on the manuscript. The samples were furnished by E. Buehler.

[1]A. Menth, E. Buehler, and T. H. Geballe, Phys. Rev. Letters 22, 295 (1969).

[2]L. M. Falicov and J. C. Kimball, Phys. Rev. Letters 22, 997 (1969).

[3]J. C. Nickerson and R. M. White, to be published.

[4]E. E. Vainshtein, S. M. Blokhim, and Yu. B. Paderno, Fiz. Tverd. Tela 6, 2909 (1964) [Soviet Phys. Solid State 6, 2318 (1965)].

[5]J. H. Van Vleck, Theory of Electric and Magnetic Susceptibilities (Oxford Univ., New York, 1959).

[6]SmB_6 has a cubic CsCl structure centered on octahedra of six boron atoms. Each Sm ion is surrounded by eight of these octahedra.

[7]J. A. White and J. H. Van Vleck, Phys. Rev. Letters 6, 412 (1961).

[8]The systematics of free-ion energy levels show that the $4f^5 6s$ configuration lies 1 eV below the $4f^5 5d$ state. In the crystal the greater overlap of the 6s wave function with the ligand charge distribution should remove most of this difference. A realistic detailed model should include hybridization of the $5d^x 6s^y$ wave function with that of the electrons on the boron ions; i.e., $x+y \neq 1$.

[9]For example, in the approximation of strong L-S coupling within the $4f$ shell, moderate exchange between the 6s and $4f$ electrons, and weak crystal field, the ground state of $4f^5 6s$ would be $J=2$, which has a nonmagnetic Γ_3 state in the cubic crystal field.

MANY-BODY EFFECTS IN PHOTOEMISSION*

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A many-body formalism utilizing a tunneling operator is proposed for the photoemission process, thereby avoiding the artificial separation of the process into distinct steps. The lowest-order term in the formalism, corresponding to surface scattering, is developed in detail for simple metals. Energy-distribution curves from this "surface term" are presented for both free and interacting electrons. Many-body effects, including plasmarons, are prominent in the latter and have tentative experimental support.

The standard model of photoemission represents the emission process as a sequence of three steps wherein the electrons are first optically excited, then proceed to the surface, possibly scattering en route, and finally escape over a surface barrier.[1] While the model has greatly facilitated interpretation of data it is, nontheless, phenomenological and does not include the possibility of many-body interactions. Several authors[2-4] have discussed the importance of such interactions in the first step, the optical excitation, although they have not departed essentially from the three-step viewpoint. In contrast, the model below incorporates many-body interaction throughout the photoemission process, inseparably intertwining the three steps. It is, I believe, the first model to treat the whole photoemission process from a unified, many-body viewpoint with results for interacting electrons.[5] In this Letter the lowest-order term in the formalism, corresponding to a surface-aided process, is developed.

Volume processes rather than surface processes are generally considered to be most significant for photoemission in metals.[3,6,7] However, it has become clear that the emitted-electron energy-distribution curves (EDC's) are very sensitive to the condition of the surface and, furthermore, that electrons emitted when the incident-photon energy is on the order of or greater than the (volume) plasmon energy ω_p originate from a very shallow mean depth, estimated to be less than 20 Å in alkali metals[7,8] and nickel.[9] It thus becomes interesting to investigate the lowest-order, surface term in the model.

The basic Ansatz in the model is that the escape of an electron from the metal into the vacuum can be mathematically represented by a tunneling operator, or transfer Hamiltonian, much as is done in superconductor and semiconductor tunneling.[10] Specifically, let H_m be the (exact) Hamiltonian of a metal of infinite extent, and H_v the Hamiltonian for free particles in a vacuum of infinite extent. The respective eigenstates occupy separate Hilbert spaces. The emission of an electron from the metal is represented as a perturbation on $H_0 \equiv H_m + H_v +$ (electromagnetic interaction with incident light) in the form

$$H = H_0 + T,$$

$$T = \sum_{k,k'} T(\vec{k}, \vec{k}') a_{k'} b_k^{\dagger} + \text{H.c.}, \qquad (1)$$

where a_k and b_k annihilate one-electron, plane-wave states of momentum $\vec{k}$ in the metal and in the vacuum, respectively. T may be viewed as a surface scattering due to overlap between the wave functions for electrons inside and outside the metal. No further Ansätze, aside from simplifying approximations, are needed in order to calculate EDC's. Physically, the approximation of using T and a metal of infinite extent neglects modifications to the photoemission which are due to the changes in the single-particle spectrum introduced by the existence of a surface. These changes include a possible peak from surface-plasmon interaction which will be discussed below, and local variations in the spectrum in the immediate vicinity of the surface; these variations should have negligible effect when the mean depth of origin of the emitted electrons is $\gtrsim 2$-5 Å, and can be considered in any case to have been largely included by appropriate modification of the matrix elements of T.

For simple metals, H_m may be approximated as the Hamiltonian of a homogeneous, interacting electron gas, H_{el}, perturbed by a static disorder potential, $U=\sum_q U(q)\rho_q{}^\dagger$, representing the effects of the crystal lattice (bands, phonons, lattice defects) and of impurities. The electromagnetic interaction with the incident beam is

$$A = e^{-i\omega t}\sum_k \{\vec{A}_{int}\cdot\vec{k}a_k{}^\dagger a_{k+q} + \vec{A}_{ext}\cdot\vec{k}b_k{}^\dagger b_{k+q}\}$$

$$\approx e^{-i\omega t}\{\vec{A}_{int}\cdot\vec{P}_{int} + \vec{A}_{ext}\cdot\vec{P}_{ext}\}. \quad (2)$$

ω and q are the photon frequency and momentum ($\hbar=1$), A_{int} (A_{ext}) is the vector amplitude of the electromagnetic A field inside (outside) the metal, and P_{int} (P_{ext}) is the total momentum inside (outside) the metal. Because of smallness of q/k_F, we put $q\approx 0$ and get the second expression above.

To compute the electron emission, it is convenient to work in the interaction representation, taking $H_{el}+H_\nu$ as the unperturbed Hamiltonian and $U+A+T$ as the perturbation. When the evolution operator is expanded in the standard way[11] in the perturbation, the lowest order nonzero contribution to the emission rate is second order in A and T, and does not depend on U. The only nonzero time ordering is that in which the action of A follows that of T; the reverse ordering gives a zero contribution, because a homogeneous system cannot undergo optical excitation without an intermediary interaction to supply momentum.[12] (Recall that A is proportional to the total-momentum operator, and the ground state of a homogeneous system is an eigenvector of the total momentum with eigenvalue zero.) Here, the surface serves as the intermediary, scattering an electron into a virtual state outside the metal, with photon absorption following. For this reason, the lowest-order contribution may be thought of as a "surface term." Its importance relative to "bulk" terms (those which do depend on U, so that U can serve as the intermediary, as in direct transitions, for example) increases as the average depth of origin of the emitted electrons decreases.[13]

The energy distribution of electrons is obtained from the emission rate by multiplying the latter by the density of states for the emitted particle. A straightforward calculation yields the following expression for the surface-term energy distribution:

$$I(\vec{k},\omega) = \text{const}\,|\vec{k}|\textstyle\sum_{k'}|T(\vec{k},\vec{k}')|^2[\vec{A}_{ext}\cdot\vec{k}-\vec{A}_{int}\cdot\vec{k}']^2$$
$$\times (1/\omega^2)\Lambda(\vec{k}', E_{kin}-\omega+\varphi), \quad (3)$$

where $E_{kin}=k^2/2m$. The work function is denoted by φ, and Λ is the negative-frequency part of the spectral density of the electron gas (proportional to the imaginary part of the one-particle Green's function). The formula is transparent, for it simply states that the emission is proportional to the square of each of the acting perturbations, the square of the intermediate-energy denominator, and the density of states of the electron gas at its residual energy and momentum.

In order to evaluate the above expression, an appropriate form for $T(\vec{k},\vec{k}')$ must be chosen. Two possible limiting forms, corresponding to uniform specular and uniform diffuse transmission, respectively, are

$$T(\vec{k},\vec{k}') = \text{const}\times\delta(\vec{k}_\parallel-\vec{k}_\parallel'), \quad (4)$$

and

$$T(\vec{k},\vec{k}') = \text{const}. \quad (5)$$

($\vec{k}_\parallel$ is the component of $\vec{k}$ lying in the plane of the surface, similarly for $\vec{k}_\parallel'$.) Specular transmission is usually assumed.[3] However, the measurements are generally performed on samples prepared by evaporation onto a polished-copper substrate. The rms surface roughness of such evaporated films is most probably greater than 30 Å; the reflection of electrons at the surface is expected to be diffuse (specularity parameter $p\approx 0$).[14] Transmission, therefore, may very well be closer to diffuse than to specular. I have consequently used the diffuse limit, Eq. (5), in numerical computations.

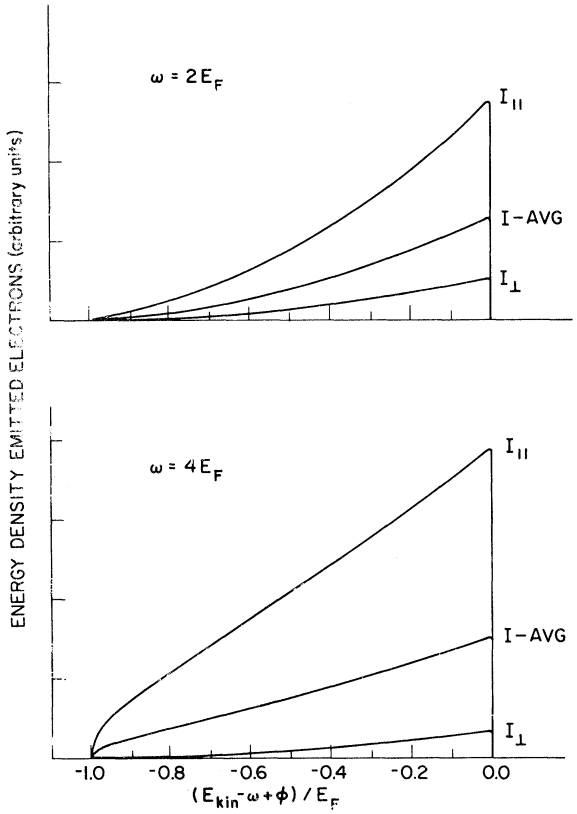

FIG. 1. EDC's, referred to initial electron energy, calculated from Eq. (3) for a free-electron gas at photon energies 2 and 4 times the Fermi energy. E_F = Fermi energy, $I_\parallel$ and $I_\perp$ are the EDC's for electrons emitted parallel and perpendicular to the photon A vector, respectively, and I-AVG is the appropriate hemispherically averaged EDC.

Equation (3) has been evaluated for light at normal incidence for the cases of free and interacting electrons. For free electrons,

$$\Lambda(k,\omega+\varphi) \propto \delta(\omega - k^2/2m). \quad (6)$$

Typical EDC's are shown in Fig. 1 for electrons emitted parallel to and perpendicular to the photon A vector.[15] The width of a free-electron EDC can be no wider than the conduction band of the metal, as there is no method for the electrons to lose energy.

The general expression for Λ is[11]

$$\Lambda(k,\omega+\varphi) \propto \mathrm{Im}[\omega - (k^2/2m) - M(k,\omega)]^{-1}, \quad (7)$$

where M is the mass, or proper-self-energy operator. EDC's for interacting electrons were evaluated by using the Hubbard modification of the random phase approximation (RPA) dielectric function[16] in the RPA expression for the mass operator.[17] Typical results[18] are presented in

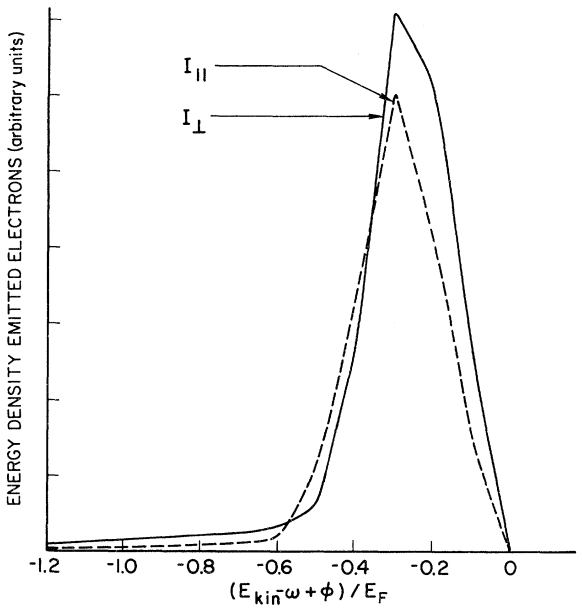

FIG. 2. EDC's calculated from Eq. (3) for an interacting-electron gas at a photon energy $\omega = 2E_F$. Notation is the same as in Fig. 1. Vertical scales for $I_\parallel$ and $I_\perp$ are different.

Figs. 2 and 3. The parameters used were those appropriate to sodium.

At low photon energies (Fig. 2) the emitted electrons are all concentrated in a primary peak near the maximum energy. Scattered electrons are absent. But the shape of the peak is qualitatively different from that obtained in the free-electron case (Fig. 1): It resembles an isosceles triangle (i.e., maximum emission does not occur

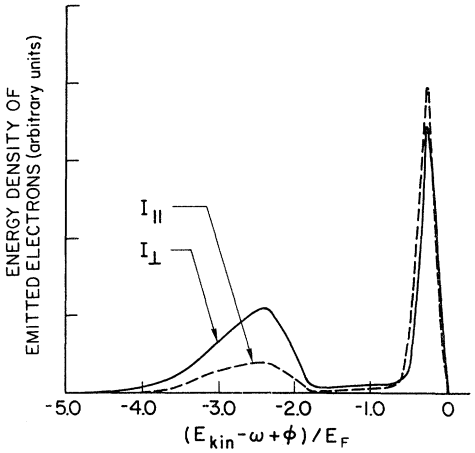

FIG. 3. EDC's calculated from Eq. (3) for an interacting-electron gas at a photon energy $\omega = 7E_F$. Notation is the same as in Fig. 1. Vertical scales for $I_\parallel$ and $I_\perp$ are different.

at the maximum energy); further, it has only $\sim\frac{1}{2}$ the width of the conduction band and is displaced toward the high-energy edge, as if the electrons near the bottom of the conduction band contributed negligibly. The isosceles shape and the narrowing of the peak are both due to the k'^2 weighting that multiplies Λ in Eq. (3) and to the modification of the free-electron dispersion relation. Both the shape and the narrowing have been observed in the alkali metals.[19] (Hopfield[2] and Smith[8] have also suggested explanations for the narrowing.)

At higher photon energies (Fig. 3) a broad peak of low-energy electrons is seen. It arises from the "plasmaron" structure in the spectral density,[8] which is due to the coherent motion of a hole and a plasma oscillation. The peak moves upward linearly with photon energy, has a (constant) width ~4 times that of the conduction-band peak, and is displaced from the latter by $\sim 1.2\omega_p$. (The leading edges of the two peaks are displaced by ω_p, but the plasmaron dispersion causes the maxima to be somewhat further apart.) The ratio of the area under the plasmaron peak to the area under the conduction-band peak increases with increasing photon energy, corresponding to the experimentally well-known fact that the proportion of scattered electrons increases with frequency. However, this peak is not due to scattered electrons, but is a true many-body effect that does not arise in a single-particle theory; it is quite similar to the polaron structure predicted theoretically and seen experimentally in metal-semiconductor tunneling.[20] The shoulder reported by Callcott and MacRae[21] at 2.8 eV below the leading edge in EDC's of Ni covered with >3 monolayers of Cs lends support to the calculations presented here.

It is of interest to note that recently, plasmaronlike structure in the spectral density of a degenerate semiconductor has been seen both at the volume-plasmon energy[22] and at the surface-plasmon energy[23] in tunneling experiments. One is thereby tempted to postulate a "surface plasmaron" peak in the spectral density of an electron gas with a boundary. The EDC's from such a peak would presumably resemble the broad peak in Fig. 3, but the leading edge would be separated from the leading edge of the high-energy peak by ω_s, the surface plasmon energy. The postulate has physical interest, because the photoemission data on the alkali metals show just such a broad secondary peak displaced by ω_s from the leading peak.[19] (A peak displaced by ω_p was not seen.)

In the photoemission data, not only the leading edges are separated by ω_s but the maxima also are separated by ω_s, rather than $\sim 1.2\omega_s$. Similarly, the plasmaron peaks in the tunneling experiments (Refs. 22, 23) occur at biases equal to the plasmon energies, contrary to the theoretical prediction, at least for the volume-plasmon case, of a somewhat larger separation. It has been suggested that the shift may be due to nonzero plasmon damping (reducing the effective critical wave vector, thus the dispersion) and to small electron mean free paths.[22] The same explanations, if correct, would also apply to the photoemission data; however, it is questionable whether damping mechanisms would shift the structure all the way from $\sim 1.8\omega_p$ to ω_p in the tunneling experiment. A possible alternative explanation is that an improved calculation of the spectral density would show the plasmaron peak shifted by exactly ω_p from the quasihole peak, rather than by a somewhat greater amount.[24]

I would like to express my gratitude to Professor J. J. Hopfield, under whose supervision this work was carried out, for his constant guidance and interest. I also wish to thank W. E. Spicer and N. V. Smith for many helpful discussions and B. Lundqvist for making his results available in tabular form.

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[1]C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1030, A1044 (1964).

[2]J. J. Hopfield, Phys. Rev. 139, A419 (1965).

[3]R. K. Nesbet and P. M. Grant, Phys. Rev. Letters 19, 222 (1967).

[4]B. I. Lundqvist, Physik Kondensierten Materie 7, 117 (1968), and references therein.

[5]EDC's for noninteracting electrons have been calculated from a many-body formalism by N. W. Ashcroft and W. L. Schaich, in Material Research Symposium on Electronic Density of States, Washington, D. C., November 1969 (unpublished).

[6]A. Meessen, Phys. Status Solidi 26, 125 (1968).

[7]F. J. Piepenbring, in Optical Properties and Electronic Structure of Metals and Alloys, edited by F. Abelés (North-Holland, Amsterdam, 1966), p. 316.

[8]N. V. Smith and W. E. Spicer, Phys. Rev. 188, 593 (1969).

[9]D. E. Eastman, J. Appl. Phys. 40, 1387 (1969).

[10]C. B. Duke, Tunneling in Solids (Academic, New York, 1969).

[11]See, e.g., D. A. Khirznits, Field Theoretical Me-

thods in Many-Body Systems, translated by A. J. Meadows (Pergamon, New York, 1967).

[12]Although this is no longer strictly true when the photon momentum is nonzero, any optical excitation arising from the direct absorption of photons is expected to be negligible.

[13]The next nonzero set of terms is second order in A, T, and U, and comprises a "volume" contribution to the photoemission. The formalism for this set of terms will be described elsewhere. There is no interference between the surface and volume terms.

[14]H. E. Bennett, private communication.

[15]Directionality effects in the EDC's here and in the interacting-electron gas should not be taken seriously, first because all bulk processes are being neglected, second, because the effects are very sensitive to the detailed form of $T(\vec{k},\vec{k}')$.

[16]J. Hubbard, Proc. Roy. Soc. (London), Ser. A 243, 336 (1957).

[17]J. J. Quinn and R. A. Ferrell, Phys. Rev. 112, 812 (1958). The approximation $M(k,\omega)=M_{\mathrm{RPA}}(k,\omega+E_F+\varphi)$ was used (cf. Ref. 8).

[18]No further approximations, other than a finite grid size, were made. The computation requires about 30 min on an IBM 360/91 computer.

[19]N. V. Smith and W. E. Spicer, Phys. Rev. Letters 23, 769 (1969).

[20]Duke, Ref. 10, p. 255 ff.

[21]T. A. Callcott and A. U. MacRae, Phys. Rev. 178, 966 (1969).

[22]C. B. Duke, M. J. Rice, and F. Steinrisser, Phys. Rev. 181, 733 (1969).

[23]D. C. Tsui, Phys. Rev. Letters 22, 293 (1969).

[24]I would like to thank J. W. Wilkins for this comment, a calculation for which has been performed by D. C. Langreth for the case of a flat band.

ANGULAR DEPENDENCE OF SURFACE SCATTERING*

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Calculations of the rf surface impedance of a thin metal plate as a function of a dc magnetic field applied parallel to the faces of the plate reveal that one can measure experimentally the critical angle of collision with the surface, if such an angle exists, below (above) which electron surface scattering is mostly specular (diffuse).

The influence of surface scattering on the response of thin metal plates to external fields has been described by a phenomenological model, first proposed by Fuchs in the study of the static conductivity of thin films,[1] in which a single specularity parameter p is supposed to describe the surface-scattering mechanism. In this model, p is the probability that an electron will be specularly scattered at the surface (the component of the velocity normal to the surface changing sign upon reflection), while $1-p$ is the probability for diffuse scattering. Diffuse scattering means that for any given angle of incidence the angle of reflection is random so that the drift velocity of the electron after collision with the surface is zero on the average and the subsequent contribution of that electron to the conductivity vanishes.

It is desirable to generalize the Fuchs specularity parameter into a specularity function[2,3] $S(\theta)$ which will depend on θ, the angle of collision with the surface (see Fig. 1), for the following reason. Even if the surface is rough on the atomic scale only, electrons with large angles of collision will be expected to be diffusely scattered as their wavelength normal to the surface is comparable with the scale of roughness. On the other hand, electrons with small angles of collision have wavelengths normal to the surface which can be much larger than the scale of surface roughness. These "grazing incidence" electrons are expected not to "see" the details of the surface and thus have a high probability of being specularly reflected.[4] On the basis of these arguments we have extended the path-integral solution of the Boltzmann equation[5] to include specularity functions $S(\theta)$ which will be nearly equal to unity (zero) below (above) a critical angle θ_0. The correct functional form of $S(\theta)$, if indeed this phenomenological description of surface scattering is at all valid, will have to be settled by experiment in the absence of a detailed microscopic theory of surface scattering.

In this Letter we propose the following simple experiment by which one can probe the angular dependence of surface scattering. An rf coil wrapped around a metal plate of thickness d sets up (antisymmetrically) surface-current layers, $\vec{j}=j(z)e^{-i\omega t}\hat{y}$, of effective thickness δ just inside the two plate surfaces which are normal to the z axis.[6] An external dc magnetic field is applied in the plane of the plate and in the transverse direction with respect to the rf current, $\vec{H}=H\hat{x}$. This magnetic field curves the trajectories of