tions are shown in Fig. 3(b), and the direction of the vectors in the inset. There appears to be no *a priori* way of choosing between these. At the peak of the resonance one solution is closely parallel to E_0, with a phase shift $\delta = 180°$ at the in-phase point. It remains within 5° of E_0 over the whole resonance region. The other solution at the resonance peak points between k_p and K, with a phase shift $\delta = 0°$ at the in-phase point. Off resonance E_p varies from this direction but seemingly in no way related to φ or the direction of k_p. The first solution seems the more realistic.

Analyzing the $\theta = 50°$, $n = 1$ data of Fig. 2(a), we have found that the direction of the major axis swings further away from E_0 as one goes through the resonance. One solution for E_p is about 30° off E_0; the other lies between k_p and K. δ in both cases varies through 180°. In this case it is not evident which is the most likely solution. For the $\theta = 70°$ data of Fig. 2 the point of $\delta = 180°$ occurs near the center of the resonance. For the $\theta = 50°$ data, δ equals 180° on one side of the resonance with s-polarized light, on the other with p-polarized light. This produces the line-shape distortion which has been referred to already above. Such line-shape distortion may account for the deviations of k_p from the predicted values found by Teng and Stern and Ritchie *et al.*

The resonance anomalies may be considered as arising from virtual excitation of surface plasmons. The residual incoherent signal must come from spontaneous emission by real plasmons. After excitation these propagate for a short while before scattering from the grating into outgoing waves. The emission process is separate from the excitation process, and the emitted light is therefore incoherent with the incident light. For the $n = 1$ plasmons the incoherent light is sharply peaked at φ_p, but for the $n = 2$ it is peaked more towards φ_d. At present it is not clear whether this is an angle of incidence effect, since the $n = 2$ anomalies tend to occur at smaller angles of incidence, or an order effect.

We are continuing studies of the line shape of the spontaneous emission and of the interference effects in the diffracted beams as well as the specular beam. We have enjoyed conversations with Dr. Michael Greene and many others in our laboratory.

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NATURE OF OPTICAL TRANSITIONS IN COPPER AND Cu:Ni ALLOYS*

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The direct $L_{2'} \rightarrow L_1$ transition is very apparent in photoemission data from pure Cu; however, as might be expected, there is no evidence for this transition in 87% Cu–13% Ni alloys. In contrast, structure in ϵ_2 for $h\nu \geq 2.1$ eV for the alloy and pure Cu is qualitatively similar. These observations support the assignment of major structure in ϵ_2 of pure Cu to nondirect transitions from the d states and argue against the 5.0 eV peak being due principally to the $L_{2'} \rightarrow L_1$ transition.

In their pioneering work on the optical properties of metallic copper, Ehrenreich and Philipp[1] attributed structure in the optical constants characterizing the interband absorption to direct, or $\vec{k}$-conserving, transitions. Berglund and Spicer[2] and Krolikowski and Spicer[3] on the basis of photoemission data have emphasized the dominance of nondirect transitions, or transitions in which conservation of $\vec{k}$ does not provide an important selection rule in the usual one-electron sense, in determining the optical absorption of copper. In particular, in transitions from the d-derived states they found no evidence that conservation of $\vec{k}$ provided an important selection rule; however, a well-defined direct transition was found between s- and p-derived states near the L symmetry point of the Brillouin zone. The question of the importance of direct transitions in copper is still quite controversial.

The study of alloys of noble metals with transition metals, such as copper-nickel alloys, can provide additional information on the importance of direct or nondirect transitions. Since the electrons of the transition-metal impurity atoms form virtual bound states, one would expect the crystal potential to be strongly disturbed, hence removing $\vec{k}$ as a meaningful quantum number. Thus it would be expected that any direct transitions would disappear from the optical spectra of the alloys and that the nondirect transitions might be little affected. An independent experimental check of the disappearance of direct transitions can be given by examining alloy photoemission data for evidence of the direct transition at L seen in pure copper. Here we present photoemission data from a cesiated copper-nickel alloy of composition 87% Cu–13% Ni, which indicate that there is no direct transition occurring corresponding to this L transition in pure copper. However, structure in the optical constant ϵ_2 in the vicinity of 5.0 eV, which in copper has been interpreted in terms of direct transitions near L, is still present in the 87%-Cu alloy. This suggests strongly that the structure in ϵ_2 is due to nondirect transitions both in the alloy and in pure copper.

The measurement of the kinetic energy distributions of photoemitted electrons (energy distribution curves, EDC's) provides a direct means for determining the nature and relative strengths of possible optical transitions in a material. Peaks in EDC's due to nondirect transitions either remain stationary in kinetic energy or move in energy according to the relation $\Delta E_p = \Delta h\nu$, where $\Delta h\nu$ is the change in photon energy and ΔE_p is the change in peak position. On the other hand, structure due to direct transitions appears suddenly at one photon energy and moves in energy with increments which are usually different from the increments in photon energy. This difference in behavior with varying $h\nu$ enables the two types of transitions to be distinguished from one another. The fact that the optical absorption (ϵ_2) at any photon energy is the sum of all possible types of transitions to all available final energy states makes the separation into direct and nondirect contributions difficult from examination of ϵ_2 alone. Differential reflectance techniques, such as piezoreflectivity,[4-6] measure the effects of direct transitions at points in $\vec{k}$ space of high symmetry but may be insensitive to any nondirect transitions. Therefore, these techniques cannot estimate accurately the relative importance of the two types of transitions.

In Fig. 1 several normalized EDC's for copper, taken from the work of Berglund and Spicer,[2] are shown for photon energies $4.1 \leqslant h\nu \leqslant 5.3$. The curves are plotted versus the initial-state energy, $E - h\nu + e\varphi$. On this type of plot structure due to nondirect transitions which follow $\Delta E_p = \Delta h\nu$ superimposes for different $h\nu$ while structure due to direct transitions does not necessarily superimpose.

These data were obtained from evaporated films of copper with a surface monolayer of cesium. The cesium monolayer lowered the vacuum level to 1.55 eV and enabled transitions to a wider range of final states to be observed than would have been possible in uncesiated copper. For $h\nu \leqslant 4.4$ eV two peaks are uncovered in the EDC's: a weak peak at about -0.35 eV and a second peak at -2.4 eV due to transitions from the copper d states. Both of these peaks superimpose for different $h\nu < 4.4$ eV and are therefore attributed to nondirect transitions. For $h\nu = 4.4$ eV a large, pronounced peak suddenly appears in the EDC's at about -0.4 eV. With further increase in the photon energy, this peak does not superimpose but changes energy position. Both of these observations—the sudden appearance of the peak for $h\nu = 4.4$ eV and the fact that $\Delta E_p \neq \Delta h\nu$—indicate that this peak is due to direct transitions. By utilizing the calculated band structure for

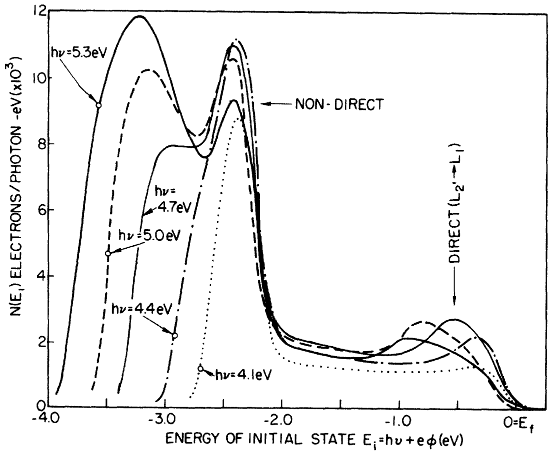

FIG. 1. Normalized EDC's for cesiated copper from the work of Berglund and Spicer (Ref. 2). The curves are plotted against the initial-state energy for 4.1 eV $\leqslant h\nu \leqslant 5.3$ eV. Photoelectrons created by the $L_{2'} \rightarrow L_1$ direct transition are observed between 0 and -1.0 eV.

copper[7] and other information deduced from the photoemission data, Berglund and Spicer identified this direct transition as occurring between initial states in the vicinity of $L_{2'}$ (located 0.35 eV below E_F) and final states near L_1 (4.05 eV above E_F). It should be noted that while the direct transition increases the magnitude of the EDC's by 30-40% near the leading edge, the number of electrons involved in the direct transitions near L is only a small fraction of the total number of electrons excited (including electrons excited to final states below the vacuum level and hence not observed in photoemission). It has been estimated that less than 10% of the optical-transition strength is associated with the L direct transition.

We have previously reported[8] photoemission data for uncesiated copper-nickel alloy samples of composition 87% Cu–13% Ni and 77% Cu–13% Ni (in the previous publication the composition of the 87% Cu sample was incorrectly reported as being 90% Cu–10% Ni). In the clean alloy samples, structure due to excitation of the copper d-derived states resembled closely the d-state structure in pure copper. The addition of nickel caused a buildup of states in the energy region between the copper d states and the Fermi level. Remeasurement of the clean 87%-Cu alloy has yielded sharper structure than previously reported because of better surface preparation. Photoemission data have also been obtained from these alloy samples with a monolayer of cesium on the surface. After obtaining data from the clean material, cesium was deposited by firing cesium generators for short periods of time. EDC's were obtained after each firing of cesium to detect the vacuum-level change and the process was repeated until the vacuum level was reduced to less than 2.0 eV. In this way the work function of the 87%-Cu sample was reduced to 1.8 eV.

In Fig. 2 we show normalized EDC's for $4.1 \leq h\nu \leq 5.3$ eV, plotted versus the initial-state energy. The curves exhibit a strong peak at −2.7 eV due to excitations of the copper d-derived states and a peak at about −1.2 eV due to nickel d electrons existing in virtual bound levels. Both peaks superimpose and have the characteristics expected of nondirect transitions. From photoemission data obtained from the clean, uncesiated alloy sample we estimate that approximately one-third of the height of the peak at −1.2 eV is due to excitations of the nickel virtual bound levels, the rest of the height being due to excitations of s- and p-like electrons.

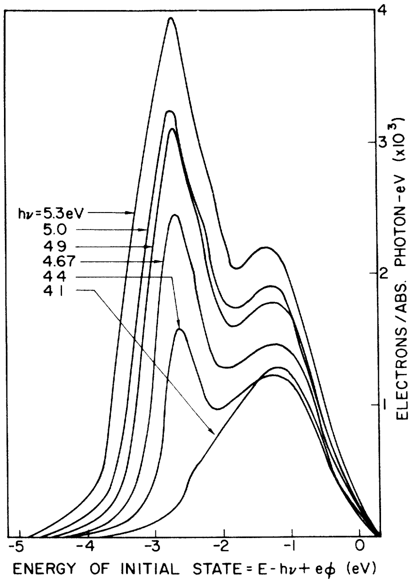

FIG. 2. Normalized EDC's for cesiated 87% Cu–13% Ni, 4.1 eV ≤ $h\nu$ ≤ 5.3 eV. All observed structure superimposes in energy and can therefore be attributed to nondirect transitions; no direct transitions are observed.

Close inspection of the curves in Fig. 2 indicates that there is no additional structure which appears suddenly and then moves with $\Delta E_p \neq \Delta h\nu$; all of the structure that is observed superimposes and varies smoothly in magnitude. Thus, these data indicate that there is no $L_{2'} \rightarrow L_1$ direct transition occurring in the alloy in the photon-energy range where the $L_{2'} \rightarrow L_1$ direct transition occurred in pure copper. Additional excitations from the nickel virtual bound levels in the alloy should not be of sufficient magnitude to mask any direct contribution as large as that occurring in pure copper. Similarly, in data from cesiated 77% Cu–23% Ni no direct transition corresponding to $L_{2'} \rightarrow L_1$ in pure copper is observed. Waldén[9] has found no evidence for direct transitions in a cesiated sample of Ag:Mn.

From measurements of the near-normal-incidence reflectivity of the 87% Cu–13% Ni sample[7] we have deduced the optical constants for this material by using a Kramers-Kronig analysis. The optical constant ϵ_2 is shown in Fig. 3; ϵ_2 for pure copper from the work of Beaglehole[10] is also shown. ϵ_2 for copper exhibits two peaks, one at 2.4 eV and the second at 5.0 eV.[11] Various explanations for the origin of the second peak have been given. Ehrenreich and Philipp,[1] on the basis of optical-constant data and Segall's[7]

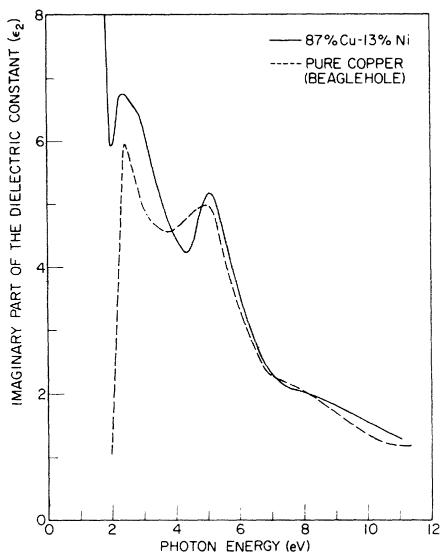

FIG. 3. ϵ_2 for 87% Cu–13% Ni and pure copper (Beaglehole, Ref. 10). For $h\nu \geq 2.1$ eV, structure in the two curves is quite similar, suggesting that the nature of optical transitions in the two materials is the same.

copper band calculations, attributed this peak to direct transitions near L and/or X. Cooper, Ehrenreich, and Philipp[12] concluded from model calculations that the 5.0-eV peak arose from direct transitions $X_5 \rightarrow X_4'$. Beaglehole[9] suggested that direct transitions at L might give an important contribution, but he also pointed out that a unique assignment of the peak's origin would be difficult because of the existence of several possible contributions. Mueller and Phillips[13] calculated ϵ_2 for copper assuming direct transitions and concluded that the second peak was due to $L_{2'} \rightarrow L_1$ transitions. From piezoreflectivity data, Gerhardt, Beaglehole, and Sandrock[5] attributed the second peak in ϵ_2 of copper to direct transitions $L_{2'} \rightarrow L_1$. Thus, most present interpretations based on direct transitions attribute the second peak to transitions at L. Krolikowski and Spicer,[3] on the other hand, have shown that both peaks in ϵ_2 can be fairly well accounted for by using a nondirect-transition model and an optical density of states deduced from photoemission data obtained from clean and cesiated copper.

The alloy data presented here confirm the predominantly nondirect nature of the optical transitions in copper. ϵ_2 for the 87%-Cu alloy (Fig. 3) bears a quite close resemblance to that for copper—both exhibit strong structure at 2.4 and 5.0 eV. At low photon energies ϵ_2 for the alloy differs from that of copper because of the large contribution of transitions from nickel d electrons in virtual bound levels, but the peaks at 5.0 eV are quite similar. Transitions for photon energies near 5.0 eV in the alloy are not direct, because of the fact that no direct transition is observed in the alloy photoemission data (Fig. 2). Of course, on fundamental grounds, direct transitions cannot be expected to occur in the alloy, since the alloy is a disordered system where the electronic states cannot be characterized by a single $\vec{k}$. Therefore, transitions in the alloy giving the 5.0-eV peak in ϵ_2 must be nondirect in nature (with possible variations in matrix elements). The close resemblance, both qualitative and quantitative, of the 5.0-eV peak in copper to that in the alloy indicates that this peak in copper must also be predominantly due to nondirect transitions. The relatively small contribution of the direct L transition in copper may provide some absorption in the photon-energy range 4.0-4.8 eV, where there is a sharp dip in the alloy absorption.

The lack of periodicity in the crystal potential would be sufficient to explain the apparent nonexistence of direct transitions in optical excitations of 87% Cu–13% Ni; however, the lack of importance of the $\vec{k}$-conservation rule for optical excitations of the d-derived states in pure copper must have a more fundamental cause. As suggested previously,[7] the resonant nature of the d-derived bands may provide for localization of the hole created by optical excitation for sufficient time to break the periodicity of the system and invalidate the $\vec{k}$-conservation criterion. Or this requirement may be removed by strong electron-electron interactions in the d-derived states, which would reduce the symmetry of the crystal Hamiltonian so that one-electron $\vec{k}$ vectors are not valid quantum numbers.[14] It does seem clear from the present data and the previous interpretations of copper photoemission data that nondirect transitions give the major contribution to structure in ϵ_2, with only a small contribution (<10%) from direct transitions near L.

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HIGH-RESOLUTION METHOD FOR CALCULATING SPECTRA OF SOLIDS

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A general method for calculating spectra of solids is developed, and the analytical expressions required for it are obtained and given. This procedure gives high resolution in the computed spectra, is at the same time also rapid and accurate, and has a wide range of applicability in fields of solid-state physics.

In a series of papers[1-4] a new method for calculating densities of states in solids has been described. This method has proved to be of much higher resolution, speed, and accuracy in comparison with the traditional root-sampling method. In its early stages this method was mainly applied to calculations of phonon densities of states of cubic,[2] hexagonal,[3] and tetragonal[4] crystals, but recently use has been made of it for the computation of electron densities of states[5-7] in solids. It can also be applied to other excitation densities of states such as magnons. The same procedure with some necessary modifications can be applied in principle to a variety of problems such as the computation of impurity modes in solids, tunneling conductance, vibronic transitions, incoherent inelastic scattering of slow neutrons, optical transitions in solids, etc. To these properties we refer here as spectra of solids. It can also be applied to thermodynamic quantities, Debye-Waller factors, thermal conductance, resistivity, and other properties which are obtained from averages over densities of states. This method has already been successfully applied to the computation of some of these spectra in numerous works, which will take too much space to be listed here. There is however one common inadequacy in these calculations which is explained presently. All the above-mentioned spectra consist of two factors, one of which is the relevant density of states and the other the transition probability, which is usually given by a square of some off-diagonal matrix element. Now in many experiments it is possible to measure the spectrum with high resolution, and one is in need of a procedure by which one can compute the spectrum to at least the same resolution. Such a resolution has so far been obtained only for the first factor, while the transition probability was taken into account in a much cruder way. The result of this is that the fine details of the computed spectrum could be significantly distorted. It is the purpose of the present Letter to show how to take the transition probability into account to the same accuracy as the density of states. In what follows we assume that the spectrum amplitude $I(\omega)$ is given by

$$I(\omega)=C\sum_j\int_{\mathrm{IBZ}}d^3\vec{q}\,F_j(\vec{q},\omega)\delta(\omega-\omega_j(\vec{q})), \tag{1}$$

where the integration is made over the irreducible part of the first Brillouin zone (IBZ). The summation over j is for the various eigenvalues $\omega_j(q)$ at each wave vector $\vec{q}$, as explained in I. ω is the angular frequency for which $I(\omega)$ is computed, and $F_j(\vec{q},\omega)$ represents the transition probability. C is some arbitrary normalization constant. In the following treatment we assume