Theoretical study of Auger-photoelectron coincidence, Auger-electron, and x-ray emission spectra of Ni metal and related systems

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The Auger-photoelectron coincidence spectroscopy (APECS) spectrum is formulated in a one-step model, using the real-time nonequilibrium Green's-function method. The APECS L_{23}-VV spectra of Ni metal and alloys are analyzed, using a semiempirical configuration interaction (CI) model approach. For Ni metal and alloys, the L_2-L_3V Coster-Kronig (CK) decay rate ratios are obtained from the coincidence spectra. The ratio increases upon alloying due to more localized valence holes. The initial shakeoff-preceded L_3V-VVV transition contributes significantly to the L_2-L_3V-VVV APECS spectra of Ni metal and Ni_xFe_y ($x=80\%$, $y=20\%$) but not for Ni_xFe_y ($x=y=50\%$). The shakeoff intensity is most likely shifted towards smaller shakeoff energy in the latter system. The satellite intensity variation in the L_{23}-VV Auger-electron spectroscopy (AES) and L_{23}-V x-ray emission spectroscopy (XES) spectra of Cu metal, Cu halides, and Cu oxides (including high T_c superconductors) is explained in terms of the L_2-L_3V-VVV and $L_{23}V$-VVV decays and the final-state interaction. The initial shakeup state does not relax to the lowest-energy state before the core decay starts. [S0163-1829(98)00643-2]

I. INTRODUCTION

Nonadiabatic photoionization induces not only a relaxed state but also a number of excited states. When the excited states such as shakeup states cannot ''relax'' to the relaxed state of the same symmetry before the core decay starts, they can decay independently. Then the analysis of deexcitation spectra such as the Auger-electron spectroscopy spectrum (AES) becomes complicated. By changing the photoionization energy, one can select a particular initial state and decompose the spectrum according to the initial states, when the initial states are well separated. The shakeoff intensity depends on the photoionization energy.[1] Near the photoionization threshold, the shakeoff probability approaches zero. Thus the initial shakeoff-preceded decay rates could be much reduced compared to those at higher incident energy. The other method is to use coincidence spectroscopy such as the Auger-photoelectron coincidence spectroscopy (APECS).[2-4] By the Auger electron coincidence spectrum (AECS) one measures the Auger electron in coincidence to a particular initial state so that one can identify the final state(s) corresponding to the selected initial state. The spectrum is not influenced by the initial-state lifetime broadening and essentially consists of the final-state spectral functions, weighted by the Auger decay rate ratios. By the photoelectron coincidence spectrum (PECS) one measures the photoelectron in coincidence to a particular final state so that one can identify the initial state(s) corresponding to the selected final state. The spectrum is the initial-state spectral function (e.g., XPS initial core-hole spectrum) multiplied by its decay rate ratio to the selected final state and the spectral function of the selected final state. When the ''relaxation'' time from the excited states to the relaxed state is comparable to or faster than the decay time, one selects a particular final state available only for the decay from the relaxed state. Then the PECS will show the spectral lines at the initial excited states. For

the selected initial excited states the AECS will show the spectral lines at the final states which are available only for the decay from the relaxed state. The PECS (AECS) intensity is given in terms of the ''relaxation'' rate ratio so that one can estimate the ''relaxation'' time from the excited states to the relaxed state. Such a study is possible also by changing the photoionization energy.

Bennett *et al.*[5] measured the Ni L_3-VV AES of Ni metal and alloys. With increasing dilution of Ni, the ^1G term narrows, and the pronounced bulge to higher kinetic energy in the Ni metal spectrum changes to a concave shape, more pronounced for electropositive partner metals. This is correlated with the fact that the Ni d bands become narrower and pull away from the Fermi level. The spectral feature below the ^1G term is interpreted as a result of L_2-L_3-V CK preceded L_3V-VVV decay.[5,6] Whitefield *et al.*[7] investigated the mechanisms that lead to states with three and four $3d$ holes following L-shell photoionization of Ni metal with synchrotron radiation. They obtained the relative spectral intensities of Ni L_3-VV Auger satellites from three-and four-hole final states to the two-hole final state. They interpreted the three-hole final state in terms of L_2-L_3V-VVV decay and initial shakeup/off preceded L_3V-VVV decay. Recently, Thurgate *et al.*[8,9] studied the origins of three- and four-hole final states of Ni metal and NiFe alloys, using APECS. The L_2-L_3V-VVV and L_3V-VVV Auger energy coincide almost with the L_3-VV Auger energy. For NiFe alloy the bandlike final state disappears. The satellite below the ^1G term is due to the final-state shakeup/off. In Ni alloy the L_3V(shakeup)-VVV decay is more likely to occur than the L_2-L_3V-VVV decay. The L_3V(shakeoff)-VVV decay is much larger than the L_3V(shakeup)-VVV and the L_2-L_3V-VVV decay.

In the present paper using a simple configuration-interaction (CI) model approach, the AES and APECS of Ni metal and alloys are analyzed, in particular to obtain the

L_2-L_3V/L_2 decay rate ratios of Ni metal and alloys. In Sec. II we formulate the APECS by the real-time nonequilibrium Green's-function method, including the case when the ''relaxation'' time is comparable to or faster than the decay time. We describe the CI model approach and how we obtain the parameter values for Ni metal and alloys. In Sec. III we discuss the results. In Sec. IV we report the L_{23}-VV AES (XES) satellite/main line intensity ratios for different decay channels and corresponding decay energies and the L_2-L_3V decay rate ratios of Cu metal, Cu halides, and Cu oxides, including the high T_c superconductors. They are semiempirically evaluated. We discuss the origins of the satellite intensity variations in the L_{23}-VV AES and L_{23}-V XES spectra. In the Appendix we formulate the competition between the ''relaxation'' and decay of a two-state system, using the density-matrix formalism.

II. FORMULATION OF THE APECS

A. Theory

Using the nonequilibrium real-time Green's-function method,[10–12] which is suitable to describe the photoionization processes, the AES intensity $I_\omega(\varepsilon_A)$ for decay from the initial core-hole state c to the final states f is given by

$$I_\omega(\varepsilon_A) = \frac{-i}{2\pi} \sum_f \int |Z_c(\varepsilon)|^2 G_c^{++}(\varepsilon - \omega)$$
$$\times V_{cf}(\varepsilon_A) G_f^{+-}(\varepsilon + \varepsilon_A - \omega)$$
$$\times V_{cf}^*(\varepsilon_A) G_c^{--}(\varepsilon - \omega) d\varepsilon, \qquad (1)$$

$$G_c^{++}(\varepsilon - \omega) = \left(\varepsilon - \omega - \varepsilon_c - \sum_c (\varepsilon - \omega) \right)^{-1}, \qquad (2)$$

$$G_c^{--}(\varepsilon - \omega) = [G_c^{++}(\varepsilon - \omega)]^*, \qquad (3)$$

$$G_f^{+-}(\varepsilon + \varepsilon_A - \omega) = 2i \, \text{Im} \, G_f^{++}(\varepsilon + \varepsilon_A - \omega)$$
$$= 2i \, \text{Im} \left(\varepsilon + \varepsilon_A - \omega - \varepsilon_f \right.$$
$$\left. - \sum_f (\varepsilon + \varepsilon_A - \omega) \right)^{-1}. \qquad (4)$$

Here, Z_c is the dipole matrix element, G_c is the initial-state Green's function, V_{cf} is the Auger decay matrix element, and G_f is the final-state Green's function. (+) denotes the forward leg of the scattering process ($-\infty$ to ∞) and (−) the return leg ($+\infty$ to ∞). Σ_c is the self-energy of the core hole and ε_A, ε, and ω are Auger-energy, photoelectron energy, and photon energy, respectively. ε_c and ε_f are the unperturbed core-hole energy and the unperturbed final-state hole energy, respectively. Equation (1) can be rewritten as

$$I_\omega(\varepsilon_A) = \sum_f \int |Z_c(\varepsilon)|^2 A_c(\varepsilon - \omega) \frac{\pi |V_{cf}(\varepsilon_A)|^2}{\text{Im} \sum_c (\varepsilon - \omega)}$$
$$\times A_f(\varepsilon + \varepsilon_A - \omega) d\varepsilon. \qquad (5)$$

The AES is a superposition of the initial-state spectral function A_c convoluted by the final-state spectral function A_f, weighted by the decay rate ratio, $\pi |V_{cf}|^2/\text{Im} \, \Sigma_c$. Thus the initial- and final-state many-body effects cannot be separated. If either A_c or A_f is replaced by the δ function, one can separate the initial- and final-state many-body effects. The AECS is given by replacing A_c by $I_c \delta(\varepsilon - \omega - \tilde{\varepsilon}_c)$, where $I_c = A_c(\tilde{\varepsilon}_c)$. $\tilde{\varepsilon}_c$ is the core-hole energy of the selected initial state,

$$I_\omega(\varepsilon_A) = |Z_c(\tilde{\varepsilon}_c + \omega)|^2 \sum_f I_c \frac{\pi |V_{cf}(\varepsilon_A)|^2}{\text{Im} \sum_c (\tilde{\varepsilon}_c)} A_f(\tilde{\varepsilon}_c + \varepsilon_A).$$
$$(6)$$

The AECS is a superposition of the final-state spectral functions, weighted by the decay rate ratios. When the final-state interaction is negligible, the spectral intensity ratio is the decay rate ratio. Compared to the AES, in principle, the AECS is *not* broadened by the initial-state lifetime broadening. One of the important final-state interactions is the hole-hole interaction. Switching on the effective hole-hole interaction U for the two-hole Green's function within the framework of the Ladder approximation, the two-hole spectral function A_{lm} is given by

$$A_{lm}(\varepsilon) = \frac{1}{\pi} \, \text{Im} \, G_{lm}(\varepsilon) = \frac{N(\varepsilon)}{[1 - I(\varepsilon)U]^2 + [\pi U N(\varepsilon)]^2}.$$
$$(7)$$

I and $\pi N(\varepsilon)$ are the real and imaginary part of the unperturbed two-hole Green's function, respectively. $N(\varepsilon)$ is the density of two-hole states neglecting the electron-electron interaction and is therefore a convolution of the calculated one-particle density of states for a single hole $l(m)$. The singularities of G as a function of ε occur when $1 - I(\varepsilon)U = 0$. If the strength of perturbation U were such as to put $\varepsilon_r[1 = I(\varepsilon_r)U]$ well inside the band, then the resonance would be broad (resonance state in the band). As ε_r moves toward either edge of the band, $N(\varepsilon_r)$ decreases and the resonance becomes sharper. As we go outside the band, $N(\varepsilon_r)$ vanishes and ε_r has become the energy of a true bound state. The localization of the final two-hole state was theoretically studied by Sawatzky and Cini.[13,14] The only energy preventing the degeneration of the localized hole state into a purely delocalized hole state is the binding energy of the hole to its associated hole of the final two holes. By freeing the hole from another hole at the same site, we gain an energy of order $\sim Zb$ [here Z is a number of atoms at the nearest neighborhoods, b is the transfer (hopping) integral, thus Zb is the bandwidth], but we lose the energy U and have only a second-order energy $\sim Zb^2/U$ gained by allowing virtual transitions of the hole away from its site. Thus we may estimate $Zb \sim U$ as a reasonable value of the transition point from the delocalization of the two-hole state. When b is large, dielectric screening becomes a problem and U is naturally smaller. This is actually quite analogous to the exciton mechanism which changes from the localized one (Frenkel exciton) to the delocalized one (Wannier exciton) with the ratio between the bandwidth and U (here U is the electron-hole attraction).[15] The localization is also analogous to that of the impurity state[16] and to the ill behavior of the t matrix

of the normal state with respect to the Cooper pairing in the presence of an attractive two-body potential.[17]

For the PECS, instead of integration by photoelectron energy in Eq. (1), we replace the Auger energy ε_A by the selected one $\widetilde{\varepsilon}_A$,

$$I_\omega(\varepsilon) = |Z_c(\varepsilon)|^2 A_c(\varepsilon - \omega) \frac{\pi |V_{cf}(\widetilde{\varepsilon}_A)|^2}{\mathrm{Im} \sum_c (\varepsilon - \omega)} A_f(\varepsilon + \widetilde{\varepsilon}_A - \omega). \tag{8}$$

The PECS is the initial-state spectral function (e.g., the initial XPS core-hole spectrum) multiplied by its decay rate ratio and the final-state spectral function. When the final-state spectral function width is narrower than the initial-state spectral function width, the PECS width becomes narrower than the latter width. We consider the case of a two-step decay process such as L_2-L_3V-VVV decay. The AES for the $i \rightarrow j \rightarrow f$ decay process is given by

$$I_\omega(\varepsilon_A) = \frac{-i}{2\pi} \sum_{j,f} \int |Z_i(\varepsilon)|^2 G_i^{++}(\varepsilon - \omega) V_{ij}(\varepsilon_1) G_j^{++}(\varepsilon_1 + \varepsilon - \omega) V_{jf}(\varepsilon_A) G_f^{+-}(\varepsilon_1 + \varepsilon_A + \varepsilon - \omega) V_{jf}^*(\varepsilon_A)$$

$$\times G_j^{--}(\varepsilon_1 + \varepsilon - \omega) V_{ij}^*(\varepsilon_1) G_i^{--}(\varepsilon - \omega) d\varepsilon \, d\varepsilon_1. \tag{9}$$

Here, Z_i, G_i, V_{ij}, G_j, V_{jf}, and G_f are the dipole matrix element, the initial-state hole Green's function, the i to j decay matrix element, the intermediate-state Green's function, the j to f decay matrix element, and the final-state Green's function, respectively. ε_1, ε_A, ε, and ω are the i to j decay energy, the j to f decay energy, photoelectron energy, and photon energy, respectively. Equation (9) becomes

$$I_\omega(\varepsilon_A) = \sum_{j,f} \int |Z_i(\varepsilon)|^2 A_i(\varepsilon - \omega) \frac{\pi |V_{ij}(\varepsilon_1)|^2}{\mathrm{Im} \sum_i (\varepsilon - \omega)} A_j(\varepsilon_1 + \varepsilon - \omega) \frac{\pi |V_{jf}(\varepsilon_A)|^2}{\mathrm{Im} \sum_j (\varepsilon_1 + \varepsilon - \omega)} A_f(\varepsilon_1 + \varepsilon_A + \varepsilon - \omega) d\varepsilon \, d\varepsilon_1, \tag{10}$$

$$\mathrm{Im} \sum_i (\varepsilon - \omega) = \sum_j \pi \int |V_{ij}(\varepsilon_1)|^2 A_j(\varepsilon - \omega + \varepsilon_1) d\varepsilon_1, \tag{11}$$

$$\mathrm{Im} \sum_j (\varepsilon_1 + \varepsilon - \omega) = \sum_f \pi \int |V_{jf}(\varepsilon_A)|^2 A_f(\varepsilon_1 + \varepsilon - \omega + \varepsilon_A) d\varepsilon_A. \tag{12}$$

Here A_i, A_j, and A_f are the initial-state, intermediate-state, and final-state spectral functions, respectively. $\pi |V_{ij}|^2 / \mathrm{Im} \Sigma_i$ and $\pi |V_{jf}|^2 / \mathrm{Im} \Sigma_j$ are the decay rate ratios for i and j states, respectively. The AES can be interpreted as a "convolution" of AES for each transition (i to j and j to f). We note that the self-energies for the single-hole state i and the-two-hole state j are not simply given by the second-order Golden Rule formula anymore [Eqs. (11) and (12)]. The XPS spectrum is given by

$$I_\omega(\varepsilon) = |Z_i(\varepsilon)|^z A_i(\varepsilon - \omega). \tag{13}$$

The AECS and PECS are given by

$$I_\omega(\varepsilon_A) = \sum_{j,f} \int |Z_i(\widetilde{\varepsilon}_c + \omega)|^2 I_i \frac{\pi |V_{ij}(\varepsilon_1)|^2}{\mathrm{Im} \sum_i (\widetilde{\varepsilon}_c)} A_j(\varepsilon_1 + \widetilde{\varepsilon}_c) \frac{\pi |V_{jf}(\varepsilon_A)|^2}{\mathrm{Im} \sum_j (\varepsilon_1 + \widetilde{\varepsilon}_c)} A_f(\varepsilon_1 + \varepsilon_A + \widetilde{\varepsilon}_c) d\varepsilon_1, \tag{14}$$

$$I_\omega(\varepsilon) = \sum_j \int |Z_i(\varepsilon)|^2 A_i(\varepsilon - \omega) \frac{\pi |V_{ij}(\varepsilon_1)|^2}{\mathrm{Im} \sum_i (\varepsilon - \omega)} A_j(\varepsilon_1 + \varepsilon - \omega) \frac{\pi |V_{jf}(\widetilde{\varepsilon}_A)|^2}{\mathrm{Im} \sum_j (\varepsilon_1 + \varepsilon - \omega)} A_f(\varepsilon_1 + \widetilde{\varepsilon}_A + \varepsilon - \omega) d\varepsilon_1. \tag{15}$$

The formulas derived so far are valid when the "relaxation" time from the excited states to the relaxed state is much longer than the decay time so that each initial state decays by its own decay channels. Now we consider the case when the "relaxation" time is comparable to or faster than the decay time, particularly when a shakeup state "relaxes" to the relaxed state and then decays. The AES intensity increase for the decay from the relaxed state by the "relaxation" from the shakeup state is given by

$$I_\omega(\varepsilon_A) = \frac{-i}{2\pi} \sum_f \int |Z_s(\varepsilon)|^2 G_s^{++}(\varepsilon - \omega) V_{sM} G_M^{++}(\varepsilon + \varepsilon' - \omega) V_{Mf}(\varepsilon_A) G_f^{+-}(\varepsilon + \varepsilon' - \omega + \varepsilon_A) V_{Mf}^*(\varepsilon_A) G_M^{--}(\varepsilon + \varepsilon' - \omega)$$

$$\times V_{sM}^* G_S^{--}(\varepsilon - \omega) d\varepsilon \, d\varepsilon'. \tag{16}$$

Here Z_S, G_s, V_{SM}, G_M, V_{Mf}, and G_f are the dipole matrix element, the initial-state Green's function, the ''relaxation'' matrix element, the intermediate-state Green's function, the Auger decay matrix element, and the final-state Green's function, respectively. ε', ε_A, ω, and ε are the ''relaxation'' energy, Auger energy, photon energy, and photoelectron energy, respectively. Equation (16) can be rewritten as

$$I_\omega(\varepsilon_A) = \sum_f \int |Z_S(\varepsilon)|^2 A_S(\varepsilon-\omega) \frac{\pi|V_{sM}|^2}{\operatorname{Im}\sum_s(\varepsilon-\omega)} \left(\int A_M(\varepsilon+\varepsilon'-\omega) \frac{\pi|V_{Mf}(\varepsilon_A)|^2}{\operatorname{Im}\sum_M(\varepsilon+\varepsilon'-\omega)} A_f(\varepsilon'+\varepsilon-\omega+\varepsilon_A)d\varepsilon' \right) d\varepsilon. \tag{17}$$

The AES intensity increase is given by a convolution of the ''extra'' AES of the intermediate state with the XPS spectrum of the initial shakeup state, weighted by its ''relaxation'' rate ratio. In contrast to the ''normal'' AES for the relaxed state, A_M, the integrated spectral intensity of the intermediate state is 1.0, not equal to the XPS spectral intensity of the relaxed state because the former is not an interacting state anymore. Thus when the final state is not interacting and the energy dependence of the imaginary part of the self-energy is negligible, the AES intensity increase is given by a superposition of the intermediate-state spectral function, weighted by its Auger decay rate ratios, the initial-state spectral intensity, and the ''relaxation'' rate ratio.

So far we considered only one initial shakeup state. However, when several shakeup states can ''relax'' to the relaxed state, the AECS or PECS will be much more useful. When we select the initial shakeup state and study the final states of the decay channel available *only* for the relaxed state, the AECS is given by

$$I_\omega(\varepsilon_A) = \sum_f |Z_S(\tilde\varepsilon_c+\omega)|^2 I_S \frac{\pi|V_{SM}|^2}{\operatorname{Im}\Sigma_S(\tilde\varepsilon_c)} \int A_M(\tilde\varepsilon_c+\varepsilon') \frac{\pi|V_{Mf}(\varepsilon_A)|^2}{\operatorname{Im}\sum_M(\tilde\varepsilon_c+\varepsilon')} A_f(\varepsilon'+\tilde\varepsilon_c+\varepsilon_A)d\varepsilon'. \tag{18}$$

When the final state is not interacting and the energy dependence of the imaginary part of the self-energy is negligible, the AECS is given by a superposition of the spectral function of the intermediate state, weighted by its Auger decay ratios, the spectral intensity of the initial state, and the ''relaxation'' rate ratio. When we select the final state available only for the decay from the relaxed state, the PECS is given by

$$I_\omega(\varepsilon) = |Z_S(\varepsilon)|^2 A_S(\varepsilon-\omega) \frac{\pi|V_{sM}|^2}{\operatorname{Im}\sum_S(\varepsilon-\omega)} \left(\int A_M(\varepsilon+\varepsilon'-\omega) \frac{\pi|V_{Mf}(\tilde\varepsilon_A)|^2}{\operatorname{Im}\sum_M(\varepsilon+\varepsilon'-\omega)} A_f(\varepsilon'+\varepsilon-\omega+\tilde\varepsilon_A) \right) d\varepsilon'. \tag{19}$$

When the selected final state is not interacting and the energy dependence of the imaginary part of the self-energy is negligible, the PECS is given by the initial-state spectral functions, weighted by its ''relaxation'' rate ratio and the Auger decay rate ratios for the intermediate state. Once the Auger decay rate ratio of the relaxed state and the XPS spectral intensities of the initial states are known, from either PECS or AECS one can obtain the ''relaxation'' rate ratios for the initial excited states. So far the experimental study of competition between the ''relaxation'' and decay is very limited. The synchrotron study of the C (core level)-VV AES spectra of adsorbates such as CO on a Ni metal surface was made. However, this study is focused on the fast relaxation from the resonantly core-level excited state to the core-level ionized state by the delocalization of the resonantly excited electron to the metal substrate before the decay starts. We refer to Refs. 18 and 19 for details.

In the present approach, we write the ground-state configuration of Ni metal as a linear combination of atomic Ni d^9 and d^{10} wave functions,

$$|g\rangle = \cos\theta_0|d^9\rangle - \sin\theta_0|d^{10}\rangle. \tag{20}$$

The $|d^n\rangle$ includes the appropriate s electrons and must be nearly degenerate in the ground state because with 9.4 elec-

trons in the Ni d band both configurations contribute to the ground state. The core-hole state is $c|i\rangle$, where c annihilates a core electron and the indices i refer to various possible configurations. The only influence of the core hole is to introduce a potential which changes the energetics of the various possible configurations relative to the energies in the ground state. Then the valence electron configurations describing the core-hole states are determined by a linear combination of the same valence electron configurations as those describing the ground state. We thus write the initial main line state $|m\rangle$ and the satellite state $|s\rangle$ as

$$|m\rangle = \cos\theta_c|cd^9\rangle - \sin\theta_c|cd^{10}\rangle, \tag{21}$$

$$|s\rangle = \sin\theta_c|cd^9\rangle + \cos\theta_c|cd^{10}\rangle, \tag{22}$$

In the sudden approximation, the spectral intensity is given by the overlap between the ground state and the core-hole states. We consider the decay channel starting from $|cd^9\rangle$ ($|cd^{10}\rangle$), where a state like $|d^7\rangle$ ($|d^8\rangle$) is reached. These states, however, cannot be directly identified as the final states, since they are coupled. The final states $|fm\rangle$ and $|fs\rangle$ are given by

$$|fm\rangle = \cos\theta_f|d^7\rangle - \sin\theta_f|d^8\rangle, \tag{23}$$

$$|fs\rangle = \sin\theta_f|d^7\rangle + \cos\theta_f|d^8\rangle. \tag{24}$$

To calculate V_{ij} $[i=|m(s)\rangle$, $j=|fm(fs)\rangle]$, we introduce $\langle cd^{10}|V|d^8\rangle=V_m$ and $\langle cd^9|V|d^7\rangle=V_s$. So far the final-state interaction is neglected. In the present case, $|fm\rangle$ ($|fs\rangle$) state is dominated by the $|d^8\rangle$ ($|d^7\rangle$) configuration. Thus the final-state interaction is approximately described also by Eqs. (23) and (24) by approximating $|fm\rangle$ ($|fs\rangle$) by $|d^8\rangle$ ($|d^7\rangle$). We consider only the $|m\rangle$ to $|fm\rangle$ and $|s\rangle$ to $|fs\rangle$ decay channels because the rest of the decay channels, including the interference terms, are very small. We neglect the energy dependence of the decay rates.

B. Numerical procedure

1. Metal Ni

The Ni metal ground-state d population is 9.4 and θ_0 is obtained from Eq. (20). The L_2 and L_3 XPS satellite/main line spectral intensity ratios of Ni metal semiempirically obtained by Whitefield et al.[7] are 0.49 ± 0.05 and 0.42 ± 0.04, respectively, while those obtained by Hillebrecht et al.[20] are 0.39 ± 0.02 and 0.41 ± 0.02, respectively. We use the former values to obtain θ_c because the satellite intensity is expected to be smaller for the L_3 level.[21] The L_{23}-VV AECS of Ni metal consists of the bandlike state, the two-hole bound state, and the three-hole shakeup state, whose relative spectral intensity ratios are not reported.[9] The ratios estimated from the spectrum are 0.45, 1.0, and 0.267, respectively. θ_f is obtained from Eqs. (23) and (24) by using the third ratio. Z is given by the cross sections calculated by Scofield.[22] To evaluate the L_3-VV and L_3V-VVV AES intensity, the decay widths of L_3 and L_3V are assumed to be the same. The V_s/V_m ratio is obtained by calculating the L_3V-VVV/L_3-VV AES intensity ratio and comparing with the experimental one (0.419 ± 0.04).[7] Then the L_2-L_3V decay rate ratio is obtained by calculating the L_3V-VVV/L_2-L_3V-VVV AES intensity ratio and comparing with the experimental one (1.44).[7] We calculate the L_2-L_3V-VVV/L_2-VV AECS intensity ratio. For the L_2-L_3V-VVV transition, the $|cd^{10}\rangle$ ($|cd^9\rangle$) ($c=L_2$) decays to $|cd^9\rangle$ ($|cd^8\rangle$) ($c=L_3$) by L_2-L_3V decay and then decays to $|d^7\rangle$ ($|d^6\rangle$). As the mixing between $|d^7\rangle$ ($|cd^9\rangle$) and $|d^6\rangle$ ($|cd^8\rangle$) ($c=L_3$) is small, the intermediate (final) state can be assumed to be dominated by $|cd^9\rangle$ ($|d^7\rangle$). Then only $|cd^{10}\rangle$ of the initial main line state will contribute to decay to $|d^7\rangle$ and the L_3V-VVV transition rate will be given by $|V_s\sin\theta_c|^2$ ($\sin\theta_c$ is the weight of $|cd^{10}\rangle$ in the initial L_2 hole state).

2. Ni alloy

Thurgate et al. measured the PECS and AECS of two kinds of Ni alloy.[8,9]

(i) Ni_xFe_y ($x=80\%$, $y=20\%$).[8] The L_2-L_3V-VVV/L_3-VV PECS intensity ratio is 0.37 ± 0.05 (see Sec. III B for how this ratio is obtained). The L_3V-VVV/L_2-L_3V-VVV PECS intensity ratio is 1.6 ± 0.2. The ratio does not include the L_3V-VVV decay from the L_3V shakeoff state. The XPS satellite/main line intensity ratio is not reported. The ratio estimated from the spectrum is about 0.6. We use this ratio to obtain θ_c. The ratios for the L_2 and L_3 levels are assumed to be the same. For θ_f the final-state shakeup intensity is assumed to be the same as that for Ni_xFe_y ($x=y=50\%$). The L_3 and L_3V total decay rates are assumed to be the same. The product of the L_2-L_3V-VVV/L_3-VV PECS intensity ra-

TABLE I. The ionized state d population, the L_2-L_3V decay rate ratio, and the L_2-L_3V-VVV/L_2-VV AECS intensity ratio of Ni metal.

State	d population
ground state	9.4
initial main line state	9.91 (L_3) 9.93 (L_2)
initial satellite state	9.09 (L_3) 9.07 (L_2)
final main line state	7.84
final satellite state	7.16

	Theory	Experiment (Ref. 8)
L_2-L_3V-VVV/L_2-VV AECS	1.62	4.0
V_s/V_m ratio	1.02	
L_2-L_3V/L_2 decay rate ratio	0.63	

tio and the L_3V-VVV/L_2-L_3V-VVV PECS intensity ratio is the L_3V-VVV/L_3-VV PECS intensity ratio. The V_s/V_m ratio is obtained by calculating the L_3V-VVV/L_3-VV PECS intensity ratio and comparing with the experimental one. The L_2-L_3V decay rate ratio is obtained by calculating the L_3V-VVV/L_2-L_3V-VVV PECS intensity ratio and comparing with the experimental one. We calculate the L_2-L_3V-VVV/L_2-VV AECS intensity ratio. The ground-state d population is assumed to be either 9.4 or 9.6.

(ii) $Ni_xFe_y(x=y=50\%)$.[9] The estimated relative spectral intensity of the three-hole shakeup state to the two-hole state is 0.259, while the one for Ni metal is 0.267. There is hardly any change in the final-state shakeup probability on alloying. The estimated L_3 XPS satellite intensity increase from Ni metal is about 20%. For a comparison of the XPS satellite intensity with the Ni metal one, Thurgate et al.[9] used the L_3V-VVV and L_3-VV PECS spectrum of Ni metal. Unless the Auger decay branching ratios are the same, the L_3V-VVV/L_3-VV PECS intensity ratio is not equal to the XPS satellite/main line intensity ratio. When the final-state interaction is negligible, the ratio is equal to the L_3V-VVV/L_3-VV AES intensity ratio. Then the ratio is 0.419.[7] This ratio happens to be the same as the XPS satellite/main line intensity ratio (0.42). Then taking into account the estimated XPS satellite intensity increase from Ni metal (about 20%), the XPS satellite/main line intensity ratio is 0.504. However, a rough estimate of the ratio from the spectrum is about 0.75. We consider also this ratio. The ratio is assumed to be same for both L_2 and L_3 levels. The L_2-L_3V-VVV/L_3-VV AECS and L_3V-VVV/L_2-L_3V-VVV PECS intensity ratios are not available. Only the L_2-L_3V-VVV/L_2-VV AECS intensity ratio is available (not reported but estimated from the spectrum). Thus we assume $V_s=V_m$ and calculate the L_2-L_3V-VVV/L_2-VV AECS intensity ratio to obtain the L_2-L_3V decay rate ratio. The ground-state d population is assumed to be either 9.4 or 9.6.

III. RESULTS AND DISCUSSION

A. Metal Ni

In Table I we summarize the d populations of ionized states, the L_2-L_3V/L_2 decay rate ratio, and the V_s/V_m ratio.

As the ionized state approximately consists of a single configuration, we denote the initial main line and satellite states simply as L and LV, respectively. The calculated L_2-L_3V decay rate ratio is 0.63, while the semiempirical ratio for Cu metal[23] is 0.63. The Auger decay rate is fairly independent of Auger energy and the final-state potential because the Auger energy is large. Thus the presence of an extra valence hole does not affect the decay rate and the V_s/V_m ratio becomes nearly 1.0. Then the Auger decay branching ratios are independent of the presence of an extra hole and the L_3V-VVV/L_3-VV AES intensity ratio becomes equal to the L_3V/L_3 XPS intensity ratio. As the shakeoff intensity approaches zero near photoionization threshold, the L_3V-VVV/L_3-VV AES intensity ratio obtained at 868 eV photon energy[7] excludes a large part of the shakeoff contribution. The V_s/V_m ratio and the L_2-L_3V-VVV/L_3-VV AES intensity ratio should be independent of incident energy because the Auger energy is independent of incident energy. Then the L_2-L_3V decay rate ratio determined from the L_2-L_3V-VVV/L_3-VV AES intensity ratio, using the V_s/V_m ratio obtained from the L_3V-VVV/L_3-VV AES intensity ratio, should be incident energy independent. When $V_s = V_m$ and the L_3V-VVV decay rate is approximated by $V_s{}^2$, the L_2-L_3V-VVV/L_2-VV AECS intensity ratio is the L_2-L_3V/L_3 decay rate ratio and the L_2-L_3V-VVV/L_3-VV AECS intensity ratio is about half of the L_2-L_3V decay rate ratio (1/2 comes from the approximate ionization cross-section ratio). Thus the ratios are independent of the LV/L intensity ratio. The L_2-L_3V-VVV/L_2-VV AECS intensity ratio can be used to obtain approximately the L_2-L_3V decay rate ratio. For Cu metal the ratio estimated from the L_2-L_3V-VVV and L_2-VV AECS reported by Haak et al.[2] is about 1.6. Then we obtain the L_2-L_3V decay rate ratio of 0.62, which agrees well with the aforementioned value.[23] Wassdahl et al.[24] studied the L_{23}-V x-ray emission spectrum XES of Cu metal using photon excitation energy close to and above the ionization thresholds. From their data we obtain the L_2-L_3V decay rate ratio of 0.69. The Auger decay width of Cu metal reported by Wassdahl et al.[25] is 0.37 eV. This gives the L_2-L_3V decay width of 0.83 eV, while the authors of Ref. 23 reported the Auger decay width of 0.34 ± 0.05 eV and the L_2-L_3V decay width of 0.56 eV. From the XPS measurements the L_2-L_3V decay width is determined to be 0.68 eV.[26] The theoretical Auger decay width for a Cu atom is 0.61 eV.[27] If we use the experimental L_2-L_3V decay width and the Auger decay width, we obtain the L_2-L_3V decay rate ratio of 0.65. The ratios for Cu metal obtained from the AES and XES data are within 5% deviations from the experimental one. The theoretical Auger width for a Ni atom is 0.53 eV.[27] Scaling the experimental width of Cu metal, the estimated Auger width for Ni metal is 0.32 eV. Then we obtain the L_2-L_3V decay width of 0.55 eV for Ni metal.

The calculated L_2-L_3V-VVV/L_2-VV AECS intensity ratio (1.62) of Ni metal is quite close to the experimental Cu metal ratio (1.6) but much smaller than the estimated experimental one (4.0).[9] There is a large background in the L_2-L_3V-VVV AECS spectrum of Ni metal compared to the spectra of NiFe and Cu metal. The background is due to the final-state shakeoff. The relative final-state shakeoff intensity in the L_3-$VV(L_2$-L_3V-$VVV)$ AECS of NiFe is reduced to about one-half (one-third) of Ni metal. The shakeoff inten-

sity is determined by the weight of the unoccupied density of states of Ni $3d$ character in the presence of an extra hole(s) and its position above the Fermi level into which the electrons scatter. The Ni d–state density at the Fermi level drops as the Ni concentration is reduced. When the $3d$ band is filled, the contribution due to an unoccupied Ni $3d$ character in other bands becomes more important.[20] The localized atomiclike VV and VVV final-state energies are given by $2E_d + U$ and $3E_d + 3U$, respectively. Here E_d and U are the valence hole energy and the effective hole-hole interaction, respectively. The ‘‘self-energies’’ of the renormalized valence hole in the VV and VVV states are $U/2$ and U, respectively. The ratio of ‘‘self-energy’’/W (W is the bandwidth) increases as the number of holes increases. Then the L_2-L_3V-VVV final state is more localized than the L_3-VV one. This explains why on alloying (with localization) the L_2-L_3V-VVV AECS width decreases more than the L_{23}-VV AECS width does. We note that the AECS width is in principle due to the final-state lifetime broadening.

The L_3V(shakeoff)-VVV at the L_2 state energy can contribute to the L_2-L_3V-VVV AECS intensity. For Ni_xFe_y ($x = 80\%$, $y = 20\%$), the L_3V(shakeoff)-VVV PECS intensity at the L_2 state energy is as large as the L_3V(shakeup)-VVV PECS intensity and is 1.6 times larger than the L_2-L_3V-VVV PECS intensity.[8] Unfortunately, the L_2-L_3V-VVV and L_3V-VVV PECS of Ni metal are not available. Comparing the L_3V-VVV and L_2-L_3V-VVV PECS profile of Ni alloy with the L_2-L_3V-VVV AECS profile of Ni metal, it would be reasonable to assume that the L_3V(shakeoff)-VVV decay contributes to the rest of the L_2-L_3V-VVV AECS intensity. If so, the L_3V-VVV/L_2-L_3V-VVV PECS intensity ratio at L_2 state energy is 1.47, while that for Ni_xFe_y ($x = 80\%$, $y = 20\%$) is 1.6. The L_3V shakeoff intensity at L_2 state energy in Ni metal is as large as in Ni_xFe_y ($x = 80\%$, $y = 20\%$). The $(L_2$-L_3V-$VVV + L_3V$-$VVV)/(L_2$-$VV)$ AECS intensity ratio is approximately given by $XY(Z+1)+Z$. Here, X is the L_3/L_2 ionization cross-section ratio, Y is the relative initial shakeoff/main line intensity ratio at L_2 level ionization energy, and Z is the L_2-L_3V/L_3 decay rate ratio. For Ni metal we obtain 0.44 for the relative initial shakeoff/main line intensity ratio at L_2 level ionization energy.

The L_3VV double shakeoff state is observed at 12.5 eV by Bosch et al.[21] Their ‘‘rough’’ estimate of the L_3VV/L_3 intensity ratio is as small as 2–3%. Thus the authors of Ref. 7 neglected the L_3VV-$VVVV$ decay and concluded that the $VVVV$ state is mainly created by the L_2V-L_3VV-$VVVV$ decay. The L_3VV double shakeoff intensity is suppressed at 868 eV photon energy. The L_3VV-$VVVV$ decay can contribute to the smaller Auger-energy region where the final-state shakeoff is considered to dominate. The background intensity increase in the L_2-L_3V-VVV AECS of Ni metal compared to NiFe could be due to the L_3VV-$VVVV$ decay. The L_2-L_3V-VVV or L_3V-VVV PECS intensity of Ni_xFe_y ($x = 80\%$, $y = 20\%$) includes the L_3VV-$VVVV$ decay because the selected final state includes the $VVVV$ state.

If the L_3V state ‘‘relaxes’’ to the L_3 state before the decay starts, the L_3V-L_3-VV decay channel opens and the L_3-VV AES intensity increases by a factor of $(1+R)$, while the L_3V-VVV AES intensity decreases by a factor of $(1-R)$.

TABLE II. The ionized state d population, the L_2-L_3V decay rate ratio, and L_2-L_3V-VVV/L_2-VV AECS intensity ratio of Ni_xFe_y ($x=80\%$, $y=20\%$).

State	d population	
ground state	9.4	9.6
initial main line state	9.95	10.0
initial satellite state	9.05	9.0
final main line state	7.84	7.95
final satellite state	7.16	7.05
	Theory	Experiment (Ref. 8)
L_2-L_3V-VVV/L_2-VV AECS	7.10 6.27	7.0
V_s/V_m ratio	0.991 0.993	
L_2-L_3V/L_2 decay rate ratio	0.74 0.70	

TABLE III. The ionized state d population, the L_2-L_3V decay rate ratio, the L_2-L_3V-VVV/L_2-VV AECS and L_3V-VVV/L_2-L_3V-VVV PECS intensity ratios of Ni_xFe_y ($x=y=50\%$). An asterisk denotes the L_3V initial shakeup state.

State	d population	
ground state	9.4	9.6
initial main line state	9.93	10.0
initial satellite state	9.07	9.0
final main line state	7.84	7.95
final satellite state	7.16	7.05
	ratio	
	$d=9.4$	$d=9.6$
L_2-L_3V-VVV/L_3-VV AECS	0.36	0.38
L_3V-VVV^*/L_2-L_3V-VVV PECS	1.40	1.33
L_2-L_3V/L_2 decay rate ratio	0.73	0.72

The L_3V-VVV/L_3-VV AES intensity ratio decreases by a factor of $(1-R)/(1+R)$. R is the L_3V spectral intensity multipled by the L_3V-L_3 ''relaxation'' rate ratio [Eq. (17)]. Judging from the present results, we can conclude that the ''relaxation'' does *not* occur. The APECS spectrum of Ni metal was never discussed from this viewpoint. The APECS is one of the methods to study the ''relaxation'' time [Eqs. (17)–(19)]. This is a very important issue for the systems where the core-hole screening mechanism is governed by the charge-transfer (CT) screening (e.g., adsorbates, Cu halides, and oxides). It would be interesting to measure the C-VV PECS of CO adsorbed on Cu metal in coincidence with the ''backbonding peak'' to study whether all three initial states will contribute to the decay. The ''backbonding peak'' is the final state of Auger decay involving the electron occupied in the core-hole CT screening orbital and can be reached only from the initial core-hole shakedown (relaxed) state. If all three initial states contribute to the decay, then the other initial states relax to the shakedown state before the decay starts. The study contributes to understanding the characters of initial states. APECS can be used to classify the characters of both initial and final states.

B. Ni_xFe_y ($x=80\%$, $y=20\%$)

In Table II the present results are summarized. For $d=9.4$ and 9.6, the L_2-L_3V decay rate ratios are 0.74 and 0.70, respectively. The ratios are larger than that for Ni metal (0.63). If the Auger decay rate does not change from the metal case, then we obtain the L_2-L_3V decay rate of 0.91 and 0.75 eV, respectively. The L-LV decay rate increases from the metal case by 65% and 36%, respectively. Upon alloying, the valence band narrows and the valence hole(s) are more localized than in metal. As a result, the final-state potential becomes more attractive. The L_2-L_3V decay rate is very energy dependent near threshold. As the potential becomes more attractive, the decay rate becomes larger near threshold. The L_2-L_3V energy is small (about 10 eV) and given by ΔE-E_d-U_{cd} (here ΔE is the spin-orbit-splitting energy for the L_{23} levels and U_{cd} is the L_3 hole–valence hole interaction). As the valence hole becomes more localized, the CK energy becomes smaller. Thus the L_2-L_3V decay rate is expected to increase upon alloying. On the other

hand, the Auger decay rate is fairly independent of the final-state potential change and the decay energy. The Auger energy decrease is small (about 1 eV or less). Thus upon alloying, the Auger decay rate may decrease slightly due to the final-state potential change. The L_3 state widths of a large number of Ni alloys tend to decrease compared to Ni metal (about 5–10%).[5] Then the aforementioned L_2-L_3V decay rate decreases only by about 5–10%. The L_2 and L_3 level widths obtained by high-resolution XPS are desirable.

For $d=9.4$ and 9.6, the calculated L_2-L_3V-VVV/L_2-VV AECS intensity ratios are 2.73 and 2.41, respectively. If we include the LV(shakeoff)-VVV decay, the ratios become 7.10 and 6.27, respectively. The experimental ratio is about 7.0 (it is not reported but estimated from the AECS spectrum). The final-state shakeoff is much suppressed in the L_2-L_3V-VVV AECS as in NiFe but it is slightly more enhanced in the L_2-VV AECS than in NiFe. The present good prediction of the L_2-L_3V-VVV/L_2-VV AECS intensity ratio shows that the L_3V(shakeoff)-VVV decay contributes to the L_2-L_3V-VVV AECS intensity. Thus the AECS ratio is *not* equal to the L_2-L_3V/L_3 decay rate ratio. The conclusion that the L_2-L_3V decay rate decreases from Ni metal to NiFe because the L_2-L_3V-VVV/L_2-VV AECS intensity ratio decreases[9] appears to be incorrect. The L_3-VV PECS intensity for the main line state can be obtained by multiplying the L_3-VV PECS intensity for the selected final state by the ratio of L_3-VV AECS intensity at the main line state to that at the selected final state. From the L_2-L_3V-VVV/L_3-VV PECS intensity ratio one can obtain approximately the L_2-L_3V decay rate ratio.

C. Ni_xFe_y ($x=y=50\%$)

The results are summarized in Table III. The calculated L_2-L_3V-VVV/L_3-VV AECS intensity ratio for $d=9.4$ is 0.36(0.38), while that for $d=9.6$ is 0.38(0.39). The L_2-L_3V decay rate ratios for $d=9.4$ and 9.6 are 0.73(0.75) and 0.72(0.71), respectively. The values inside the parentheses are obtained when the L_3V/L_3 intensity ratio of 0.75 is used. The L_2-L_3V-VVV/L_3-VV AECS and the L_2-L_3V decay rate ratio are fairly independent of d population and the L_3V/L_3 intensity ratio. The ratios are similar to those of Ni_xFe_y (x

TABLE IV. Semiempirical L_2-L_3V decay energies and rate ratios, and L_{23}-VV (L_{23}-V) AES (XES) satellite/main line intensity ratios of Cu metal and Cu compounds. An asterisk indicates that the initial satellite (shakeup/off)/main line intensity ratio is assumed to be 0.18. For Cu metal $L_{23}V$-$VVV(L_{23}V$-$VV)$ satellite intensity is calculated for 1100 eV photon excitation energy.

element	energy	L_2-L_3V ratio	L_2-VV AES (L_2-V XES) initial states L_2V	L_1-L_2V	L_3V	L_3-VV AES (L_3-V XES) initial states L_2-L_3V	L_1-L_3V
Cu	4.8	0.63 (0.69)	0.36	0.22	0.13	0.33	0.05
CuCl		0.65	0.51	0.23	0.18*	0.33	0.05
CuBr		0.58	0.43	0.19	0.18*	0.30	0.05
Cu_2O		0.68	0.56	0.25	0.18*	0.35	0.05
$CuBr_2$	4.4	0.57	1.06	0.19	0.45	0.30	0.05
$CuCl_2$	4.1	0.49 (0.48)	1.16	0.16	0.60	0.25	0.04
CuF_2	3.2	0.32 (0.28)	1.18	0.12	0.80	0.17	0.03
$CuSO_4$		0.25	0.88	0.11	0.66	0.13	0.02
$Cu(acac)_2$		0.46	1.75	0.15	0.94	0.24	0.04
Cu(Pc)		0.36	0.62	0.13	0.40	0.18	0.03
CuO	5.0	0.62	1.18	0.21	0.45	0.32	0.05
YBCO	5.5	0.55 (0.59)	0.78 (0.85)	0.18	0.35	0.28 (0.30)	0.05

$=80\%$, $y=20\%$) $[0.37\pm0.05$ and $0.74(0.70)]$. Judging from a substantial background expected below the L_2 state energy (unfortunately the reported XPS spectrum of NiFe is limited only for the L_3 level[9]), it would be reasonable to assume that the L_3V-VVV decay contributes to some extent. The L_2-L_3V decay rate ratio of NiFe is unlikely to become smaller than that for Ni metal. We take the L_2-L_3V decay rate ratio of Ni metal as the minimum value. Then the L_3V-VVV/L_2-L_3V-VVV PECS intensity ratio at L_2 state energy will be in the range of 0.50(0.45) to 0.63(0.48). The values inside the parentheses are obtained when the L_3V/L_3 intensity ratio of 0.75 is used. The shakeoff (at L_2 state energy)/main line intensity ratios for Ni metal, Ni_xFe_y ($x=80\%$, $y=20\%$), and Ni_xFe_y ($x=y=50\%$) are 0.44, 0.56, and 0.17, respectively. From Ni metal to NiFe, the shakeoff intensity around the L_2 state energy decreases substantially. As high-resolution XPS spectra of NiFe alloys are not available, it is difficult to conclude about the initial shakeup/off intensity variation. We tend to consider that the shakeoff intensity is shifted towards smaller shakeoff energy in NiFe compared to Ni metal. This explains the shakeoff intensity reduction at L_2 state energy and the ''satellite'' intensity increase. Between Ni metal and Ni_xFe_y ($x=80\%$, $y=20\%$), it is difficult to draw any conclusion from the available experimental data.

IV. L_{23}-VV AES AND L_{23}-V XES OF Cu HALIDES AND HIGH-T_c SUPERCONDUCTORS

In Tables IV and V we list the L_2-L_3V decay rate ratios, the L_{23}-VV AES satellite/main line intensity ratios for different decay channels, and the Auger and radiative transition energies of Cu halides and Cu oxides. They are semiempirically evaluated. The satellite at about 5 eV *below* the L_3-VV main line of Cu halides, CuO, and $YBa_2Cu_3O_{7-\delta}$ (YBCO) is much more intense than in CuCl and Cu metal. For Cu metal, the L_2-L_3V-VVV decay is attributed to the satellite.[2,6,23] Thus the enhanced satellite is interpreted as due to the

L_3V-VVV decay, in addition to the L_2-L_3V-VVV decay.[28] According to Ramaker *et al.*[29,30] the satellite intensity remains approximately constant in the Cu halides, while the XPS satellite intensity increases sharply as one progresses up the series Br, Cl, and F. The satellite intensity also increases as one progresses from Cu, Cu_2O, CuO, LSCO ($La_{1.85}$, $Sr_{0.15}$, $CuO_{4-\delta}$) to YBCO ($YBa_2Cu_3O_{7-\delta}$), generally in the opposite direction to the XPS satellite intensity increase. They considered that the LV(shakeup)-VVV decay is not a cause of the satellite increase because the AES satellite intensity variation is opposite to that of the XPS satellite intensity. They considered also that the L_3V(shakeoff)-$VVVV$ and L_2-L_3V-VVV decay rates are independent of environmental changes because the decays are localized. Thus they concluded that the satellite intensity increase is due to the final-state interaction.

As the L_2-VV/L_3-VV AES main line intensity ratio is given approximately by the L_2/L_3 level ionization cross sections multiplied by the L_3/L_2 decay width ratio, one can obtain approximately the L_2-L_3V decay rate ratio. Except for Cu metal, the AES intensity ratios are not reported. Thus they have to be estimated from the spectra. The L_2-L_3V decay rate ratios obtained for Cu metal, $CuBr_2$, $CuCl_2$, CuF_2, and YBCO are 0.63, 0.57, 0.49, 0.32, and 0.55, respectively.[31] The estimated L_2-L_3V decay energies for Cu metal, $CuBr_2$, $CuCl_2$, CuF_2, and YBCO are 4.8, 4.4, 4.1, 3.2, and 5.5 eV, respectively. Near the threshold the L_2-L_3V decay rate increases with the CK energy increase. The variation of the L_2-L_3V decay rate ratios cannot be explained only in terms of the CK energy variation. For the Cu halides and YBCO the final-state potential becomes less attractive compared to the Cu metal case because of more delocalized (or screened) final-state hole(s). Thus the CK decay rate ratio becomes smaller in spite of the larger or similar CK energy. The calculated L_2-L_3V-VVV/L_3-VV intensity ratios for Cu metal, $CuBr_2$, $CuCl_2$, CuF_2, and YBCO are 0.33, 0.30, 0.25, 0.17, and 0.28, respectively. For Cu metal, the experimental ratio obtained at the L_2 level ionization energy, where a large

TABLE V. Experimental and semiempirical Auger and radiative decay energies of Cu metal, Cu halides, and Cu oxides (in eV). $\underline{c}$ denotes L_3 core hole. $\underline{L}$ denotes a hole in the ligand. For the $\underline{c}d^{10}\underline{L}\to d^9\underline{L}^2$ and $\underline{c}d^9\underline{L}\to d^8\underline{L}^2$ decays of the Cu halides, the energies are evaluated, assuming U (ligand hole–hole interaction)$=10$ eV. The values inside of the parentheses are obtained, assuming $U=5$ eV. The semiempirical energies are evaluated by using the Anderson Hamiltonian model approach summarized in Table I in Ref. 29. The intersite interations are neglected for the present results.

Auger decay	CuF$_2$	CuCl$_2$	CuBr$_2$	CuO	YBa$_2$Cu$_3$O$_{7-\delta}$
$\underline{c}d^{10}\underline{L}\to d^8\underline{L}$	914.6[a]	915.5[a]	917.1[a]	918.3[b]	918.5[c]
$\underline{c}d^{10}\underline{L}\to d^9\underline{L}^2$	910.6 (915.6)	913.3 (918.3)	915.4 (920.4)	914.5	916.4
$\underline{c}d^{10}\underline{L}\to d^7\underline{L}$	894.1	895.3	897.7	899.3	899.5
$\underline{c}d^9\underline{L}\to d^7\underline{L}$	910.7	911.0	913.1	913.1	914.0
$\underline{c}d^9\underline{L}\to d^8\underline{L}^2$	913.0 (918.0)	915.9 (920.9)	919.0 (924.0)	917.9	919.5
$\underline{c}d^9\to d^7$	909.2[a]	910.1[a]	911.9[a]	910.5	910.9
$\underline{c}d^9\to d^8\underline{L}$	921.8	924.3	927.1	927.2	927.3
$\underline{c}d^{10}\to d^8$				918.3	919.1
$\underline{c}d^{10}\to d^9\underline{L}$				927.9	928.7
$\underline{c}d^{10}\to d^7$				899.3	900.1

Radiative decay	CuO	YBa$_2$Cu$_3$O$_{7-\delta}$	Radiative decay	Cu metal
$\underline{c}d^{10}\underline{L}\to d^9\underline{L}$	929.7[d]	929.7[d]	$\underline{c}d^{10}\to d^9$	929.7[e]
$\underline{c}d^{10}\to d^{10}\underline{L}^2$	930.2	930.7	$\underline{c}d^9\to d^8$ (shakeup)	929.7
$\underline{c}d^{10}\underline{L}\to d^8\underline{L}$	918.3	918.5	$\underline{c}d^9\to d^8$ (shakeoff,CK)	932.9
$\underline{c}d^9\underline{L}\to d^8\underline{L}$	933.1	932.8		
$\underline{c}d^9\underline{L}\to d^9\underline{L}^2$	926.7	927.6		
$\underline{c}d^9\to d^8$	929.5	929.9		
$\underline{c}d^9\to d^7$	910.5	910.9		
$\underline{c}d^{10}\to d^9$	931.2	931.1		

[a]Reference 28.
[b]Reference 35.
[c]Reference 36.
[d]Reference 38.
[e]Reference 25.

part of the shakeup/off is suppressed, is 0.32.[32] The agreement is excellent. The L_1-L_3V-VVV/L_3-VV decay rate ratio is estimated using the theoretical L_1-L_3V decay rate ratio which is available only for Zn.[33] If the L_1 main line intensity is the same as that of the L_2 level, we obtain 0.05 for Cu metal. As the authors of Ref. 33 often overestimate the CK decay rates by a factor of 2–3, the L_1-L_3V-VVV decay is most likely small. The satellite intensity variation cannot be explained only by the L_2-L_3V-VVV decay, although the latter changes even among the Cu halides.

For Cu metal the L_3-VV AES satellite/main line intensity ratio is as large as 0.45 at 1100 eV photon energy.[32] Thus the initial satellite/main line intensity ratio ($0.13=0.45-0.32$) at 1100 eV is not small at all. When the L_3-V-VVV decay is taken into account and the L_1-L_3V-VVV decay rate is scaled by the L_2-L_3V-VVV decay rate variation, the AES satellite/main line intensity ratios for Cu metal (at 1100 eV photon energy), CuBr$_2$, CuCl$_2$, CuF$_2$, and YBCO are 0.51, 0.80, 0.89, 1.00, and 0.68, respectively. The AES satellite intensity increase is much smaller than the XPS satellite intensity increase. The experimental intensity ratios are not available. A substantial part of the satellite *below* the L_3-VV main line is due to the initial shakeup/off. Thus the initial shakeup state does not relax to the main line state before the decay.

The satellite intensity at about 5 eV *below* the main line in the L_2-VV AES of Cu halides and YBCO seems to remain

approximately constant. For Cu metal, the L_2V-VVV decay is predominantly attributed to the satellite.[32] The L_3V-VVV/L_3-VV intensity ratio is approximately given by the L_3 XPS satellite/main line intensity ratio, while the L_2V-VVV/L_2-VV intensity ratio is approximately given by the L_2 XPS satellite/main line intensity ratio multiplied by $(1-R)^{-1}$. Here, R is the L_2-L_3V decay rate ratio. The latter is enhanced by a factor of $(1-R)^{-1}$ compared to the former because the Auger decay branching ratio for L_2V cannot be approximated by that for L_2 due to the presence of the L_2-L_3V decay for the latter. This explains why the satellite is much more enhanced in the L_2-VV than in the L_3-VV. For Cu metal, CuBr$_2$, CuCl$_2$, CuF$_2$, and YBCO $(1-R)^{-1}$ are 2.73, 2.35, 1.94, 1.48, and 2.22, respectively. At 1000 eV photon energy, the L_3V-VVV/L_3-VV ratio for Cu metal is about 0.08 ($=0.4-0.32$). The calculated L_2V-VVV/L_2-VV intensity ratios for Cu metal (at 1000 eV), CuBr$_2$, CuCl$_2$, CuF$_2$, and YBCO are 0.22, 1.06, 1.16, 1.18, and 0.78, respectively. The experimental ratio for Cu metal at 1000 (970) eV photon energy is about 0.40 (0.20),[32] while the experimental L_2V-VV/L_2-V XES satellite/main line intensity ratio for Cu metal measured at 970 eV is 0.19.[24] We note a good agreement between the experimental AES and XES ratios. The L_1-L_2V-VVV/L_2-VV intensity ratio is approximately obtained by using the theoretical L_1-L_2V decay rate

ratio.[33] The ratios for Cu metal, CuBr$_2$, CuCl$_2$, CuF$_2$, and YBCO are 0.22, 0.19, 0.16, 0.12, and 0.18, respectively. They are much larger than the L_1-L_3V-VVV/L_3-VV ratios because of the $(1-R)^{-1}$ factor. They could be much overestimated as in the case of L_2-L_3V-VVV decay rates. The satellite/main line intensity ratios for Cu metal (at 1100 eV), CuBr$_2$, CuCl$_2$, CuF$_2$, and YBCO are 0.58, 1.25, 1.32, 1.30, and 0.96, respectively. The L_2-VV AES satellite/main line intensity ratios of the Cu halides remain constant, but much more enhanced compared to Cu metal. A large part of the satellite intensity *below* the main line in the L_2-VV AES is due to the initial shakeup/off. Thus the initial shakeup state does not relax to the main line state before the decay.

The L_2-V/L_3-V XES total intensity ratio can be used to estimate the L_2-L_3V decay rate ratio. For the L_2-V XES the L_2-V and L_2V-VV decays occur, while for the L_3-V XES the L_3-V, L_3V-VV, and L_2-L_3V-VV decays occur. Then the L_{23} XES intensity ratio is approximately given by $(1-IR)/(X+IR)$. Here, X is the L_3/L_2 ionization cross-section ratios, I is the core XPS main line intensity, and R is the L_2-L_3V decay rate ratio. From the experimental data,[34] the L_2-L_3V decay rate ratios obtained for CuSO$_4$, Cu(II)acetyleacetonate[Cu(acac)$_2$], Cu(II)phthalocyanine-[Cu(pc)], CuCl$_2$, CuF$_2$, and CuO are 0.25, 0.46, 0.36, 0.48, 0.28, and 0.62, respectively. The ratios for CuCl$_2$ and CuF$_2$ agree well with those obtained from the AES data, namely 0.49 and 0.32, respectively. We note that the ratio from the AES is obtained without the presence of satellites, while the ratio from the XES is obtained in the presence of satellites. From the XES data by Wassdahl *et al.*[24] we obtain the L_2-L_3V decay rate ratios of 0.69 and 0.59 for Cu metal and YBCO, respectively. The ratios agree well with those derived from the AES data. The calculated L_3-VV AES satellite/main line intensity ratio for CuO by the L_3V-VVV and L_2-L_3V-VVV decays is 0.77, while that for YBCO is 0.63 (0.65). These ratios are expected to be the same for the L_3-$M_{23}V$ AES. According to Ramaker *et al.*,[29,30] the L_3-$M_{23}V$ satellite intensity remains constant from CuO to YBCO. They interpreted the satellite as due to the L_3V(shakeoff)-MVV and L_2-L_3V-MVV decay because they considered that the two decay processes are localized and the decay rates are independent of environmental changes. However, the experimental satellite intensity decreases from CuO to YBCO, in agreement with the present prediction. For the Cu halides the satellite intensities for CuF$_2$ and CuCl$_2$ are larger than that for CuBr$_2$. The initial shakeup state does not relax to the main line state before the decay starts because the satellite change is predominantly due to the initial shakeup.

van der Laan *et al.*[28] interpreted the satellite at about 7 eV *above* the main line in the L_3-VV AES of the Cu halides as the final state $3d^9\underline{L}^2$ reached by covalent mixing with the $3d^8\underline{L}$ ($\underline{L}$ denotes a hole in the ligand). They considered that the observed satellite intensity decrease from CuF$_2$ to CuBr$_2$ is consistent with the expected decrease in the mixing because of the increase in the $d^8\underline{L}$ and $d^9\underline{L}^2$ splitting. The latter is caused by the decrease in the ligand hole energies. For CuF$_2$, CuCl$_2$, and CuBr$_2$ the experimental two-hole bound state ($d^8\underline{L}$) energies are 22.0, 19.1, and 16.0 eV, respectively, while the one-hole state ($d^9\underline{L}^2$) energies are 16.0

$+U$, 11.3$+U$, and 7.7$+U$, respectively. Here, U is the ligand hole-hole interaction. In order to interpret the satellite as $d^9\underline{L}^2$, U must be nearly equal to zero. U is expected around 10 eV. Then the $2p^{-1}3d^{10}\underline{L} \rightarrow d^9\underline{L}^2$ transition energy lies around the satellite *below* the main line. It is unreasonable to interpret the satellite *above* the main line as $d^9\underline{L}^2$. Most likely, $d^9\underline{L}^2$ will be degenerate with $d^8\underline{L}$ so that the broadening of the two-hole bound state ($d^8\underline{L}$) arises from its mixing with delocalized band states ($d^9\underline{L}^2$). This is analogous to the ''dissociational broadening'' proposed to explain the final-state broadening of Ni alloys.[5] Then the shoulder on the larger kinetic-energy side of the main line which originates from the ^3F multiplet should be broadened. We note that the satellite enhancement occurs in both L_2-VV and L_3-VV AES. The final-state shakeup/off leads to $2p^{-1}3d^{10}\underline{L} \rightarrow 3d^7\underline{L}$. The decay energies range from 894 to 898 eV. The final-state shakeup/off is not large. The energy of the $2p^{-1}3d^9 \rightarrow 3d^8\underline{L}$ decay, which involves the final-state charge-transfer screening of the initial shakeup $2p^{-1}3d^9 \rightarrow 3d^7$ decay, coincides with the satellite above the main line. However, the $3d^7 \rightarrow 3d^8\underline{L}$ splitting energy is too large (13 to 15 eV) to induce the mixing. The CK decay preceded $2p^{-1}3d^9\underline{L} \rightarrow 3d^7\underline{L} \rightarrow 3d^8\underline{L}^2$ decay will not explain the satellite unless the U is less than 5 eV.

Ramaker *et al.*[29,30] interpreted the intensity ''variation'' of the satellite at about 6 eV *below* the main line in the L_{23}-VV AES of CuO and high T_c superconductors also as the final-state interaction between $d^8\underline{L}$ and $d^9\underline{L}^2$. The experimental $d^8\underline{L}$ energies for CuO and YBCO are 15.2 and 14.6 eV, respectively, while the present predicted $d^9\underline{L}^2$ energies are 19.0 and 16.7 eV, respectively. The intensity will increase from CuO to YBCO with the expected increase in the mixing because of the decrease in the $d^8\underline{L}$ and $d^9\underline{L}^2$ splitting. The L-VV AES of YBCO by Ramaker *et al.*[29,30] resembles the spectrum of Ref. 35. However, both spectra are considerably different from the spectrum reported by van der Marel *et al.*[36] The former spectra are much more broadened compared to the latter so that the satellite is somehow smeared out, while the latter spectrum greatly resembles the spectra of CuO and the Cu halides. There is no significant satellite intensity variation from CuO to YBCO. The L_3V-VVV and L_2-L_3V-VVV decay energy falls in the satellite region and the relative intensity to the main line intensity decreases from CuO (0.82) to YBCO (0.70). The final-state interaction increases the relative satellite to the main line intensity more for YBCO so that the intensity may not change from CuO to YBCO.

The satellite at about 7 eV *above* the main line of the Cu halides exists also in CuO and YBCO. There seems to be a very close resemblance between CuO (YBCO) and CuBr$_2$. The satellite *above* the main line could be $d^9\underline{L}$ due to the charge-transfer screening of the d^8 final state reached by the decay from the resonantly core-level excited $2p^{-1}3d^{10}$ state. The latter state lies about 2 eV below the core ionized main line state and can be reached from the latter by the ''shakedown.'' The former state, which is the ''best'' screened core-hole state, could be created upon core-level ionization so that we do not need to talk about the ''relaxation.'' The $2p^{-1}3d^{10} \rightarrow 3d^8 \rightarrow 3d^9\underline{L}$ decay coincides with the satellite at about 6 eV *above* the main line, which cannot be explained

only in terms of the L_2V-VVV initial shakeup/off, L_2-VVV final shakeup/off, and $2p^{-1}3d^9$-$3d^8\underline{L}$ decay. The third decay which involves the final-state screening is negligible because of a large energy separation between d^7 and $\underline{d}^8\underline{L}$. The $2p^{-1}3d^{10} \rightarrow 3d^8$ decay energy coincides with the $2p^{-1}3d^{10}\underline{L} \rightarrow 3d^8\underline{L}$ decay energy so that both processes cannot be distinguished in the normal AES.

For Cu metal using the L_2-V XES satellite/main line intensity ratio (0.19) obtained at 970 eV photon energy[24] and the L_2-L_3V decay rate ratio of 0.69, we obtain the initial satellite/main line state intensity ratio of 0.06. At 970 eV, the L_3-VV AES satellite/main line intensity ratio is 0.37.[32] As the L_2-L_3V-VVV/L_3-VV intensity ratio is 0.32, we obtain 0.05 for the L_3V-VVV/L_3-VV intensity ratio. The agreement is good. The calculated L_3-V XES satellite/main line intensity ratio is 0.41, while the experimental one is 0.43.

Kawai and Maeda[37] interpreted the main lines of the L_3-V XES spectra of the Cu halides, CuO, and YBCO as due to the $2p^{-1}3d^{10}\underline{L} \rightarrow 3d^9\underline{L}$ decay, while the hump at about 4 eV above the main line as due to the $2p^{-1}3d^9$(shakeup)$\rightarrow 3d^8$ decay. However, the above two emissions overlap (Table V). The hump is also interpreted as due to the charge-transfer screened final state $d^{10}\underline{L}^2$.[38] The 4 eV satellite is seen also in the Cu metal spectrum.[39] The present semiempirical radiative transition energies of Cu metal (Table V) show that the satellite must be due to the L_3V(shakeoff)-VV and L_2-L_3V-VV decays. The L_3V(shakeup)-VV decay energy coincides with the main line energy. This is also the case with CuO and YBCO. The L_3-V XES of Cu halides and Cu oxides tends to show a hump at about 1 eV above the main line. This spectral feature coincides with the Cu L_3 absorption peak whose intensity will be very sensitive to self-absorption effects.[38] The energy of $2p^{-1}3d^{10}\underline{L}$-$3d^9\underline{L}$-$3d^{10}\underline{L}^2$ decay which involves the final-state charge-transfer screening coincides with the 1 eV satellite. The energy of the $2p^{-1}3d^{10}$-$3d^9$ transition from the "best" screened core ionized state coincides also with the 1 eV satellite. Kawai and co-workers[34,37] studied the correlation between the core XPS satellite intensity and the full width at half maximum (FWHM) and at $\frac{1}{3}$ maximum of the L_3-V XES main line. However, the widths are larger than those of the spectra in Ref. 38 by a factor of 2–4. The former widths are unusually broad. Finally we note that the L_2-L_3V decay rate ratio will not be affected even when the decay from the "best" screened core ionized state overlaps with that from the "better" screened core ionized state because their Auger (and radiative) decay branching ratios are similar.

Ramaker et al.[29,30] argued that the initial shakeup does not produce satellites in the AES or XES spectra because the shakeup state generally "relaxes" to the primary states of the same symmetry before the decay. Such a relaxation is expected when the shakeup energy is larger than the core-level width. However, the present analysis of the APECS of Ni metal shows that this is not the case. It is not the shakeup energy but the coupling strength between the shakeup state and the lowest energy state which determines the relaxation time (see the Appendix).

V. THE L_{23}-VV AES OF Fe METAL AND FeAl

For metallic Fe, Sarma et al.[40] concluded that the L_3V-VVV satellite intensity is negligible, while the L_3-VV/L_2-VV AES spectral intensity is significantly larger than 2, suggesting that L_2-L_3V CK decay occurs in metallic Fe. They suggested that the occurrence of L_2-L_3V CK decay and the absence of Auger satellites can be reconciled if the $3d$ hole hops away prior to the decay of the L_3 core hole. This spectral study is confirmed by Unsworth et al.[41] Unsworth et al. studied the L_{23}-VV AES of FeAl with synchrotron radiation. For FeAl the L_3V-VVV satellite is observed due to the localized $3d$ hole in the L_2-L_3V CK decay. The L_2-L_3V CK decay rate is expected to decrease in the absence of an extra $3d$ hole (when the $3d$ hole delocalizes before the L_3 hole decays) because of the less attractive final-state potential and small CK decay energy. Moreover, the L_2-L_3V-VVV decay can be the L_2-L_3V-VV decay because of fast $3d$ hole delocalization. Thus the spectral intensity transfer from the satellite to the main line is expected to occur for the L_3-VV AES of metallic Fe. The fast delocalization is expected because of bandlike behavior of the L_{23}-VV AES. With localization of the $3d$ hole in the L_3V state, the spectral intensity of the main line will be transfered back to the satellite line. The L_3-VV/L_2-VV main line intensity ratio seems to increase from metallic Fe to FeAl, indicating the increase of the L_2-L_3V CK decay rate from metallic Fe to FeAl. The L_2 AECS of metallic Fe (Ref. 4) shows a significant spectral intensity in the L_3-VV main line region. There should be two contributions to this structure: One is the L_2-L_3V-VVV (which is essentially L_2-L_3V-VV) decay and the other is the L_3V(shakeoff)-VVV. The latter can be interpreted also as L_3-VV when the delocalization of the valence hole is very effective. The PECS study should resolve this puzzle. The APECS will be useful when a competition between the delocalization of a valence hole and decay is involved.

VI. CONCLUSION

The APECS spectra are formulated in a one-step model, using the real-time nonequilibrium Green's-function method. The competition between the relaxation from the initial excited states to the lowest-energy relaxed state and the core-hole decay is discussed. The possibility of obtaining the relaxation time by using the APECS is discussed. Using a CI model approach the APECS spectra of Ni metal and alloys are analyzed. Because of a lack of complete experimental data, it is difficult to draw any definite conclusion. However, the analysis indicates that the L_2-L_3V CK decay rate ratio increases about 10–20 % from Ni metal to Ni alloy due to the more localized valence holes on alloying. The CK decay rate variation is analyzed in terms of both decay energy and final-state potential changes. The L_2-L_3V-VVV/L_2-VV AECS intensity ratio does not necessarily reflect the L_2-L_3V decay rate ratio because of a large contribution by the initial shakeoff preceded L_3V-VVV decay. The initial shakeoff intensity for Ni metal is as large as in Ni$_x$Fe$_y$($x=80\%$, $y=20\%$). However, in Ni$_x$Fe$_y$($x=y=50\%$) the intensity is much reduced. The L_3V-VVV and L_2-L_3V-VVV PECS of Ni metal and Ni$_x$Fe$_y$($x=y=50\%$) are desirable. In the latter system, the shakeoff intensity appears to be shifted towards smaller shakeoff energy, compared to the former. The high-resolution L_{23} XPS spectra of the systems of current interest are also desirable. The L_{23}-VV AES (L_{23}-V) XES satellite/main line intensity ratios by different decay channels and

corresponding decay energies, and the L_2-L_3V decay rate ratios of Cu metal, Cu halides, and Cu oxides, are semiempirically evaluated. To provide a consistent explanation of the satellite intensity variations of both AES and XES, it is necessary to take into account the initial shakeup/off processes. In these systems the initial shakeup state does not relax to the lowest-energy state before the decay starts. The lowest-energy main line state may consist of the ''best'' screened state $2p^{-1}3d^{10}$ and the ''better'' screened state $2p^{-1}3d^{10}\underline{L}$. The APECS study will provide very useful and significant information about the relaxation and decay of the charge-transfer systems. Such experimental studies are really necessary for the further understanding of the decay and charge-transfer screening mechanism.

APPENDIX

We consider a two-state system. The density-matrix element is defined as

$$\rho(t)=\sum_{n,n'}\rho_{nn'}|n\rangle\langle n'|. \tag{A1}$$

The equation of motion for the density matrix element is given by

$$\frac{\partial\rho}{\partial t}=\frac{1}{i\hbar}[H,\rho]+\left(\frac{\partial\rho}{\partial t}\right)_{\text{relax}}. \tag{A2}$$

The last term is the relaxation term which describes the interaction between heat bath and the electronic system. The equations of motion for ρ_{ba}, ρ_{aa}, and ρ_{bb} are

$$\dot{\rho}_{ba}=-i\omega_{ba}\rho_{ba}-\frac{i}{\hbar}H'_{ba}(\rho_{aa}-\rho_{bb})-\Gamma_{ba}\rho_{ba}, \tag{A3}$$

$$\dot{\rho}_{aa}=(1-\gamma)P-\Gamma_a\rho_{aa}-\frac{i}{\hbar}(H'_{ab}\rho_{ba}-\rho_{ab}H'_{ba}), \tag{A4}$$

$$\dot{\rho}_{bb}=\gamma P-\Gamma_b\rho_{bb}-\frac{i}{\hbar}(H'_{ba}\rho_{ab}-\rho_{ba}H'_{ab}). \tag{A5}$$

Here, H' is the interaction between states $|a\rangle$ and $|b\rangle$. We assume that the ionized states $|a\rangle$ and $|b\rangle$ are created by the ratios of $(1-\gamma)P$ and γP, respectively. γ corresponds to the spectral intensity of state $|b\rangle$. $\Gamma_{a(b)}$ and Γ_{ab} are the diagonal and nondiagonal parts of the decay (relaxation) rates of state $|a\rangle$ ($|b\rangle$), respectively. By adiabatic approximation, the nondiagonal part ρ_{ba} is given by

$$\rho_{ba}=\frac{H'_{ba}(\rho_{aa}-\rho_{bb})}{\hbar(\omega-\omega_{ba}+i\Gamma_{ba})}, \tag{A6}$$

$$\hbar\omega_{ba}\equiv E_b-E_a. \tag{A7}$$

We consider the case where the observation time is much longer than the decay time of states $|a\rangle$ and $|b\rangle$. Then setting $\dot{\rho}_{aa}=\dot{\rho}_{bb}=0$, we obtain quasistationary solutions for ρ_{aa} and ρ_{bb},

$$\rho_{aa}=\frac{(1-\gamma)\Gamma_b+g}{\Gamma_a\Gamma_b+g(\Gamma_a+\Gamma_b)}P, \tag{A8}$$

$$\rho_{bb}=\frac{\gamma\Gamma_a+g}{\Gamma_a\Gamma_b+g(\Gamma_a+\Gamma_b)}P, \tag{A9}$$

$$g=\frac{|H'|^2}{\hbar^2\Gamma_{ba}}. \tag{A10}$$

To obtain Eq. (A10), we used the resonance condition $\omega=\omega_{ba}$ and neglected the nonresonant term. From Eqs. (A8) and (A9) we obtain

$$\Gamma_a\rho_{aa}+\Gamma_b\rho_{bb}=P. \tag{A11}$$

Equation (A11) shows that all atoms $[P=N$ (number of atoms)$]$ become either state $|a\rangle$ or $|b\rangle$. When g is large (i.e., the coupling between states $|a\rangle$ and $|b\rangle$ is large),

$$\rho_{aa}=\rho_{bb}=\frac{P}{\Gamma_a+\Gamma_b}. \tag{A12}$$

The populations of states $|a\rangle$ and $|b\rangle$ become the same and the system saturates. This is because of inherent effect of ''detailed balance'' in Eqs. (A3)–(A5). On the other hand, if we assume that the transition from state $|b\rangle$ to $|a\rangle$ is not possible (we assume $\gamma>1-\gamma$ and state $|b\rangle$ is a lower-energy ionized state), we set $\rho_{bb}=0$ in Eq. (A6). Then we obtain

$$\rho_{aa}=\frac{1-\gamma}{g+\Gamma_a}P, \tag{A13}$$

$$\rho_{bb}=\left\{\frac{\gamma}{\Gamma_b}+\frac{(1-\gamma)g}{(g+\Gamma_a)}\frac{1}{\Gamma_b}\right\}P. \tag{A14}$$

The meaning of Eqs. (A13) and (A14) is that state $|a\rangle$ decays with the increased width $g+\Gamma_a$ (g describes the relaxation from state $|a\rangle$ to $|b\rangle$). In the case of state $|b\rangle$, the first term of Eq. (A14) describes the decay of state $|b\rangle$ independent of the decay of state $|a\rangle$ and the second term describes the decay of state $|b\rangle$ reached by relaxation from state $|a\rangle$ [$g/(g+\Gamma_a)$ describes the partial decay rate ratio of state state $|a\rangle$ to $|b\rangle$]. When g is very large,

$$\rho_{aa}=0, \tag{A15}$$

$$\rho_{bb}=\frac{P}{\Gamma_b}. \tag{A16}$$

All of state $|a\rangle$ relaxes to state $|b\rangle$ before it decays by Γ_a. In the system where g is very large, the system relaxes to the lowest-energy state before the system decays and the deexcitation (decay) process is entirely activated from state $|a\rangle$.

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