*Present address: Institut de Physique Expérimentale, Université de Lausanne, Lausanne, Switzerland.

[1]K. Fuchs, Proc. Cambridge Phil. Soc. 34, 100 (1938).
[2]See, e.g., J. E. Parrott, Proc. Phys. Soc. (London) 85, 1143 (1965).
[3]R. F. Greene and R. W. O'Donnell, Phys. Rev. 147, 599 (1966).
[4]S. B. Soffer, J. Appl. Phys. 38, 1710 (1967).
[5]J. F. Koch and T. E. Murray, Phys. Rev. 186, 722 (1969).
[6]G. F. Juras, Phys. Rev. Letters 24, 390 (1970).
[7]B. B. Soffer Helv. Phys. Acta (to be published).
[8]D. C. Larson and B. T. Boiko, Appl. Phys. Letters 5, 155 (1964).

PHYSICAL REVIEW B VOLUME 2, NUMBER 10 15 NOVEMBER 1970

Many-Electron Theory of Nondirect Transitions in the Optical and Photoemission Spectra of Metals*

S. Doniach
Department of Applied Physics, Stanford University, Stanford, California 94305
(Received 1 December 1969)

The theory of the singular readjustment of a conduction band to a hole formed in an x-ray absorption event is extended to the case where the hole has finite mass, as in the *d* band of Cu. Although the resulting recoil removes the singularity, the effect may still be quite large, and results in an electron-induced Debye-Waller-factor reduction of the intensity of direct (*k*-conserving) optical or photoemission events. This reduction depends on the mass of the *d*-band hole, and is accompanied by inelastic contributions in which the photon energy is shared between an interband transition and a number of low-energy electron-hole pairs.

I. INTRODUCTION: HOLE PROPAGATOR

When an x ray is absorbed by a core electron in a metal, the consequent readjustment of the Fermi-gas conduction electrons to the hole potential has the singular character of an infrared divergence. This singularity was discovered by Mahan[1] and further investigated by Nozières and co-workers.[2,3]

In the present paper we suggest that a similar effect, though not singular as in the x-ray case, will occur when electrons in a narrow band (such as a *d* band) lying below the Fermi level are excited by some sort of radiation.

In the core-state case, Doniach and Sunjic[4] showed that the infrared singularity (suitably smeared by lifetime effects) would show up directly in the form of the low-energy tail in the line shape of emitted photoelectrons from the metal. In the present narrow-band case, too, we show that the relaxation of the Fermi sea of electrons around the narrow-band hole will lead to enhancement of weakly inelastic (1–2 eV)events during a uv photoemission process. The magnitude of this effect depends on the strength of the effective screened potential for conduction-electron-hole scattering, which is not known at the present time, but the effect possesses certain characteristic qualitative features which should allow it to be distinguished from other inelastic photoproduction mechanisms in the metal.

In the core-state case the infrared divergence is found theoretically from a study of the hole correlation function, or propagator (whose Fourier transform is directly related to the spectrum of photoelectrons in a photoemission experiment):

$$g(t)=i\langle b(t)b^{+}(0)\rangle \ , \tag{1}$$

where b^+ is a creation operator for the core-state hole. The divergence shows up as a power-law behavior $g(t)\sim t^{-\alpha}$for long times, which may be thought of as resulting from the fact that the production of zero-energy electron-hole pairs at the Fermi surface becomes infinitely probable; i.e., the lower the energy of the pairs, the more that will be produced. In the case of hole states in a narrow band, the hole creation operators are now labeled by a momentum suffix $b_K^\dagger$. The change in the physics is that the hole undergoes recoil during the emission and reabsorption of low-energy pairs, and the resulting recoil energy removes the zero-energy denominators, which lead to the divergence in the infinite-mass case. However, we suggest that the many low-energy pair scatterings will still be enhanced in the case of large hole mass (narrow hole band) relative to the perturbation-theory result (for a single electron-hole pair), leading to a propagator with spectral density of the form [Fourier transform of (1)]

$$\operatorname{Im} g_K(\omega)=A_K\delta(\omega-E_K)+\varphi_K(\omega) \ , \tag{2}$$

where hole-lifetime effects due to recombination and scattering have been neglected.

The above result is based on a "pseudoharmonic" treatment of the perturbation of the electron-gas density by the hole potential. The reduction of the δ function part by the factor A_K is a kind of electron-gas "Debye-Waller" effect. In the photoemission case it leads to a reduction of the direct or k-conserving transition probability. We show below that in a weak-coupling approximation

$$A_K \approx (m/M_{\text{hole}})^{\alpha} \text{ as } m/M_{\text{hole}} \to 0 , \tag{3}$$

where $\alpha = [N(0)v]^2$ and v is an electron-hole scattering potential parameter. [Following Nozières and de Dominicis,[3] it seems likely that $N(0)v$ will be replaced by δ/π, where δ is the electron-hole scattering phase shift in the strong-coupling case.] Thus we reach the important conclusion that the probability of the direct k-conserving process in the photoemission experiment will depend on the mass of the hole state involved.

$\varphi_K(\omega)$ in Eq. (2) is an inelastic part leading in the photoemission experiment to a spectrum of inelastic electrons associated with a given transition. We show below that for high hole mass, $\varphi_K(\omega)$ may be quite strongly enhanced in the relatively low-energy-loss range, thus providing possible additional inelastic structure in the photoemission electron energy distribution curves. This possibility should be kept in mind when examining photoelectron data for metals with narrow bands below the Fermi level.

II. INELASTIC PROCESS IN PHOTOEMISSION

The above mechanism is only one out of a number of possible processes for nondirect (k-nonconserving) photoemission events in metals. In this section we proceed to consider other possible processes in a qualitative way and point out special distinguishing features of the mechanism of Sec. I.

Excluding surface effects, we can classify nondirect photoemission events as follows:

(a) Electron induced; energy loss from the emitted photoelectron by excitation of electron-hole pair states. This is the usual mean-free-path mechanism, and has been carefully discussed by Berglund and Spicer.[5]

(b) Hole-induced excitation of electron-hole pair states; the mechanism of Sec. I.

(c) Electron- and hole-induced collective excitations of the many-electron system (plasmons) or of the electron-ion system (phonons).

(d) Quantum interference effects between hole-induced and electron-induced transitions.

The distinguishing features of the hole-induced mechanism (b) are the following:

(1) *Threshold behavior.* From consideration of the kinematics of the process it may be seen that for photons at a direct-interband-transition threshold, when there is a k-conserving transition between the maximum in a d band and a minimum in a higher band (i.e., at $K=0$), then the only inelastic events which can occur are those costing more photon energy than needed for the direct transition. Therefore, as the photon energy is increased, such direct-transition edges should come in sharply, broadened only by lifetime effects, but not broadened by the above inelastic effects. This will apply both to electron-induced (a) and hole-induced (b) processes. However, for photoelectrons away from $K=0$, or for a case where the band structure precludes a direct transition at $K=0$ (see Fig. 1), the kinematics of the situation show that in the hole-induced mechanism there will also be inelastic transitions with photon energies *below* the direct-transition energy in addition to those above. This is because, whatever the momentum transfer $\vec{K}-\vec{K}'$ involved, it is always possible to excite an electron across the Fermi surface with momentum transfer $\vec{K}-\vec{K}'$ and zero energy transfer. So in general the direct-transition δ function will come in the middle of the inelastic "mush" rather than on the low-energy threshold. This type of inelastic precursor could not occur in case (a), where the direct transition takes place first and the photoelectron scatters inelastically at a later time.

(2) *Mass dependence of the direct (k-conserving) transition probability.* This was discussed in Sec. I (and will be discussed in more detail in Sec. III).

As a result of the mass dependence of A_K [Eq. (20)], we may expect that the characteristic peaks

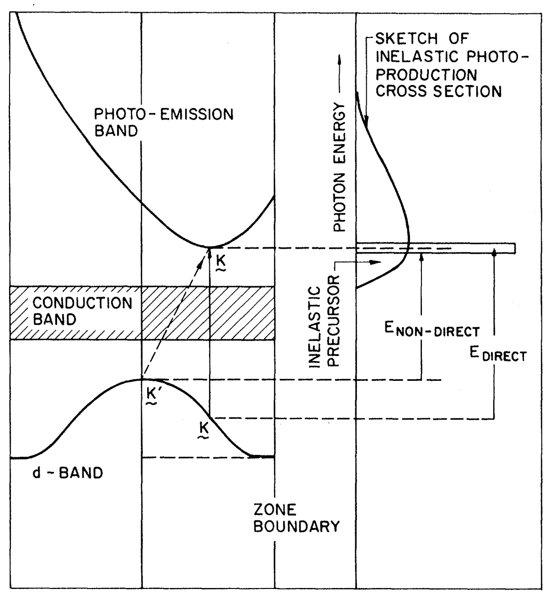

FIG. 1. Schematic diagram of inelastic contribution to the photoelectron production cross section resulting in the case where nondirect-transition photon energy is less than direct-transition photon energy, for fixed outgoing photoelectron state. The reader should note that this type of distribution curve refers to the inelastic spectrum (as a function of photon energy) associated with a *given* photoelectron final state. The latter has then to be integrated over all momentum at fixed photon energy, to give an observed photoelectron distribution curve (EDC).

expected in the k-conserving part of the photoelectron distribution curves (see, for instance, Smith[6]), which result from flat regions of the d band, will be just those parts of the spectrum most affected by mechanism (b). Again, this effect could not result from mechanism (a), where the energy loss is via the photoelectron scattering, and thus will not depend on the hole state. It would also not result in plasmon emission [via (a) or (b)], as here the energy denominators are large, and hole recoil would only lead to very small corrections.

(3) *Enhancement of low-energy-loss inelastic process*. We now argue that in the 0–2-eV energy-loss region the hole-induced loss mechanism (b) is much more effective than electron-induced mechanism (a). The reason is the low-energy multipair enhancement effect mentioned in Sec. I and discussed in detail in Sec. V. What we show is that this enhancement becomes increasingly effective as the hole mass increases. Thus, for the electron-produced final-state pairs of mechanism (a), the recoil of the fast electron during the scattering event will shift the system far off the infrared-type divergence discussed above, and the enhancement effect will not occur. Under these conditions the perturbation-theory approach of Berglund and Spicer[5] is correct and shows a relatively low probability for low-energy-loss events. For energy-loss events in the intermediate-energy range, however (4–6 eV for Cu), the Berglund-Spicer mechanism appears to account rather well for the observed characteristic low-energy tail of photoelectrons.[5,7]

Phonon emission events will also contribute to low-energy-loss events: Multi-phonon effects seem likely to be small in metals, where the electron-phonon interaction is strongly screened. Single-phonon events will in general only involve very small energy transfers ($\lesssim 0.1$ eV) and may be responsible (cf. Nesbet and Grant[8]) for some k-nonconservation, but one would expect these effects to be fairly temperature dependent, which does not appear to be the case in transition-metal photoemission experiments.

Events of type (d) constitute an interesting generalization. Physically one might describe them as events where the mean-free-path picture in which scattering of the escaping photoelectron is treated independently of its birth process has broken down. Hopfield's[9] decay of a virtual plasmon is an example of this type of event. Their importance for low-energy-loss processes is not clear to the author at the present time.

Finally, the effects discussed above will apply equally to the usual optical absorption spectra of metals for transitions in which the final-state electron (which need not escape from the metal) is not too close to the Fermi surface. Thus we may expect interband transition peaks in the optical spectra of metals such as Cu to be shifted and changed in shape by the nondirect contributions accompanying inelastic absorption events. Correlation of data with direct-transition joint density of states calculations should be examined with this possibility in mind.

For optical transitions to states very close to the Fermi surface, additional nearly singular scattering of the final-state electron with the hole will occur as in the x-ray case. This is not considered in the present paper. In a recent paper Gavoret *et al.*[10] extended their treatment of the x-ray problem (different from the one adopted here) to the case of finite hole mass and applied it to a discussion of exciton states in degenerate semiconductors. Presumably many of their conclusions will also apply to metals. However, they did not discuss the present case of transitions in which the final-state electron is far from the Fermi surface.

III. OPTICAL ABSORPTION AND PHOTOEMISSION CROSS SECTIONS

The electromagnetic field will interact with the metal via a current operator $j(\vec{x})$. For simplicity we will neglect the detailed momentum dependence of the matrix elements of this operator, although this will be important in real energy bands. The electromagnetic absorption cross section may then be found by examining the current-current correlation function

$$\langle j(t) j(0)\rangle . \tag{4}$$

In terms of the hole creation operator $b_K^\dagger$ and electron creation operator $c_K^\dagger$, this may be written

$$\sum j_K j_{K'} \langle c_K^\dagger(t) b_K^\dagger(t) b_{K'}(0) c_{K'}(0)\rangle , \tag{5}$$

where the Heisenberg time dependence is dictated by the full Hamiltonian. In order to discuss the hole-induced loss mechanism, a number of simplifying assumptions are now introduced. The electron-electron interaction which is important for discussing both electron-induced loss events and plasmon loss events will be assumed to be screened out in the usual way and the electron-hole interaction will be replaced by a self-consistently screened short-range interaction of strength v. If one were discussing large energy transfers via the hole, then the energy dependence of the screening would be important. However, as emphasized above, the present mechanism involving many pairs is essentially a low-energy process and this energy dependence will be ignored. The model Hamiltonian then becomes

$$H = \sum_p \epsilon_p c_p^\dagger c_p + \sum_K \left(E_g + \frac{K^2}{2M_{\text{hole}}} \right) b_K^\dagger b_K + \frac{v}{N} \sum_{pp'q} c_{p+q}^\dagger c_p b_{p'-q}^\dagger b_{p'} . \tag{6}$$

Here M is the hole mass, assumed to be large, and v is the screened potential for scattering of the conduction electrons from the hole. In the last term, band suffixes for the scattered electrons $c_p^\dagger$ have been omitted for simplicity. For electrons involved in transitions near the Fermi surface, in a material such as Cu, only one band will be involved. For higher-energy transitions, interband events will also be important, but we neglect them in the present simplified discussion. We now make the "single-hole approximation," which is the same basic approximation as that made in the x-ray problem, namely, that the hole–conduction-band-gap energy E_g is relatively large compared to other energies in the problem, so that only the hole produced by the photon excitation energy need be considered, and all virtual excitations of the hole may be neglected. This restriction, which is a shortcoming of the present theory, will become increasingly worse as the d band being considered comes close to the Fermi surface. The problem of at what value (relative to ϵ_F) of the hole excitation energy and coupling parameter v the present treatment of the hole propagator breaks down and the usual perturbation expansion of the mass operator takes over (in the weak-coupling limit) is a fundamental one which is not resolved in this paper. Within this approximation scheme (6) may be rewritten as

$$\sum_K |j_K|^2 \langle e^{iH_0 t} c_K^\dagger b_K^\dagger e^{-iHt} b_K c_K \rangle, \tag{7}$$

where

$$H_0 = \sum_p \epsilon_p c_p^\dagger c_p + \sum_K (E_{\text{gap}} + K^2/2M) b_K^\dagger b_K \ . \tag{8}$$

Now consider the evaluation of the correlation function (7). If we restrict ourselves to hole-induced loss events, as discussed in Sec. II, the c_K operators in (9) can be taken out, with their appropriate energy dependence $e^{i\epsilon_K t}$. For lower-energy photoelectrons and for optical transitions, we have two regimes to consider: (A) near threshold, where the excited electron $c_K^\dagger$ is very close to the Fermi level of the conduction band, and (B) away from threshold.

In regime (A), we know from the x-ray problem that scattering of the excited electron from the hole is very singular in character and cannot be neglected. In regime (B), on the other hand, although interactions with high-energy excitations in the electron gas (plasmons, etc.) will be of general importance, the singular scattering of the electron with the accompanying heavy hole will have died away. Furthermore, as will appear from the discussion to follow, the scattering of the escaping electron from the *low-energy* excitations of the electron gas, which would be singular if the electron had high mass, will be considerably weakened by the large recoil (i.e., low mass) of the electron, so it can be satisfactorily treated by perturbation theory. Since in the present paper we are mainly concerned with the strong-interaction effects of many low-energy pairs on the absorption process, we will therefore leave aside the question of the electron interaction, and, provided we are away from regime (A) (the threshold regime), we will just focus attention on the *hole correlation function*:

$$g_K(t) = \langle e^{iH_0 t} b_K^\dagger e^{-iHt} b_K \rangle . \tag{9}$$

In terms of g_K, the optical absorption probability in regime (B) may be represented by

$$\epsilon(\omega) = \sum_K \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, |j_K|^2 e^{i\omega t} g_K(t) \ . \tag{10}$$

The photoemission cross section for ingoing photon energy ω and outgoing photoelectrons in state $\vec{K}$ with energy $\epsilon_{\vec{K}}$ [which is bound to be in regime (B), since it is at least a work function away from ϵ_F] comes out as

$$\frac{d\sigma}{d\epsilon_K d\omega} \propto |j_K|^2 \frac{1}{\pi} \int_0^{\infty} dt\, e^{i(\omega - \epsilon_K)t}\, \mathrm{Re}\, g_K(t) \ . \tag{11}$$

The measured photoelectron intensity will then involve a sum over directions of $\vec{K}$, together with a work-function reduction of energy in the direction normal to the surface:

$$N(\epsilon, \omega) = \sum_K \delta(\epsilon - \tilde{\epsilon}_K(\phi)) \frac{d\sigma}{d\epsilon_K d\omega} \ , \tag{12}$$

where $\tilde{\epsilon}_K(\phi)$ contains the appropriate work-function reduction effect.

IV. PSEUDOHARMONIC APPROXIMATION

The approach of this paper to the calculation of g [Eq. (9)] is to try and estimate the effects of hole recoil on the singular perturbation of the Fermi sea which occurs in the x-ray case. Schotte and Schotte[11] have emphasized the analogy between the latter situation and that of a set of 1-dimensional Tomonaga electron-density oscillators coupled to the hole potential. Rather than work in terms of the Tomonaga coordinates, we stay in the fermion representation. But our central assumption is that it is reasonable to make the analogous approximation for the finite-hole-mass case to that in the Schotte paper in our evaluation of the hole correlation function.

What we do is observe that the Schotte-Schotte approximation is the first term in a cumulant expansion, in powers of v, of the hole Green's function. We term this a "pseudoharmonic" approximation, in the sense that if the electron-density operator combinations occurring in Eq. (6) obeyed Bose commutation rules, then the cumulant expansion of (9) would terminate at the first term and the resulting formula would be exact. In the infinite-mass-hole case the Schotte-Schotte approximation is exact (i.e., agrees with the formula of Nozières and de Dominicis) in the weak-coupling limit $vN(0) \ll 1$. What the work of Nozières and de Dominicis shows is that the cumulant treatment would still work if the Born-approximation scattering length $vN(0)$ is replaced by the phase shift δ/π.

In the present case we expand $g_K(t)$ to order $[vN(0)]^2$ to give

$$g_K(t) = \langle b_{0K}^\dagger(t) b_{0K}(0)\rangle - v^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \times \langle b_{0K}^\dagger(t) H_1(t_1) H_1(t_2) b_{0K}(0)\rangle , \tag{13}$$

where $b_{0K}^\dagger(t)$ is the interaction representation form. Writing

$$g_K(t) = e^{-iE_K t} e^{-C_K(t)} , \tag{14}$$

where

$$E_K = E_{\text{gap}} + K^2/2M, \tag{15}$$

we therefore have

$$C_K(t) = \frac{v^2}{N^2} \sum_{pp'} \left(\frac{it}{\Delta_K(pp')} + \frac{e^{i\Delta_K(pp')t} - 1}{[\Delta_K(pp')]^2} \right) \times f_p(1 - f_{p'}) f_{K+p'-p} , \tag{16}$$

where

$$\Delta_K(pp') = \{\epsilon_{p'} - \epsilon_p + E_{K+p'-p} - E_K\} . \tag{17}$$

The first term in (16) represents a renormalization of the hole energy (zero if one assumes electron-hole symmetry), while the second term contains the infrared divergence in the limit that $E_K \to$ const (infinite-mass limit).

To check the equivalence with Schotte and Schotte we first evaluate (16) in this limit. Then one has

$$\frac{d^2C}{dt^2} = -\int_0^E d\epsilon_1 \int_{-E}^0 d\epsilon_2\, e^{i(\epsilon_1 - \epsilon_2)t}\, vN(\epsilon_1) vN(\epsilon_2) , \tag{18}$$

where we have put the Fermi level in the middle of the conduction band, of width $2E$. For large t the dominant contribution comes from the region of the Fermi surface, so that (see Appendix A)

$$\frac{d^2C}{dt^2} \cong (1/t^2)[vN(0)]^2 . \tag{19}$$

Integrating over t, we obtain the large-t behavior

$$C(t) \cong [vN(0)]^2 \ln(it) . \tag{20}$$

Hence for $M_h \to \infty$ the present approximation gives the result of Schotte and Schotte and of Nozières and de Dominicis,

$$g(t) \cong (1/it)^\alpha . \tag{21}$$

Conversely in the *low*-mass limit, the singular character of (16) disappears, and we can expand g directly in powers of v to give

$$g(K, t) = g_0(t) + \int_{-\infty}^t dt_1\, g_0(t - t_1)\pi_2(t_1), \tag{22}$$

where $\pi_2(t)$ is the hole self-energy due to emission and reabsorption of a pair:

$$\pi_2(t) = \left(\frac{v}{N}\right)^2 \sum_{pp'} \frac{n_p(1 - n_{p'})\, e^{i\Delta(pp'K)t}}{\Delta(pp'K)} . \tag{23}$$

Thus, on integrating over t_1 in (23), and setting $g_0(t)$ equal to a unit step function (normalizing to the hole energy), we see that (16) reproduces the usual perturbation-theory result in this limit.

V. EFFECT OF RECOIL ON LINE SHAPE

We now study the effect of recoil on the time dependence of the hole propagator for finite hole mass, in terms of our pseudoharmonic approximation (16). For the case of hole momentum $\vec{K}$ equal to zero, the asymptotic time dependence of integrals is relatively easy to estimate. We have (renormalizing the energy-shift term)

$$\frac{d^2C(t)}{dt^2} = -\left(\frac{v}{N}\right)^2 \sum_{p_1 p_2} f_{p_1}(1 - f_{p_2}) e^{i(\epsilon_{p_1} - \epsilon_{p_2})t} e^{it(p_1 - p_2)^2/2M} . \tag{24}$$

For long times the main time dependence comes from the $\epsilon_1 \epsilon_2$ factor and we can replace p_1 and p_2 by p_F to give

$$\frac{d^2C}{dt^2} \cong \alpha \int_0^E d\epsilon_1 \int_{-E}^0 d\epsilon_2\, e^{i(\epsilon_1 - \epsilon_2)t} e^{i\beta t}\, \frac{\sin\beta t}{\beta t} , \tag{25}$$

where

$$\beta = (2m/M)\epsilon_F .$$

Again for large times, the small $\epsilon_1 \epsilon_2$ terms dominate. But it may now be seen that the $\sin\beta t/\beta t$ factor has the effect of *damping out* the $\ln t$ divergence of Eq. (20). Thus $\lim C(t)$, as $t \to \infty$, is now finite, and the Fourier transform of $g(t)$, which determines the line shape for a given direct transition to final electron state $\epsilon_{K=0}$, still contains the direct-transition δ function. However, its weight is reduced by a factor

$$A_{K=0} = e^{-C(K=0,\, t=\infty)} \tag{26}$$

analogous to the Debye-Waller factor. Since we have the general sum rule [from Eq. (9)]

$$\int d\omega\, g(\omega) = \lim g(t) = 1 \quad \text{as } t \to 0 , \tag{27}$$

we may conclude A_K determines the relative weight of the direct transitions to the total yield of state ϵ_K (integrated over photon energy). In Appendix A we show that, for $K = 0$, and $M/m \gg 1$, Eq. (25) may be integrated to give

$$\lim_{t\to\infty} C(K = 0, t) = -\alpha \ln[\gamma(m/M)] , \tag{28}$$

where, for large M/m, $\gamma(m/M) \propto m/M$. Thus at the band edge, $K = 0$, direct-transition weight is given by Eq. (2):

$$A_{K=0} = \{\gamma(m/M)\}^\alpha \approx (m/M)^\alpha \quad \text{as } M \to \infty.$$

To calculate the line shape we write

$$g(t)=e^{iE_{\text{direct}}t}e^{-C(\infty)}+e^{iE_{\text{direct}}t}[e^{-C(t)}-e^{-C(\infty)}], \quad (29)$$

so that, if we set the zero of photon energy ω at the direct-transition energy, the Fourier transform of the real part of (29) is given by

$$g(\omega)=A_K\delta(\omega)+\varphi_K(\omega)\ , \quad (30)$$

where

$$\varphi_K(\omega)=\frac{1}{\pi}\operatorname{Re}\int_0^\infty dt\, e^{-i\omega t}[e^{-C(t)}-e^{-C(\infty)}]\ . \quad (31)$$

Evaluation of (31) using the integral of Eq. (25) needs more numerical work, and to avoid this (at the present time) we try and get some idea of the line shape by making an ansatz for $C(t)$. We choose

$$C_{K=0}(t)\approx\tfrac{1}{2}\alpha\ln[(\gamma^2t^2-1)/t^2]\ . \quad (32)$$

This has the virtue of possessing the right value in both the limits: (a) $\beta\rightarrow 0$, where it gives the result (21), and (b) $t\rightarrow\infty$, where it gives the result (28). Neither this form nor the long-time approximation (21) of Nozières and de Dominicis is good in the small-t ($\lesssim 1/\epsilon_F$) region, so the resulting approximate line shapes do not satisfy the sum rule (27) and are not to be trusted for $\omega\gtrsim\epsilon_F$. Using the simulation formula (29), we have

$$g(K=0,\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\, e^{-i\omega t}\operatorname{Re}\left[\left(\frac{\gamma^2t^2-1}{t^2}\right)^{\alpha/2}-\gamma^\alpha\right], \quad (33)$$

where the branch of the root must be chosen so that the integral converges at the $t\rightarrow\infty$ limit. We show in Appendix B that (33) may be rewritten as

$$g(\omega)=0 \quad (\text{for}\quad \omega<0)$$

$$=\frac{2\sin\frac{1}{2}\pi\alpha}{\pi\omega^{1-\alpha}}F(\omega/\gamma)\quad(\text{for}\quad\omega>0)\ , \quad (34)$$

where

$$F(E)=\frac{1}{E^\alpha}\int_0^E dx\sin x\left(\frac{E^2-x^2}{x^2}\right)^{\alpha/2}\ . \quad (35)$$

The resulting line shapes are plotted in Fig. 2 for $\alpha=0.25$.[12] For Cu, the hole effective mass may be of order 10 in some regions of the d band, so that Fig. 2 suggests there will be quite a large low-energy inelastic contribution associated with such hole states. Unfortunately the crude nature of the simulation formula (29) leads to rather unphysical wiggles in the resulting Fourier transform. However, it does point up the importance of the hole mass in accentuating the low-energy inelastic contributions. Because of the poor nature of the form (29) in the small-t (high-energy) region, Fig. 2 almost certainly overestimates the high-energy inelastic scattering strength. Inelastic events with energy more than $2\epsilon_F$ above the direct-transition energy will tend to be cut down kinematically (they would need too much momentum transfer). The sum rule will then tend to heap up the absorption at lower energies, so Fig. 2 may give an underestimate of the inelastic strength at $\omega<\epsilon_F$. More numerical work needs to be done on Eq. (24) to improve this approximate form.

For finite $\vec{K}$, which is physically the more important case, the integration leading to (24) cannot be done easily, and one needs to study (16) numerically to get a quantitative picture of the resulting line shape. One can, however, get some idea of it from the kinematic constraints on the energy transfer to a pair, as discussed in Sec. II.

VI. CONCLUDING REMARKS

From the discussion of Sec. V it may be seen that the situation here is somewhat analogous to what happens in the Mössbauer effect or in diffuse x-ray scattering. The direct transitions persist in the finite-hole-mass case but with reduced intensity. However, there is an important difference in the form of the inelastic transitions from that in the phonon problem. Owing to the infrared catastrophe for low-energy pair production, it is no longer a reasonable approximation to expand this part in powers of the coupling α, i.e., the contributions to the large inelastic peaks in Fig. 2 come from rapid variation of $e^{-\alpha C(t)}$, which represents *many-pair* final states. The one-pair approximation would correspond to $e^{-\alpha C(t)}\approx 1-\alpha C(t)$. What our calculations have shown is that this would be a bad approximation, even for small (but finite) α, when the ratio of hole mass to conduction-band mass becomes large compared to 1.

The detailed application of the above theory to analysis of the photoemission data for metals such

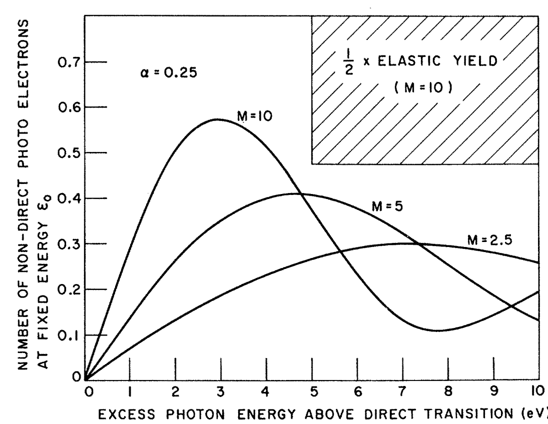

FIG. 2. Photoelectron production cross section given by the simulation line-shape formula (33) for $\alpha=0.25$, as a function of photon energy ω for a given photoelectron state of energy $\epsilon_{\vec{k}}$. Half of the direct-transition δ-function weight, reduced by the inelasticity factor of (4), is shown in the hatched box. The vertical scale is normalized so that the full sum-rule weight would be exhausted by a box of height 1.0 and width ϵ_F ($\cong 5$ eV for Cu).

as Cu must await numerical work on the k dependence of the line shape for real band structures. However, empirical evidence for nondirect (k-non-conserving) transitions in photoemission processes in d-band metals in terms of the lack of strong dependence of the peaks in electron distribution curves on photon energy has been emphasized in a series of papers by Spicer and co-workers.[13] In view of the specific enhancement due to the effect described in this paper in narrow-band situations, it therefore seems plausible that some of the observed reduction of the EDC peaks in transition and noble metals may result from the hole-induced energy-loss mechanism described here.

ACKNOWLDGMENTS

The idea for this approach to the problem grew out of discussions with Marijan Sunjic, and I would like to express my indebtedness to him for his help. I would also like to thank Bill Spicer and Neville Smith for a number of very stimulating discussions, and Bob Nesbet for pointing out the importance of the pair mechanism in absorbing momentum from an interband transition process. I am grateful to Gerard Toulouse for pointing out an error in the original draft of this paper.

APPENDIX A: ASYMPTOTIC VALUE OF HOLE GREEN'S FUNCTION

First we show the logarithmic dependence of $C(t)$ in the infinite-mass case [Eq. (20)]; then we establish the $t\to\infty$ limit of $C(k=0, t)$ in the finite-mass case [Eq. (28)].

Starting from Eq. (18), we use the fact that only the small-t dependence of d^2C/dt^2 is important to replace $N(\epsilon)$ by its value at the Fermi level:

$$\frac{d^2C}{dt^2} = -\alpha(e^{iEt}-1)^2/t^2 . \qquad \text{(A1)}$$

Integrating once by parts, and noting that the divergence cancels at $t=0$, we have

$$\frac{dC}{dt} = -\alpha\left(\frac{2e^{iEt}-1-e^{2iEt}}{t} - 2iE\int_0^t dt' \frac{e^{iEt}-e^{2iEt}}{t}\right) . \qquad \text{(A2)}$$

At large t we use the asymptotic forms

$$\int_0^t \frac{\sin x}{x}\,dx = \tfrac{1}{2}\pi - \frac{\cos t}{t}, \quad \int_t^\infty \frac{\cos x}{x}\,dx = -\frac{\sin t}{t} \qquad \text{(A3)}$$

to rewrite Eq. (A2) as

$$\frac{dC}{dt} \to \alpha\left[\frac{1}{t} + 2i\left(\frac{\sin Et}{t} - \frac{\sin 2Et}{2t}\right)\right] + O\left(\frac{1}{t^2}\right) \quad \text{as } t\to\infty. \qquad \text{(A4)}$$

Hence, using the fact that $dC/dt \to 0$ as $t\to 0$, we can integrate for large t to give

$$C(t) \to \alpha(\ln t + \tfrac{1}{2}i\pi) + O(1/t) \quad \text{as } t\to\infty , \qquad \text{(A5)}$$

so that

$$C(t) \to \alpha \ln(it)$$

from which

$$g(t) \to (1/it)^\alpha .$$

We now want to study how this is modified by the factor $e^{i\beta t}(\sin\beta t)/\beta t$ in Eq. (25). Using the same limits as in (A1), we have

$$\frac{d^2C(k=0, t)}{dt^2} = -\alpha e^{i\beta t}\frac{\sin\beta t}{\beta t}\;\frac{(e^{iEt}-1)^2}{t^2} . \qquad \text{(A6)}$$

The real part of this is

$$\mathrm{Re}\frac{d^2C}{dt^2} = \frac{\alpha}{\beta t^3}\sin\beta t[\cos(2E+\beta)t - 2\cos(E+\beta)t + \cos\beta t]$$
$$= \frac{\alpha}{2\beta t^3}[\sin(2E+2\beta)t - \sin(2Et) - 2\sin(E+2\beta)t + 2\sin Et + \sin 2\beta t]. \qquad \text{(A7)}$$

So we need to evaluate integrals of the type

$$\int_\epsilon^\infty dt \int_\epsilon^t dt_1 \frac{\sin At_1}{t_1^{\,3}} , \qquad \text{(A8)}$$

where $\epsilon > 0$ and will approach 0 after summing over the terms in (A7). Now we integrate (A8) by parts and use

$$\int_\epsilon^\infty dt \frac{\sin At}{t^3} \to -A\ln(A\epsilon) + O(1) \quad \text{as } \epsilon\to 0 \qquad \text{(A9)}$$

and

$$\int_\epsilon^\infty dt\,\frac{\cos At}{t} = -\ln A\epsilon + O(1). \qquad \text{(A10)}$$

[There is also a term $\int_0^\infty dt \sin(At)$ which converges and does not contribute to the divergence as $\beta\to 0$.] So from (A7) we have

$$C(\infty) = \lim_{\epsilon\to 0}\frac{\alpha}{2\beta}\sum_i p_i \ln(A_i\epsilon), \qquad \text{(A11)}$$

where p_i and A_i are the appropriate coefficients in (A7). In the limit $\beta \ll 1$ (high mass) this reduces to

$$C(\infty) \to \alpha\ln(\beta/B) = -\alpha\ln[(M/m)B/2\epsilon_F] \quad \text{as } \beta\to 0, \qquad \text{(A12)}$$

where B is a constant. To determine B reliably, the above asymptotic evaluation is not good enough and we have integrated (A7) numerically using

$$\mathrm{Re}C(K=0, t=\infty) = -\mathrm{Re}\int_0^\infty dt\int_t^\infty dt_1\left(\frac{d^2C}{dt^2}\right) . \qquad \text{(A13)}$$

The results are given in Table I, where we have set

$$\lim C(K=0, t) = \ln[\gamma(m/M)] \quad \text{as } t\to\infty. \qquad \text{(A14)}$$

APPENDIX B: EVALUATION OF LINE-SHAPE FORMULA (33)

To perform the integral (33),

$$g(\omega) = \frac{1}{\pi}\,\mathrm{Re}\int_0^\infty dt\,e^{i\omega t}\left[\left(\frac{\gamma^2t^2-1}{t^2}\right)^{\alpha/2} - \gamma^\alpha\right], \qquad \text{(B1)}$$

TABLE I. Values of $\lim C(t)$ as $t\to\infty$ as function of hole mass.

M/m	2.5	5	10
$\ln\gamma$	−0.578	−0.955	−1.442
γ	0.561	0.385	0.236

where $\gamma=\gamma(m/M)$ is defined in (A14), we write

$$x=|\omega|t \text{ for } \omega>0,\ \omega<0,$$

so that

$$g(\omega)=\frac{\gamma^\alpha}{|\omega|}\int_0^\infty dx\,\frac{1}{\pi}\,\mathrm{Re}\,e^{ix}\left[\left(\frac{x^2-E^2}{x^2}\right)^{\alpha/2}-1\right] \text{ for } \omega>0 \tag{B2}$$

$$=\frac{\gamma^\alpha}{|\omega|}\int_0^\infty dx\frac{1}{\pi}\,\mathrm{Re}\,e^{-ix}\left[\left(\frac{x^2-E^2}{x^2}\right)^{\alpha/2}-1\right] \text{ for } \omega<0. \tag{B3}$$

Here $E=|\omega|/\beta$. Note that the branch of the $\frac{1}{2}\alpha$ power is fixed by the requirement that the integral converges as $x\to\infty$.

Now consider

$$h(E)=\int_0^\infty dy\,e^{-y}\left[\left(\frac{y^2+E^2}{y^2}\right)^{\alpha/2}-1\right] \tag{B4}$$

and deform the line of integration either up to $y=+i\infty$ or $y=-i\infty$ to give

$$h(E)=-i\int_0^E dx\,e^{-ix}\left[e^{i\pi\alpha/2}\left(\frac{E^2-x^2}{x^2}\right)^{\alpha/2}-1\right]-if(E), \tag{B5}$$

where

$$f(E)=\int_E^\infty dx\,e^{-ix}\left[\left(\frac{x^2-E^2}{x^2}\right)^{\alpha/2}-1\right] \tag{B6}$$

and

$$h(E)=i\int_0^E dx\,e^{ix}\left[e^{-i\pi\alpha/2}\left(\frac{E^2-x^2}{x^2}\right)^{\alpha/2}-1\right]. \tag{B7}$$

Hence for $\omega<0$

$$\bar{g}(E)=(1/\pi)\mathrm{Re}[-ih(E)]=0, \tag{B8}$$

since h is real from (B4) [we have set $\bar{g}(E)=(|\omega|/\gamma^\alpha)g(\omega)$], while for $\omega>0$

$$\bar{g}(E)=\frac{1}{\pi}\,\mathrm{Re}\left\{\int_0^E dx\,e^{ix}\times\left[e^{i\pi\alpha/2}\left(\frac{E^2-x^2}{x^2}\right)^{\alpha/2}-1\right]+f^*(E)\right\}$$

$$=\frac{2\sin\frac{1}{2}\pi\alpha}{\pi}\int_0^E dx\,\sin x\left(\frac{E^2-x^2}{x^2}\right)^{\alpha/2} \tag{B9}$$

using (B5).

Using the fact that

$$\bar{g}(E)\cong E^\alpha\int_0^\infty\frac{\sin x}{x^\alpha}\,dx \text{ as } E\to\infty,$$

we can rewrite

$$g(\omega)=\frac{\gamma^\alpha E^\alpha}{|\omega|}\,F(E)$$

$$=\frac{2\sin\frac{1}{2}\pi\alpha}{\pi|\omega|^{1-\alpha}}\,\frac{1}{E^\alpha}\int_0^E dx\,\sin x\left(\frac{E^2-x^2}{x^2}\right)^{\alpha/2} \tag{B10}$$

as used in Eq. (34).

*Research supported by the Advance Research Projects Agency through the Center for Materials Research at Stanford University and by U. S. Army Research Office, Durham, N. C.

[1]G. D. Mahan, Phys. Rev. 163, 612 (1967).
[2]B. Roulet, J. Gavoret, and P. Nozières, Phys. Rev. 178, 1072 (1969); 178, 1084 (1969).
[3]P. Nozières and C. T. de Dominicis, Phys. Rev. 178, 1097 (1969).
[4]S. Doniach and M. Sunjic, J. Phys. C 3, 285 (1970).
[5]C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1030 (1964); 136, A1030 (1964).
[6]N. V. Smith, Phys. Rev. Letters (to be published).
[7]D. E. Eastman and J. K. Cashion, Phys. Rev. Letters 24, 310 (1970).
[8]R. K. Nesbet and P. M. Grant, Phys. Rev. Letters 19, 222 (1967).
[9]J. J. Hopfield, Phys. Rev. 139, A419 (1965).
[10]J. Gavoret, P. Nozières, B. Roulet, and M. Combescot, J. Phys. Radium (to be published).
[11]K. D. Schotte and U. Schotte, Phys. Rev. 182, 479 (1969).
[12]Saturation of the Friedel sum rule by the conduction electrons would give $\delta/\pi\cong 0.5$ – if the hole did not form a magnetic state, giving $\alpha\cong 0.25$.
[13]See, for instance, the discussion by W. E. Spicer (and references therein) in Phys. Rev. 154, 385 (1967), who points out the importance of final-state interactions between hole and conduction band in leading to nondirect transitions.