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[6] Of course, $\Phi_{k_1+k_2}$, $\Phi_{k_1+k_1}$, and $\Phi_{k_2+k_2}$ all have second-order terms, but there is no echo associated with these terms.

[7] The $\partial f_0/\partial v$ term in Eq. (4) looks like it makes the integrand diverge for large imaginary v, but this term is actually canceled by a similar term hidden in $\epsilon(-k_1, ik_1v)$.

NONDIRECT PROCESSES AND OPTICAL PROPERTIES OF METALS

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Recent photoemission studies of noble and transition metals show a predominance of "nondirect" electronic excitations and indicate an anomalous density-of-states peak below the expected d-band. We attribute these observations to second-order (and higher) processes involving secondary phonon- and electron-pair excitations.

Photoemission studies of the noble and transition metals by Spicer and collaborators[1] imply, contrary to the expected selection rule for photon absorption, that the dominant absorption mechanism involves electron excitations that do not conserve wave vector $\vec{k}$. In addition to this "nondirect" character of the excitation process, an anomalous peak in the valence density of states is deduced to lie several volts below observed d-band structure. The d-band structure itself appears to be in good agreement with theoretical computations. It has been shown,[1] particularly for Cu and Ni, that the photoemission results, including the anomalous peaks, are in agreement with optical-reflectance data. X-ray emission data on Ni have been interpreted by Phillips[2] to provide confirmation for the photoemission results, but Cuthill, McAlister, and Williams[3] dispute this interpretation. They associate the observed large x-ray emission peak with the d-band density of states, while Phillips identifies this peak with the anomalous peak observed several electron volts below the d-band structure in optical and photoemission data. Ion-neutralization spectra[4] of Cu and Ni indicate prominent d-band density-of-states peaks, with an anomalous peak in Cu at the same energy as the anomalous optical peak, but with no second peak in Ni.

We shall not attempt to resolve the questions raised by existing inconsistencies among experimental data. However, we shall point out additional evidence for the importance of nondirect optical transitions in metals, and we propose a general mechanism for the appearance of anomalous shifted peaks in effective densities of states deduced from optical data.

If optical experiments on metals really measure nonlocal bulk properties and not surface effects, then $\vec{k}$ conservation must be assumed for the over-all absorption process. Observation of nondirect processes implies that second-order (or higher) processes are involved, so that nondirect electronic excitations are coupled to secondary excitations that make up the necessary $\vec{k}$ vector. If nondirect processes are observed in any part of the spectrum, the dipole sum rule implies that the observed intensity is borrowed from first-order direct electronic excitations. It follows from this that any nondirect process has the effect of decreasing the relative intensity of direct processes, thus increasing the relative strength of other nondirect transitions.

Any intrinsic absorption below the threshold for direct excitation must be due to a nondirect process. In particular, the well-known classical Drude theory of free electron absorption corresponds in the quantum theory to a second-order indirect process in which $\vec{k}$ is conserved by phonon emission or absorption. The quantum theory of such indirect processes has been applied by Nettel[5] to describe not only the Drude absorption but also the anomalous structure observed in Na below the threshold for direct one-electron excitation.[6] Similar structure observed in other alkali metals shows temperature dependence that is not yet accounted for,[6] but, as pointed out above, such structure must be attributed to a nondirect excitation process because it lies below the direct excitation threshold. It has been shown by Ferrell[7] that an indirect electronic excitation from the Fermi surface to the Brillouin zone boundary would give a reasonable value for the energy of this anomalous structure in potassium. Energy-band calculations by Ham[8] indicate that Fermi-surface to zone-boundary transitions are in the same energy range as the anomalous structure observed for other alkali metals. Photoemission data on the alkali metals[9] are very similar to the low-energy results of Spicer *et al.* on the noble metals.

We conclude from this that indirect interband transitions, as described by Nettel,[5] should be a universal phenomenon in metals, just as is the Drude absorption.

In addition to phonon processes, secondary electronic excitations can also occur in the usual theory of metals. We attribute the nondirect character of the transitions observed by Spicer *et al.* to a combination of phonon indirect processes and of secondary excitation of low-energy electron-hole pairs. The transfer of oscillator strength from direct excitations to nondirect processes is apparently so extensive that the nondirect processes predominate.

Secondary electronic excitations correspond to inelastic scattering of an electron or hole produced in a primary virtual direct excitation. This is to be thought of as a second-order term in perturbation theory, so virtual pairs of arbitrary energy contribute to the transition amplitude. The final state describes a nondirect one-electron excitation accompanied by a secondary excitation of the many-electron system. In fact, a large background of low-energy electrons is observed in photoemission experiments, but it is attributed to single scattering of primary electrons.[1,10] Hole scattering, similar to the Auger effect, also occurs.[1] Much of this observed low-energy background could be due to secondary electrons excited in second-order processes.

Since the inelastic scattering of an electron or hole is involved in the intermediate virtual state of a second-order process, the excitation of secondary pairs or, more generally, of collective excitations should lead to shifts of density-of-states structure by energies comparable with characteristic energy-loss peaks. Spicer *et al.*, after correcting for the background of low-energy secondary electrons, analyze the observed distribution $N(E)$ of photoelectrons at energy E in terms of the formula[1,10]

$$N(E)=CT(E)N_c(E)N_v(E-\hbar\omega). \tag{1}$$

Here C is a constant, $T(E)$ is the escape function for emission from the surface of the metal, and $N_c(E)$ and $N_v(E)$ are the inferred "optical" densities of electronic states in the conduction and valence bands, respectively. If there is a narrow characteristic loss peak at ΔE_α, it will contribute to $N_v(E-\hbar\omega)$ by adding in a contribution of $N(E)$ from electrons originating at $E-\hbar\omega+\Delta E_\alpha$ rather than at the assumed $E-\hbar\omega$. In general, this changes Eq. (1) to

$$N(E)=\sum\nolimits_\alpha C_\alpha T(E)N_c(E)N_v^{(0)}(E-\hbar\omega+\Delta E_\alpha), \tag{2}$$

where $N_v^{(0)}$ is the true valence-electron density of states. Elastic scattering, direct excitation, and secondary photon processes can be included in a term with $\Delta E_\alpha=0$. The optical density of states deduced from Eq. (2) would be

$$N_v(E-\hbar\omega)=\sum\nolimits_\alpha (C_\alpha/C)N_v^{(0)}(E-\hbar\omega+\Delta E_\alpha). \tag{3}$$

This formula shows explicitly the folding together of the true density of states and the characteristic loss spectrum, assumed here for the sake of simplicity to consist of a number of sharp lines at the energies ΔE_α. Only those characteristic loss peaks due to volume effects (excluding lowered plasma losses) should contribute. Plasma excitations would have no special significance compared with general interband-loss peaks.

The energy-loss spectra of Fe, Co, Ni, and Cu have been measured by Robins and Swan[11] and that of Ag and Pd by Robins.[12] From Eq. (3), anomalous peaks E_a might be expected to occur in the optical densities of states for these metals at energy values shifted below the highest-energy d-band peak E_{d1} by the amount of the lowest characteristic energy loss ΔE_1. Observed values of $E_{d1}-E_a$ and ΔE_1 are compared in Table I. Since the second peak observed in the d-band optical density of states of these metals[1] might itself be an anomalous peak due to low-energy secondary electron pairs, it would not necessarily lead to corresponding structure in the main anomalous peak. The agreement between the last two columns of Table I is striking, both for those cases in which an anomalous peak is observed in photoemission data (Fe, Co, Ni, and Cu) and those in which it is not (Ag, Pd). For Ag, the anomalous peak should appear around -8.3 eV; however, the photoemission data terminate above this energy. For Pd, an anomalous peak is expected near -7.0 eV, if the characteristic loss at 6.8 eV is a volume

Table I. Comparison of the anomalous photoemission peak with observed low-energy characteristic energy-loss peaks. E_a refers to the energy of the anomalous peak with respect to the Fermi level, E_{d1} to the highest-energy d-band photoemissive peak, and ΔE_1 to the lowest energy-loss peak. All energies are in eV.

Metal	E_a	E_{d1}	$E_{d1}-E_a$	ΔE_1
Fe	-5.5^{a}	-0.3^{a}	5.2	5.3 ± 0.4^{c}
Co	-5.1^{a}	-0.3^{a}	4.8	4.6 ± 0.4^{c}
Ni	-4.6^{a}	-0.3^{a}	4.3	4.3 ± 0.4^{c}
Cu	-6.2^{b}	-2.1^{b}	4.1	4.5 ± 0.2^{c}
Ag	$<-7.0^{b}$	-4.2^{b}	>2.8	4.1 ± 0.1^{d}
Pd	$\sim-7.0?^{a}$	-0.2^{a}	6.8	6.8 ± 0.2^{d}

[a] A. Y.-C. Yu and W. E. Spicer, Phys. Rev. Letters 17, 1171 (1966) (see especially Ref. 11).

[b] W. E. Spicer, in Optical Properties and Electronic Structure of Metals and Alloys, edited by F. Abelès (John Wiley & Sons, Inc., New York, 1966), pp. 296-315.

[c] J. L. Robins and J. B. Swan, Proc. Phys. Soc. (London) 76, 857 (1960).

[d] J. L. Robins, Proc. Phys. Soc (London 78, 1177 (1961).

effect and not a lowered plasma loss. Although photoemission data do not extend to this energy, Yu and Spicer[1] indicate the presence of an optical reflectivity peak at −7.0 eV and do not rule out the possibility of a photoemission peak at this energy.

It should be emphasized that our proposed explanation of the observed anomalous peaks does not attribute them directly to the electronic density of states. On physical grounds, we argue that such peaks should occur as a consequence of energy loss to secondary excitations, and therefore that the observed "optical" density of states should correspond qualitatively to the result of folding the characteristic loss spectrum into the true density of states. The relative magnitude of these secondary peaks depends on the strength of interactions that are not directly related to the true density of states. This is compatible with the observed wide variation of the relative strength of the anomalous peaks in different transition metals.[1]

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DIRECT ELECTROMAGNETIC GENERATION OF ACOUSTIC WAVES*

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A recent Letter by Larsen and Saermark[1] describes the electromagnetic generation of acoustic waves in aluminum. They explain their experimental results on the basis of the helicon-phonon interaction. The present paper presents evidence that rf-ultrasonic coupling can occur near the surface of a metal in the presence of a magnetic field, independent of helicon propagation. The results of our experiments are consistent with a model which assumes that the external electromagnetic fields couple directly with the electromagnetic fields of the acoustic wave.

The experimental arrangement is shown in