to the value of 15 eV usually quoted from keV transmission data.[1,2,16,18] Although the origin of this discrepancy is not known, we note that Kunz[19] has reported 14-eV thresholds for certain thin films in his transmission experiments. Our assignment of $\hbar\omega_b \cong 14$ eV is clearly required by the ILEED data on both Al(111)[14,15] and Al(100).[20]

Beck's random-phase approximation (RPA)

calculations[10] predict $C_1 \cong 4$ eV Å, $C_2 \cong 3$ eV Å^2, $\Gamma_s = 0$, $D_1 = 0.1$ eV Å, and $D_2 \cong 0.1$ eV Å^2 for a background charge density comparable to that of aluminum. These values are typical of those predicted by other microscopic models.[9-11] A detailed analysis of ILEED data on both Al(111) and Al(100) using these parameters may be found elsewhere.[8]

Our model is an extension of that proposed by Duke and Laramore for two-step diffraction.[6,7] The incident electron's scattering from the solid is described as a "two-step" process in which elastic diffraction is followed by an energy-loss process or vice versa. The elastic diffraction is described by the Born approximation to the s-wave inelastic-collision model.[21,22] Details of the calculation are given elsewhere.[6-8]

We next specify our procedure for analyzing the data. The inelastic-scattering cross sections are functions of six independent variables: the energy, polar angle, and azimuthal angle of both the incident (E, θ, ψ) and scattered (E', θ', ψ') beams. For a variety of reasons[10,11] we analyze the "angular" (vary θ', all other variables fixed) and "loss" (vary $w \equiv E - E'$, all other variables fixed) profiles of the specular beam ($\theta' = \theta$, $\psi' = \psi$ for elastic scattering, $w = 0$). We examine the data at the energy ($E = 51 \pm 1$ eV in our case[8,14,15]) of a primary Bragg peak, in the profile of elastic intensity versus incident energy.

Having selected the parameters of the incident electron beam, we analyze the angular profiles (for fixed w) to estimate C_2. The results of a typical analysis are illustrated in Fig. 1. The $w = 14.4$ eV angular profile is most influential in determining C_2. Once a value of C_2 has been chosen, the next step is the calculation of loss profiles, for various θ', as functions of $\hbar\omega_s$, C_1, and Γ_s. These calculations are repeated until the "best-fit" loss profile as well as the probable uncertainties in $\hbar\omega_s$, C_1, and Γ_s are determined. Our final results for two different dispersion relations are shown in Fig. 2. This analysis gives us the best values of the parameters $\hbar\omega_s$, C_1, Γ_s consistent with a particular C_2. This procedure is repeated for a grid of values of C_2 to obtain bounds on its values which provide a satisfactory description of the $w = 12.4$ and 14.4 eV angular profiles. The final selection of C_2 is made on the basis of a comparison of the angles of predicted and observed maxima in the angular profiles.

An intrinsic limitation on the above procedure is its lack of sensitivity to the behavior of the

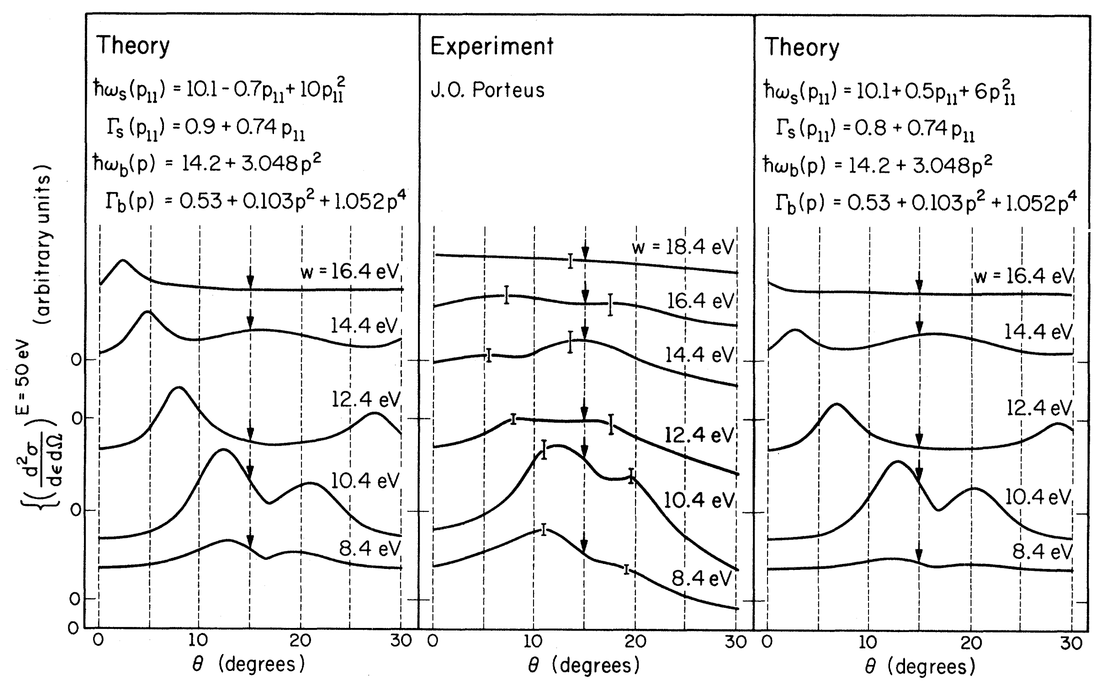
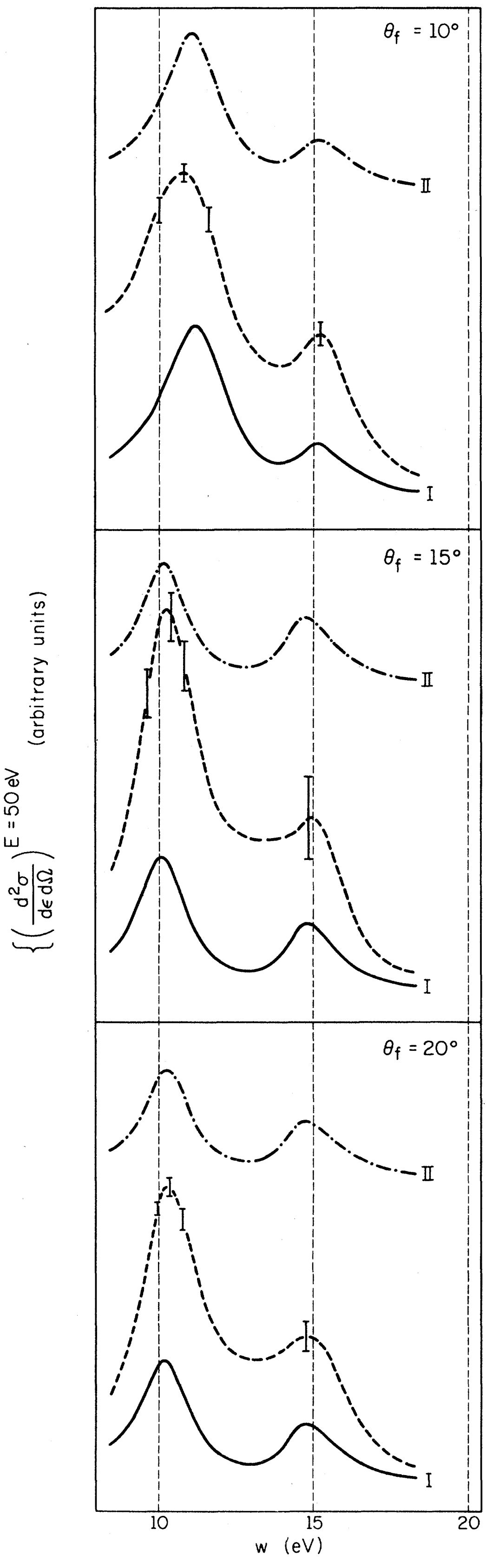


FIG. 1. Theoretical and experimental (Ref. 15) angular profiles for electrons incident on Al(111) with a primary energy E of 50 eV and diffracted inelastically in the (00) direction for a number of loss energies, w. Arrows indicate the direction of specular reflection ($\theta_i = 15°$) and bars the experimental uncertainty. Two sets of theoretical curves are given. Their dispersion relations are noted in the figure. Elastic electron–ion-core scattering is described by the s-wave inelastic-collision model with $\lambda_{ee} = 6$ Å, $V_0 = 14.7$ eV, and $\delta = \pi/4$.



surface-plasmon dispersion relation for $p_{\parallel} \lesssim 0.2$ Å^{-1}. In the present case, the consequences of the most serious ambiguity resulting from this fact are displayed in Figs. 1 and 2. If, in accordance with most theoretical expectations, we constrain $C_1 > 0$, then we obtain the alternative "best-fit" dispersion relation

$$\hbar\omega_s(p_{\parallel}) = 10.1 + 0.5p_{\parallel} + 6p_{\parallel}^2 \tag{7}$$

$$\Gamma_s(p_{\parallel}) = 0.8 + 0.74p_{\parallel}. \tag{8}$$

The difficulty with this dispersion relation is the too rapid movement of the surface-plasmon peak in the angular profile with increasing loss energy w, which is caused by the small value of C_2. The relative merits of the two dispersion relations (1) and (7) may be assessed from Figs. 1 and 2. We think that (1) is clearly preferable.

Finally, using the above procedure we have tried to assess the uncertainty in the values of the various parameters we derive from ILEED data. The coefficient of the quadratic term, C_2, is accurate to about 20%. For the other surface-plasmon parameters, we believe the following ranges to be representative: $\hbar\omega_s = 10.1 \pm 0.1$ eV, $C_1 = 0.7 \pm 0.3$ eV Å, and $\Gamma_s = 0.7 \pm 0.3$ eV. We also mention that the surface-plasmon dispersion relation and damping given by Eqs. (1) and (2) describes reasonably well within our theory other recent ILEED measurements[20] for nonspecular beams performed on Al(100).

Summarizing, we feel that the above considerations indicate clearly that ILEED can be used as a quantitative probe of the excitation spectra of solids. By analyzing ILEED data we have extracted the surface-plasmon dispersion and damping for Al(111) and thereby have demonstrated a substantial discrepancy between the experimental value of C_1 and those predicted by microscopic models.[9-11] We find that $|C_1| \sim 0.5$, and C_1 probably is negative. This conclusion is consistent with the measurements of Kunz[5] on Mg. His results have been rationalized by Bennett[23] on the basis of an empirical hydrodynamic model de-

FIG. 2. A comparison of the experimental (dashed lines) and two sets of theoretical (marked I and II) loss profiles for the (00) beam of electrons on Al(111). The primary beam energy is 50 eV, the angle of incidence 15°, and the exit angles noted by θ_f. The parameters used to describe the elastic scattering are given in the caption to Fig. 1. As in Fig. 1, curve I refers to the plasmon-dispersion relation $\hbar\omega_s(p_{\parallel}) = 10.1 - 0.74p_{\parallel} + 10p_{\parallel}^2$, $\Gamma_s(p_{\parallel}) = 0.9 + 0.7p_{\parallel}$, whereas curve II refers to $\hbar\omega_s(p_{\parallel}) = 10.1 + 0.5p_{\parallel} + 6p_{\parallel}^2$, $\Gamma_s(p_{\parallel}) = 0.8 + 0.74p_{\parallel}$.

scribing a surface with a variable thickness of the electron density.[24] We feel, therefore, that the results of our analysis together with the observations of Kunz indicate a serious systematic deficiency in existing microscopic models of surface-plasmon dispersion which predict $C_1 \cong 5 > 0$ and $\Gamma_s \equiv 0$ for electron fluids of density comparable to that of aluminum. Both measurements of C_1 are consistent with Bennett's model calculation provided a suitable electron-density profile is used in the model.

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Calorimetric Evidence for a Singlet Ground State in *Cu*Cr and *Cu*Fe†

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Heat-capacity measurements show that the entropy reduction associated with the formation of the spin-compensated state in *Cu*Cr is $R\ln(2S+1)$. The magnetic field dependence of the heat capacity of *Cu*Fe suggests that at $T \ll T_K$ the susceptibility has the form $\chi = \chi_0 \times [1 - 15(T/T_K)^2]$, which is consistent with the third law of thermodynamics.

The ground state of a single magnetic impurity in a metal continues to be an unsolved problem in spite of the attention it has received. Different theories give different physical pictures for the ground state and make different predictions for the 0-K entropy and the temperature dependences of physical properties at $T \ll T_K$, where T_K is the Kondo temperature.[1] Heat capacity measurements on both *Cu*Fe and *Cu*Cr have been interpreted as showing that ΔS, the entropy reduction associated with the formation of the spin-compensated state, is less than $R\ln(2S+1)$.[2,3] In the same systems, the temperature dependence of the magnetic susceptibility[2-5] χ, if extrapolated to $T=0$, does not satisfy the requirement of the third law of thermodynamics that $[\partial\chi/\partial T]_{T=0} = 0$. This also implies that the spin degeneracy is not completely removed at $T=0$. We report here new heat-capacity measurements on *Cu*Cr and an extension of earlier measurements[6] on *Cu*Fe to higher temperatures. In the single-impurity limit the new data show that the heat-capacity anomalies are broader than had been indicated by earlier measurements. The *Cu*Cr