# Breadths of resonant photoemission satellites and electron-excited direct-recombination emission

J. A. D. Matthew* and S. M. Girvin
*Surface Science Division, National Bureau of Standards, Washington, D. C. 20234*
(Received 21 November 1980)

Resonant photoemission involving core-hole excitation and electron emission arising from direct recombination of electron-excited resonant states are compared. At fixed photon energy the resonant emission has an energy distribution which is not broadened by the finite lifetime of the core hole and is therefore narrower than the corresponding Auger emission process. Electron-excited resonant states give rise to emission which can be isolated only if it is at a different energy from that of the main Auger channel as in the rare earths, but this emission is core-hole broadened. A coincidence experiment monitoring the energy loss of the incident electron and the energy distribution of the emitted electron is equivalent in resolution to resonant photon excitation.

There has been considerable interest recently in various effects associated with the decay of core excitations in solids. If an electron is excited from a core level to a localized state, it is possible for the system to de-excite by an autoionization process in which one electron fills the core hole and another is emitted into the continuum. The electron which was originally excited may either take part directly or remain as a spectator to the decay process. Such effects were first seen in the rare earths[1,2] where $4d^{10}4f^n \rightarrow 4d^9 4f^{n+1}$ excitations are accompanied by $4d^9 4f^{n+1} \rightarrow 4d^{10}4f^{n-1} + e$ transitions and other possible direct recombinations. Under electron excitation these appear as extra peaks on the high-energy side of the corresponding Auger transitions associated with $4d$ ionization.[1-5] The origin of such peaks was confirmed by comparison of the x-ray-excited and electron-excited Auger spectra of Sm.[2] High-energy x rays raise the $4d$ electrons to a high continuum state yielding only Auger electrons while electronic excitation produces both excitation (followed by direct recombination) and direct ionization. The dual origin of the secondary spectra of rare earths has been confirmed for EuO,[3] Er,[4] and Gd.[5]

Similar effects were seen independently in resonant photoemission in rare earths using synchrotron radiation. If the photon energy $h\nu$ is resonant with a particular $4d^{10}5p^6 4f^n \rightarrow 4d^9 5p^6 4f^{n+1}$ transition, and the excited state decays as described above, the emitted electron is at the same energy as that for direct $4f$ photoemission and Fano-type resonance profiles may occur.[6-10] The presence of resonances in the intensities of satellites in the valence-band photoemission of transition metals has been given a related interpretation[11,12]; $3p^6 3d^n \rightarrow 3p^5 3d^{n+1}$ transitions de-excite to a $3p^6 3d^{n-1}$ which would appear at first sight to lead to a $d$-band photoemission resonance, but differences in the screening for the direct and resonant processes leads to a resonant satellite offset from the main peak by the correlation energy of two $d$ holes.[13] Although there are differences in the detailed interpretation of the mechanism of the resonances, the importance of $d$-hole correlation is now fairly well established.[13-16] More recently, the phenomenon has been shown to be present, albeit in weaker form, in copper zinc,[12,17] and gallium[18] which have filled $d$ bands. One suggested mechanism involves resonant excitation to a core-hole-enhanced density of states $V^*$ just above the Fermi level[19,20] followed by decay via the $d$ electrons with the excited electron as a spectator to the process, i.e., $3p^6 3d^{10} V + h\nu \rightarrow 3p^5 3d^{10} VV^* \rightarrow 3p^6 3d^8 VV^*$. The number of electrons in the final state is different from that of direct $3d$ photoemission and the $3d^8$ state has been clearly isolated.

In GaP it has been possible to identify the $3p^5 V^*$ state as a core exciton,[18] and in this case it is also possible to observe the channel $3p^5 3d^{10} V^* \rightarrow 3p^6 3d^9$ (at the same energy as direct $3d$ photoemission). The $d^8$ final-state structure in GaP has been compared with the multiplet structure in the $M_{23}M_{45}M_{45}$ Auger process.[18] Similar effects have been observed in Zn-phthalocyanine.[17]

The purpose of this paper is to compare the information contained in photon-induced resonances and in direct-recombination emission following electron excitation by exploring properties which are in-

 

dependent of the detailed mechanisms of the various phenomena. Let us consider a simple model in which an electron is excited from a core state $A$ to an excited state $B$, which may be either a highly localized discrete state as in the rare earths or GaP or a hole-induced conduction-electron resonance at the Fermi level as in Cu, Zn, and Ga metals.[19,20] We do not consider systems in which the Auger line shape is controlled by the valence-band width due to delocalization of the final-state holes. The process under consideration is illustrated for photon excitation in Fig. 1(a) and for electron excitation in Fig. 1(b). Let us look at the following two decay channels:

(i) $A^{-1}B \rightarrow C^{-1}$ [Fig. 1(c)] in which the excited electron takes part in the nonradiative de-excitation along with an electron from state $C$. In GaP $A = 3p$, $B = V^*$, and $C = 3d$, so that this would correspond to a resonance in the $3d$ photoemission channel.

(ii) $A^{-1}B \rightarrow C^{-2}B$ [Fig. 1(d)] in which the excited electron is a spectator to the deexcitation as, for example, the $d^8$ satellite resonance in GaP or Ga metal.

Photon-induced resonances are observed in the following two ways:

(1) Constant initial-state spectroscopy which fixes the final-state excitation energy; i.e., observes the fixed electron-energy difference from the photon energy and measures the intensity versus photon energy.

(2) Fixing photon energy and observing the spectral structure in the electron emission.

The properties of a particular resonance may then be mapped on a three-dimensional intensity-relative electron-energy—photon-energy plot. We wish to point out some general properties of such "maps" by reference to some recent theoretical models[19,20] and experimental results.[18]

Let us first focus attention on decay mode (ii) and for the moment neglect the possibility of multiplet structure associated with the $C^{-2}$ final state. The intensity map will then have the general characteristics shown in the model of Davis and Feldkamp.[19] The intensity map obtained by Girvin and Penn[20] for this particular model is shown in Fig. 2, but the comments we wish to make apply quite generally to photon-induced resonances. In Fig. 2 zero photon energy corresponds to the $A \rightarrow B$ transition energy and zero *relative* electron energy (i.e., binding energy) corresponds to the peak of the resonant emission; e.g., for the $d^8$ resonance this would be $h\nu$ minus the energy required to generate two $d$ holes. The units along both axes are in terms of the hole lifetime breadth, and it is this choice of an energy unit that allows us to emphasize properties common to all such resonances.

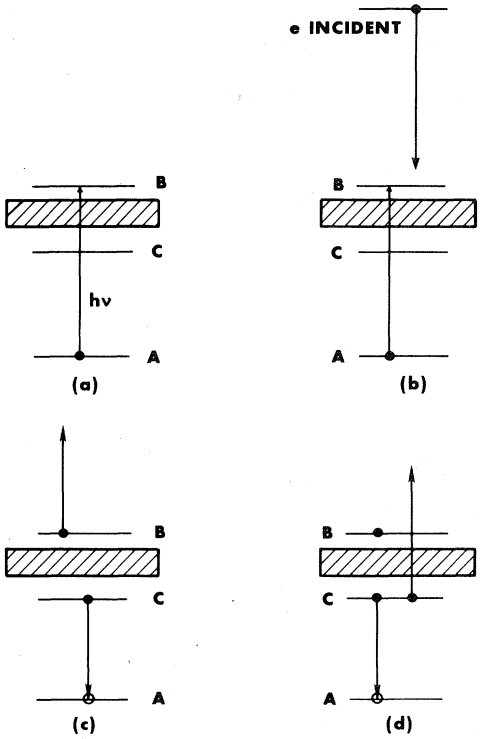


FIG. 1. (a) and (b): comparison of resonant photon excitation and electron excitation. (c) and (d): comparison of two channels of decay of the excitation.

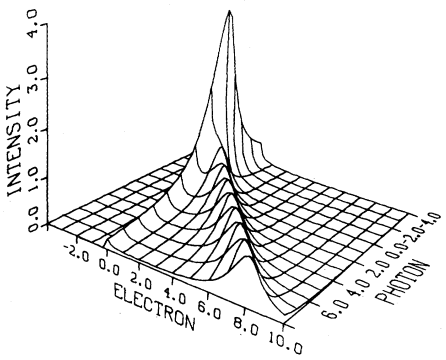


FIG. 2. Calculated secondary-electron-emission spectrum from the model of Girvin and Penn (Ref. 20). Emission intensity is plotted along the $z$ axis, the relative electron-emission energy along the $x$ axis, and the photon energy along the $y$ axis. The ridge at zero relative energy is the resonant photoemission peak, while the diagonal ridge represents the Auger spectrum. The energy units are in terms of the core-hole lifetime and a final-state $d$-hole lifetime of 0.1 units is assumed.

Let us first consider observation of the resonance by method (1). We set the electron relative energy at zero (e.g., on the $d^8$ satellite) and vary the photon energy. A broad resonance is observed whose strength is proportional to the enhancement in the optical absorption near the $A \rightarrow B$ transition energy and whose width is therefore controlled by the core-hole lifetime. In contrast, if we set the photon energy at the $A \rightarrow B$ transition energy a very sharp peak in the electron-energy distribution is found. The width of this peak is controlled by final-state lifetime effects and it does *not* carry any broadening associated with the core hole. This may be readily understood by noting that the core hole exists only as an intermediate step and is not present in the final state. The core electron is excited by a definite energy to a bound state or a sharp resonance in the continuum, and so the final state has its energy defined within the bounds of the lifetime broadening of that final state. The emission energy is then given by

$$E = h\nu - E_{\text{fin}} \tag{1}$$

so that the fluctuations in $E$ are controlled only by uncertainty in $E_{\text{fin}}$ (and broadening associated with chromaticity in the photon source). This will apply even if the excited electron does not take part in the decay as long as it remains localized for a period longer than the core-hole lifetime. If the excited electron rapidly delocalizes into the continuum, $E_{\text{fin}}$ is no longer uniquely defined and the total excitation energy is shared between the two outgoing electrons (the photoexcited electron and the Auger electron). The uncertainty in the division of this energy is controlled by the core-hole lifetime. If the core-hole lifetime is not apparent in the electron-emission breadth, it is nevertheless controlling the integrated emission intensity. As the photon energy is shifted off the peak-yield energy, the intensity of resonant emission decreases and a second peak emerges at fixed kinetic energy (not binding energy). This is the $ACC$ Auger peak following direct nonresonant ionization of $A$, and is broadened by the lifetime width of $A$ because, as mentioned above, the partitioning of energy between the core-hole state and the energy of the continuum electron is not controlled. This analysis is similar to that made by Yafet.[21] These arguments show why the core-hole width can be scaled out of the intensity map in Fig. 2. The width of the Auger peak in *electron energy* and the width of the satellite resonance in *photon energy* are both determined by the core-hole width.

Resonance path (1), which involves the excited electron in the decay, has exactly the same breadth properties. Again the breadth of the core hole helps to determine how intense the resonance is at a particular photon energy, but does not control the breadth of the emitted electron distribution. The phenomena may be rather more complicated than this in practice. It is possible that there are several resonant states due both to core-hole spin-orbit splitting and to multiplet structure in the final state. This will give rise to a number of broadened peaks along the photon axis and several resonances peaking at different energies along the electron-energy axis. In addition, the $C^{-2}$ final-state hole-hole interaction leads to multiplet structure in both the resonance and Auger decay channels, but each multiplet line will be broadened differently in its resonance and Auger structure. This phenomenon may be clearly observed in the recent experimental results of Chiang and Eastman[18] on GaP. Figure 3 reproduces a comparison of the $3p_{3/2}$ resonance decaying to a $3d^8V^*$ state excited at 106 eV (so that it avoids any substantial excitation of the $3p_{1/2}$ resonance which peaks at 110 eV) with the Auger spectrum following ionization of both the $3p_{3/2}$ and $3p_{1/2}$ states with a photon energy of 120 eV. The comparison is complicated by the fact that two different

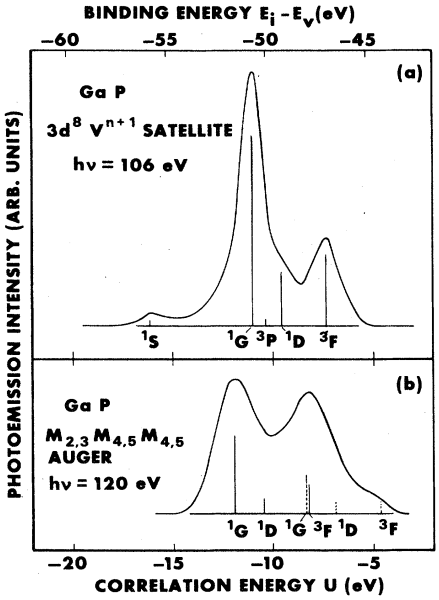


FIG. 3. Comparison of line shapes of (a) the photoemission satellite structure and (b) the $M_{23}M_{45}M_{45}$ Auger spectra of GaP after background subtraction [work of Chiang and Eastman (Ref. 18)]. Spectra are decomposed into multiplets with the length of the vertical lines representing relative intensity. The relative-energy axis represents the correlation energy $U$ as defined in Ref. 18.

core holes are excited, and by the fact that there is a shift in the final $d^8$-state excitation energies of about 1 eV due to the role of the spectator $V^*$ electron in affecting the hole-hole correlation energy. However, if we concentrate attention on the region of the $^1G$ peak at $-(12-13)$ eV relative energy, where contamination from the tails of the $M_2M_{45}M_{45}$ Auger peaks is weak, clear differences between the two spectra may be discerned. The Auger decay is broadened both by the $M_3$ core-hole lifetime of Ga of about 1.5 eV (Ref. 22) and by the lifetime broadening of the $d^8$ final state, while the resonance carries only the $d^8$ broadening and a breadth associated with imperfect monochromatization of the photon beam. Comparable effects are seen in Zn-phthalocyanine.[17]

In contrast, electron beams act rather like white-light sources as noted by Gerken *et al.*,[4] and cause both resonant excitation and ionization simultaneously. The effect is similar to carrying out an integration of intensity over photon energy in Fig. 2 and plotting the resulting intensity against *absolute* kinetic energy. This means that electron-excited direct-recombination emission is *always* broadened by the lifetime width of the core hole and so is inherently lower in resolution than a photon-excited resonance (provided that the photon energy is sharply defined).

Furthermore, whether one can distinguish direct-recombination emission from conventional Auger emission under electron excitation depends on whether the two processes peak at sufficiently different energies. Let us consider three cases.

*(a) The rare earths.* Here the $4d^{10}4f^n \rightarrow 4d^9 4f^{n+1}$ cross sections peak at an energy $E_{ex}$ well above[1,2] the $4d$ ionization threshold $W_{4d}$ and the final state involves only one $4f$ electron less than in the ground state (at an energy cost of $W_{4f}$). Hence the direct-recombination emission energy $E$ will peak at

$$E = E_{ex} - W_{4f} , \tag{2}$$

while the corresponding Auger energy is given by

$$E_{Auger} = W_{4d} - 2W_{4f} - U_{eff} , \tag{3}$$

where $U_{eff}$ is the effective Coulomb interaction between two $4f$ holes. $E - E_{Auger}$ is therefore of the order 10 eV and the direct-recombination emission can readily be resolved.[1-5]

*(b) GaP.* The $3p^5 3d^{10}V^* \rightarrow 3p^6 3d^9$ process will occur at the resonance energy (110 eV for $3p_{3/2}$) minus the $3d$ binding energy, i.e., at 91.2 eV relative to the Fermi level. This is just above the upper energy limit of the $M_2M_{45}V$ Auger process, but the resonance peak should be sharper than the broad-band-like Auger peak. On the other hand, the $M_{23}M_{45}M_{45}$ Auger peaks occur about 1 eV below the corresponding direct-recombination emission[18] and will be very difficult to separate from the main Auger peaks.

*(c) Cu, Zn, Ga.* Here the energies of the Auger and direct-recombination peaks are virtually indistinguishable, and separation of the two phenomena will not be possible.

The only way that direct recombination may then be isolated is by a coincidence experiment in which one detector measures the energy lost by the incoming electron (this is approximately equivalent to controlling the photon energy) and the other measures the energy distribution of emitted electrons, in which case core-hole broadening would *not* be observed.

In summary, resonant processes involving excitation of a core electron to a localized excited state have recently been observed using both photon and electron excitation. We have compared the two modes of excitation with particular reference to the breadths of the emitted electron distributions. The main points we wish to emphasize are as follows.

(1) At fixed photon energy the electron-energy distribution of resonantly excited-electron emission is broadened only by final-state effects and not by the width of the core hole essential to the resonance process. This has been illustrated with reference to the theoretical analysis by Girvin and Penn[20] of the Davis and Feldkamp model[19] and the experimental results of Chiang and Eastman.[18]

(2) Electron beams also cause localized excitations, but the energies of the direct-recombination emission are not always well separated from that of conventional Auger decay. Furthermore, when direct-recombination emission is well resolved as in the rare earths, it is broadened by the core-hole width.

(3) Photon-induced resonant emission is approximately equivalent to a coincidence experiment involving electron excitation where the energy loss of the incident electron is controlled so that the electron emission is then broadened only by final-state properties.

*Permanent address: Physics Department, University of York, Heslington, York, Y015DD, England.

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