

whose lattices are more anharmonic than the chlorides, exhibit much smaller discrepancies than the chlorides.

Finally, it should be emphasized that Eq. (1), and thereby Eq. (2), are based on the absolute rate theory.<sup>8</sup> Implicit in this theory is the assumption that the diffusive process can be described in terms of equilibrium statistical mechanics. Although there has been some criticism of this theory, it nevertheless has been very successful in treating diffusion and ionic conduction, and this success is generally taken as the strongest evidence for its validity.<sup>8</sup>

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## New Mechanism for Resonant Photoemission

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We present a mechanism for the resonance near the  $3p$  threshold in the photoemission associated with the two-hole bound state in metals such as Cu and Zn. It is based upon the strong interaction between the  $4s$ - $4p$  conduction-band electrons and the two bound holes (the  $3d^8$  configuration) resulting from the super Coster-Kronig decay of the  $3p$  core hole. This effect also occurs in Ni but is not dominant.

This Letter reports a new mechanism for resonant photoemission resulting from the super Coster-Kronig decay<sup>1</sup> of a  $3p$  core hole ( $3p^5 3d^{10} \rightarrow 3p^6 3d^8 \epsilon l$ ). Unlike the model described by Penn,<sup>2</sup> this mechanism is operative in metals with filled  $3d$  bands such as Cu and Zn. It is based upon the strong interaction between the  $4s$ - $4p$  conduction-band electrons and the two bound holes (the  $3d^8$  configuration) produced in the final state. Our calculations clearly exhibit a resonance in the  $3d^8$  satellite at fixed binding energy and the appearance above resonance of a separate, "Auger" peak at fixed kinetic energy.

Resonant photoemission in Ni metal was discovered by Guillot *et al.*<sup>3</sup> They observed that, for photon energy  $h\nu$  near the  $3p$  threshold (66 eV), the emission from the 6-eV satellite associated with the  $3d$  valence band was greatly enhanced.

Iwan, Himpfel, and Eastman<sup>4</sup> observed a similar, although weaker, resonance in Cu. They anticipate that such a resonance is a common feature of the row Cu, Zn, . . . , because atomic effects are important in their respective Auger spectra.<sup>5</sup> Since the Penn model gives no resonance when the  $3d$  bands are filled, it fails to explain the data in Cu. The presence of a satellite in Cu does not invalidate the Penn model for Ni, however. The mechanism proposed here is an additional effect which is probably dominant only in Cu, Zn, etc.

For simplicity, we consider only a single conduction band (analogous to the  $4s$ - $4p$  bands) into which the core electron is excited when a photon is absorbed. The Hamiltonian for this model has been described by Nozières and de Dominicis<sup>6</sup> for the x-ray edge problem. In the initial (ground)

state,

$$H_0 = \sum_{k=1}^N \epsilon_k a_k^\dagger a_k,$$

where  $a_k^\dagger$  is a creation operator for the  $k$ th orbital and  $N$  is the number of levels in the band. We assume that the energies  $\epsilon_k$  are ordered. The ground state is  $b^\dagger |\Phi_g\rangle$ , where  $b^\dagger$  creates a core electron at the origin,

$$|\Phi_g\rangle = \prod_{k=1}^L a_k^\dagger |0\rangle,$$

and  $L$  is the number of electrons in the band. The ground-state energy is

$$E_g = \sum_{k=1}^L \epsilon_k + \epsilon_c,$$

where  $\epsilon_c$  is the core energy. Following absorption, the Hamiltonian consists of  $H_0$  plus an interaction term due to the hole in the core level:

$$H = \sum_k \epsilon_k a_k^\dagger a_k - (U/N) \sum_k a_k^\dagger \sum_{k'} a_{k'}, \quad (1)$$

where  $U$  is a parameter describing the strength of the interaction. Since (1) is strictly a one-electron operator, it can easily be diagonalized<sup>7</sup>:

$$H = \sum_n \omega_n c_n^\dagger c_n, \quad (2)$$

where  $a_k = \sum_n S_{kn} c_n$  and the  $n$ th eigenvalue and eigenvector satisfy

$$(\epsilon_k - \omega_n) S_{kn} - (U/N) \sum_{k'} S_{k'n} = 0. \quad (3)$$

The  $\omega_n$  occur between the  $\epsilon_k$ , i.e.,  $\epsilon_{n-1} < \omega_n < \epsilon_n$ . The excited states of the system are

$$|\varphi_\alpha\rangle = \prod_{i=1}^{L+1} c_{n_i}^\dagger |0\rangle, \quad (4)$$

where  $\alpha$  stands for the set  $\{n_1, n_2, \dots, n_{L+1}\}$ . The energy is

$$E_\alpha = \sum_{i=1}^{L+1} \omega_{n_i}. \quad (5)$$

These states decay by super Coster-Kronig transitions into continuum states with the core

level filled but with two  $3d$  holes bound at the origin (the  $3d^8$  configuration).<sup>5</sup> Here we neglect dispersion of the two-hole state as well as its multiplet structure. The Hamiltonian for the conduction-band electrons in the presence of the two holes is the same form as (1), but with  $U$  replaced by  $U'$  which we expect to be much larger ( $U$  corresponds to  $Z=1$  and  $U'$  to  $Z=2$ ). Let us denote the eigenvalues and eigenvectors by  $\omega_{n'}$  and  $S_{kn'}$ , etc. The final states are denoted by  $|\psi_{\beta E}\rangle$  where

$$|\psi_{\beta E}\rangle = b^\dagger |\epsilon d^8 \varphi_{\beta'}\rangle, \quad (6)$$

$\epsilon$  stands for the photoemitted electron with kinetic energy  $\epsilon$ ,  $d^8$  signifies the two-hole state, and

$$|\varphi_{\beta'}\rangle = \prod_{i=1}^{L+1} c_{m_i'}^\dagger |0\rangle. \quad (7)$$

Here  $\beta$  stands for the set  $\{m_1, m_2, \dots, m_{L+1}\}$  and the energy of  $|\psi_{\beta E}\rangle$  is

$$E = \epsilon + \epsilon_c + E(d^8) + E_{\beta'}, \quad (8)$$

with

$$E_{\beta'} = \sum_{i=1}^{L+1} \omega_{m_i'}. \quad (9)$$

The energy for the creation of two bound holes is  $E(d^8)$ .

The matrix element for the decay of the discrete state  $|\varphi_\alpha\rangle$  into the continuum state  $|\psi_{\beta E}\rangle$ , denoted by  $V_{\beta\alpha}(E)$ , is

$$V_{\beta\alpha}(E) = V_0 \langle \varphi_{\beta'} | \varphi_\alpha \rangle. \quad (10)$$

Here  $V_0 \sim \langle 3p\ell | (e^2/R) | 3d3d \rangle$ , the super-Coster-Kronig matrix element (we neglect its dependence on  $\epsilon$ ). The total decay rate of  $\varphi_\alpha$  into all continua is  $\Gamma_0 = \pi |V_0|^2 (2\Gamma_0)$  ( $2\Gamma_0$  is the full width at half maximum).

The photoemission intensity  $N(h\nu, \epsilon)$  can be calculated from the general formalism for the interaction of discrete states with continuum states.<sup>8,9</sup> For the sake of brevity, the derivation is omitted here. The result is

$$N(h\nu, \epsilon) = 2\pi \sum_\beta |\sum_\alpha (\pi/\Gamma_0) (\pi^2 + Z_\alpha^2)^{-1/2} \langle \varphi_\alpha | T | \Phi_g \rangle V_{\beta\alpha}|^2 \delta(h\nu + E_g - \epsilon - \epsilon_c - E(d^8) - E_{\beta'}), \quad (11)$$

where

$$z_\alpha = \pi(h\nu + E_g - E_\alpha)/\Gamma_0 \quad (12)$$

and  $\langle \varphi_\alpha | T | \Phi_g \rangle$  is the dipole transition amplitude (it is assumed that the direct excitation of final states  $|\psi_{\beta E}\rangle$  can be neglected). The essential feature of (11) is the adding of amplitudes for the

excitation of the  $\beta$ th final state before squaring. The rate of absorption is [with use of (10) and (11)]

$$W(h\nu) = \int d\epsilon N(h\nu, \epsilon) = 2\pi (\pi/\Gamma_0) \sum_\alpha (\pi^2 + Z_\alpha^2)^{-1} |\langle \varphi_\alpha | T | \Phi_g \rangle|^2. \quad (13)$$

Threshold is at

$$h\nu_0 = E_{\alpha 0} - E_g = -\epsilon_c + \sum_{h=1}^{L+1} \omega_h - \sum_{k=1}^L \epsilon_k,$$

where  $E_{\alpha 0}$  is the lowest  $E_{\alpha}$ .

Now we let  $E^B = h\nu - \epsilon$  be the binding energy of the photoelectron. From (11), we see that the possible values of binding energy are

$$E_{\beta}^B = E(d^{\beta}) + E_{\beta}' - \sum_{k=1}^L \epsilon_k. \quad (14)$$

The lowest binding energy is

$$E_0^B = E(d^{\beta}) + \sum_{m=1}^{L+1} \omega_m' - \sum_{k=1}^L \epsilon_k,$$

which corresponds to the  $d^{\beta}$  satellite (the last two terms represent the relaxation of the conduction electrons around the two bound holes). Various authors<sup>7,10,11</sup> have discussed the numerical evaluation of finite systems of this type. A typical spectrum is shown in Fig. 1.

A strong resonance is observed at  $E^B \approx E_0^B$  as  $h\nu$  is swept through threshold  $h\nu_0$ . Physically, this corresponds to the core electron being excited to states near the Fermi energy  $\epsilon_F$  with the subsequent super-Coster-Kronig decay (one  $3d$

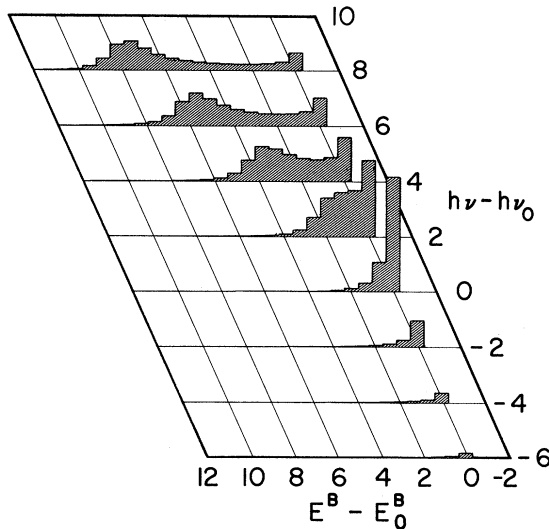


FIG. 1. Photoemission intensity vs binding energy for various photon energies near threshold. The calculation was performed for a constant density of states (band half filled,  $\epsilon_F = 10$ ) with  $U' = 10$ ,  $\Gamma_0 = 1$ , and  $N = 32$ .  $U$  was chosen to be zero so that the effects exhibited arise strictly from final-state interactions ( $U' \neq 0$ ). For  $U \neq 0$ , the absorption  $W(h\nu)$  is peaked at threshold, making the resonant peak (at fixed binding energy) even more pronounced than the Auger peak.

electron falls into the core hole while the other goes to  $\epsilon l$ ). Energy is only conserved overall, not in the intermediate absorption. Hence  $\epsilon$  tracks  $h\nu$ . Above resonance, this peak persists due to the singular nature of the off-diagonal elements of  $V_{\beta\alpha}$  [see below], and another peak develops. The latter corresponds to the core electron being excited to states with energy  $\approx (h\nu - h\nu_0) + \epsilon_F$ . The subsequent super-Coster-Kronig decay produces a photoelectron with  $\epsilon$  fixed at the Auger energy  $\epsilon_A = h\nu_0 - E_0^B$  or, equivalently, a binding energy  $E^B = h\nu - h\nu_0 + E_0^B$ . These features, which are characteristic of the experimental data, occur for a wide range of parameters and for various densities of states.

It is clear from these calculations that it makes sense to distinguish the Auger peak from the resonant peak only for  $h\nu$  well above resonance. As  $h\nu \rightarrow h\nu_0$ , the two peaks coalesce into one. A single physical process excites various final states  $\psi_{\beta E}$  with binding energy  $E_{\beta}^B$  as described above.

An interesting connection exists between the satellite peak for  $h\nu$  above resonance and the x-ray edge problem.<sup>6</sup> By evaluating the determinants  $\langle \varphi_{\beta}' | \varphi_{\alpha} \rangle$  contained in  $V_{\beta\alpha}$  [Eq. (10)] analytically, in a manner similar to that of Anderson,<sup>12</sup> we find that for  $U = 0$  and  $h\nu \gg h\nu_0$  the intensity  $I_0$  of the final state at  $E_0^B$  goes as  $N^{\lambda-1}$  in the limit  $N \rightarrow \infty$ . [Specifically, we evaluate the coefficient of the  $\delta$  function in (11) for  $\beta = 0$ .] Here  $\lambda = 2\delta'/\pi - (\delta'/\pi)^2$ , where the phase shift  $\delta'$  depends upon  $U'$ . Following arguments given by Dow and co-workers,<sup>11</sup> we find that the integrated intensity over a small interval  $\Delta E \sim W/N$  above threshold is

$$\int_{E_0^B}^{E_0^B + \Delta E} dE^B N(h\nu, h\nu - E^B) = I_0.$$

Using the dependence  $I_0 \sim N^{\lambda-1}$  and differentiating with respect to  $N$ , we obtain  $N(h\nu, h\nu - E^B) \sim 1/(E^B - E_0^B)^{\lambda}$  as  $E^B \rightarrow E_0^B$ . It is this singular behavior which causes the peak at  $E_0^B$  to persist for  $h\nu$  well above resonance.

If  $U' = U$ , then  $V_{\beta\alpha}$  is diagonal and there is only a single peak (the Auger peak) unless the absorption is peaked near threshold. In Ni,<sup>13</sup> the empty portion of the  $3d$  bands gives rise to a strong absorption over a narrow energy range and this leads to a strong resonance. For Cu, there may be a small amount of peaking due to the admixture of  $3d$  character in the conduction bands, but the consequences of  $U' \neq U$  must also be important. In Zn, this effect should be the dominant one. Although the band structure of the semi-

conductor Ge is, of course, much different from that of Cu or Zn, we nevertheless expect it to show a resonant satellite.

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## Band Theory of Metallic Polyacetylene

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*Ab initio* extended muffin-tin orbital calculations are presented for *trans*-polyacetylene heavily doped with AsF<sub>5</sub>, AsF<sub>6</sub>, SbF<sub>6</sub>, or PF<sub>6</sub>. For the hexafluoride dopants, AsF<sub>6</sub> and SbF<sub>6</sub>, hybridization of metal *s* states with polymer  $\pi$  states produces a partly filled metallic band. This provides a band model of metallic conductivity within and between chains consistent with anisotropic electric conductivity. This model should also apply to other doped conjugated polymers.

It has recently been discovered that doping can vary the electric conductivity of *trans*-polyacetylene [*t*-(CH)<sub>x</sub>] by about twelve orders of magnitude.<sup>1,2</sup> The highest conductivities (2000  $\Omega^{-1}$  cm<sup>-1</sup>) were observed after doping with 10% AsF<sub>5</sub> {*t*-[CH(AsF<sub>5</sub>)<sub>0.1</sub>]<sub>x</sub>}. AsF<sub>5</sub> and I<sub>2</sub> dopants have been most widely used but other halides and metal ions are also effective. For all these dopants, an abrupt semiconductor-metal transition takes place at 1–2% doping, and metallic conductivity is observed up to 20% doping. Recent x-ray absorption experiments<sup>3</sup> indicate that exposing *t*-(CH)<sub>x</sub> films to AsF<sub>5</sub> vapor actually leads to incorporation of AsF<sub>6</sub><sup>-</sup> as the effective dopant. ESR measurements<sup>4,5</sup> indicate that the charge carriers in lightly doped *p*-type semiconducting samples are not the usual free holes seen in inorganic semiconductors. Finally, other conjugate polymers are reportedly dopable up to metallic levels of conductivity.<sup>6–8</sup>

We present results of first-principles extended muffin-tin orbital (EMTO)<sup>9,10</sup> calculations on

pure, defect-free *t*-(CH)<sub>x</sub>, and on doped materials, denoted *t*-(CHA<sub>y</sub>)<sub>x</sub>, in the high doping regime,  $y = \frac{1}{6}$ . Dopants, *A*, studied are AsF<sub>5</sub>, AsF<sub>6</sub>, SbF<sub>6</sub>, and PF<sub>6</sub>. Our results show that heavy doping by AsF<sub>6</sub> and SbF<sub>6</sub> produces partly filled metal *s* bands which imply strong metallic conductivity along chains and weaker metallic conductivity between chains. Similar doping with AsF<sub>5</sub> yields a semiconductor with a completely filled As *s* valence band 2 eV below an empty C=C  $\pi$  conduction band. *t*-[CH(PF<sub>6</sub>)<sub>1/6</sub>]<sub>x</sub> is different in that its P *s* band is empty; charge transfer to F atoms partly empties a  $\pi$  band and implies metallic conductivity along, but not between, chains. This simple one-electron picture (a) explains anisotropic metallic conductivity; (b) substantiates the conclusion that AsF<sub>6</sub><sup>-</sup> is the effective dopant in highly conducting *t*-(CH)<sub>x</sub> films; and (c) predicts qualitatively different properties for samples doped with PF<sub>6</sub>.

Crystalline *cis*-(CH)<sub>x</sub> is known to have an orthorhombic unit cell containing two chains.<sup>11</sup> The