Post-Collision Interactions in $M_{2,3}$-Shell Energy-Loss, Autoionization, and Auger Spectra of Cr and Fe by Electron Impact near Threshold

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Large shifts were observed in the positions of the $3p$ energy-loss features for clear Cr(110) and Fe(110) surfaces, which were in parallel with shifts for the $M_{2,3}VV$ Auger "satellite," as the primary electron energy was varied. These observations are discussed in terms of the post-collision interaction and direct recombination process following the $3p \rightarrow 3d$ transition.

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Recently, inner-shell excitations of $3d$ transition metals by electron impact near the threshold have been studied in detail. After our observation[1] on the drastic change in the $3p(M_{2,3})$ energy-loss spectrum of Cr(110) with the primary-electron energy (E_p), similar phenomena were investigated also for Ti, V, and Ni by Powell and Erickson[2] who attributed new features observed at low E_p to exchange effects.[3] Bader, Zajac, and Zak[4] and we[5] pointed out the correspondence between the high-energy "satellite" of the $M_{2,3}VV$ Auger spectra and the $3p$-loss peak and suggested that this satellite is due to the direct recombination process following the $3p \rightarrow 3d$ transition, as first proposed by Bertel, Stockbauer, and Madey.[6] This Letter reports first observations of the large systematic shifts in the positions of the $3p$-loss features for Cr(110) and Fe(110) with E_p near threshold which are in accordance with the comparable shifts of the $M_{2,3}VV$ satellite (contrary to the very small shifts to the opposite direction of the $M_{2,3}VV$ Auger main peaks), supporting the previous interpretation for these satellites. We tentatively attribute the peak shifts to a post-collision interaction although exchange effects are also important.

Experimental details were described elsewhere.[5] The spectra were measured with a double-pass cylindrical-mirror analyzer with a coaxial gun. Cleaning of the samples were performed by repeated Ar-ion sputtering and annealing cycles. The amounts of impurities of well-ordered surfaces were reduced to less than 0.01 monolayer.

Figure 1 shows measured undifferentiated $3p$-loss spectra $[N(E)]$ of the clean Cr(110) for E_p near threshold. These $3p$-loss spectra show a threshold dip and three major peaks. The features in the $N(E)$ spectra are well resolved and reproducible in the second-derivative spectra $[-d^2N(E)/dE^2]$ shown in Fig. 2 (solid lines). As clearly seen in Figs. 1 and 2, the positions of the dip and three peaks are systematically shifted from ~ 39, 41, 46, and 54 eV to ~ 42, 44, 48, and 56 eV, respectively, with increasing E_p. The 41–44-eV peak is dominant at low E_p and the 46–48-eV and 54–56-eV peaks are dominant at high E_p, becoming similar to photoabsorption data which show a dip at ~ 42 eV and two peaks at ~ 49 and 56 eV.[7] The $M_{2,3}VV$ Auger spectra $[-d^2N(E)/dE^2]$ of Cr(110) for near-threshold E_p are shown in Fig. 2 (dotted lines). Auger-electron energies have been corrected for the analyzer work function of ~ 4.5 eV. The $M_{2,3}VV$ Auger spectra indicate two types of features: One is the 38.5-eV peak and 40-eV shoulder which are observed below the $3p$ binding energy (42.3 eV)[8] and shift to higher energies by ~ 0.1 eV as E_p is lowered, and the other the "satellite" indicated by the solid circle which is observed above the $3p$ binding energy and shifts to higher energy by ~ 3 eV with increasing E_p, being in a parallel shift with the loss features. The 38.5- and 40-eV peaks are due to ordinary super-Coster-Kronig (SCK) Auger processes.[9]

Similar results were obtained for the clean Fe(110) as shown in Fig. 3. The same results were obtained also for Fe(100). The $3p$-loss spectra (solid lines) show a dip and two peaks being shifted to higher ener-

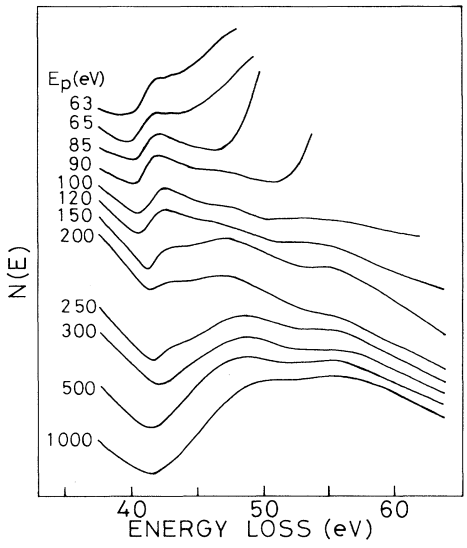

FIG. 1. $3p$ energy-loss spectra $[N(E)]$ of Cr(110) for primary-electron energies indicated.

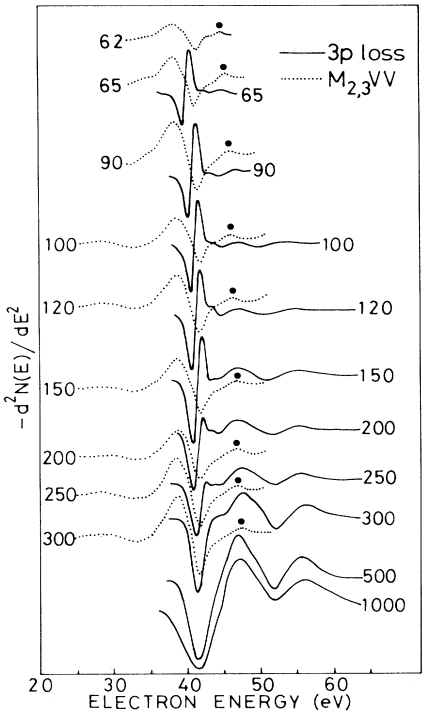

FIG. 2. Negative second-derivative $[-d^2N(E)/dE^2]$ $3p$-loss and $M_{2,3}VV$ Auger spectra of Cr(110) for primary-electron energies indicated. The solid circle marks the $M_{2,3}VV$ satellite. The Auger electron energies are now referenced to the Fermi energy.

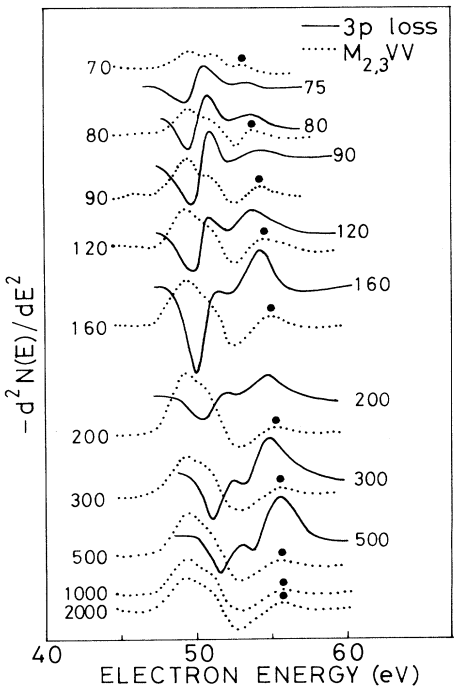

FIG. 3. Same as in Fig. 2 except the sample is now Fe(110).

gies by ~ 3 eV with increasing E_p, becoming similar to photoabsorption spectra which show a dip at ~ 52 eV (metallic phase)[7] and two peaks at ~ 54 and 56.5 eV (vapor phase).[10] The 49.5- and 51-eV ordinary $M_{2,3}VV$ (SCK) Auger peaks (dotted lines) observed below the $3p$ binding energy (52.5 eV)[8] shift to higher energies by 0.1–0.2 eV as E_p is lowered, and the "satellite" (indicated by the solid circle) observed above the $3p$ binding energy shifts to higher energy by ~ 3 eV with increasing E_p, being in a parallel shift with the loss features.

As shown in Figs. 2 and 3, the position of the $M_{2,3}VV$ satellite coincides with that of the $3p$-loss peak at the same E_p which becomes dominant at high E_p, confirming the previous interpretation of this satellite as being due to autoionization (direct recombination) emission following the resonant $3p \rightarrow 3d$ transitions (direct transfer of the $3p$-excitation energy to a $3d$ electron).[4-6] The same relationship between them was examined also for FeO(111) prepared by 100-L [1 L (langmuir) $= 10^{-6}$ Torr·sec] O_2 exposure on Fe(110) as shown in Fig. 4. Other unsuccessful interpretations such as doubly ionized $M_{2,3}$ level for the satellite have been discussed previously.[5] In a simplified atomic-configuration notation, the $3p \rightarrow 3d$ transition is represented as $3p^6 3d^n \rightarrow 3p^5 3d^n 3d^*$, which is followed by a direct recombination process, $3p^5 3d^n 3d^* \rightarrow 3p^6 3d^{n-1} + \epsilon l_{\mathrm{DR}}$, by a delocalization and subsequent SCK Auger decay, $3p^5 3d^n 3d^* \rightarrow 3p^5 3d^n + \epsilon' d \rightarrow 3p^6 3d^{n-2} + \epsilon' d + \epsilon'' l_{\mathrm{SCK}}$, or by a SCK decay with the $3d^*$ as spectator, $3p^5 3d^n 3d^* \rightarrow 3p^6 3d^{n-2} 3d^* + \epsilon''' l_{\mathrm{SCK}}$. The ϵl_{DR} autoionization emission corresponds to the $M_{2,3}VV$ satellite, the $\epsilon'' l_{\mathrm{SCK}}$ emission to the ordinary Auger emission, and the $\epsilon''' l_{\mathrm{SCK}}$ emission to the d-band satellites observed in resonant photoemission[8] ($\epsilon''' < \epsilon''$ because of screening effects).

The changes in the positions of the $3p$-loss features could be due to a number of factors. (1) *Unoccupied surface states*: The $3p$-loss spectra of Fe(110) and (100) are the same, and the $3p$-loss spectra of Fe and Cr are less sensitive to oxygen adsorption as compared with the valence-electron excitation loss spectra,[5] being against this possibility. (2) *Differences in $M_{2,3}$ binding energies for bulk and surface atoms* are known to be less than 0.2 eV for Cr and Fe.[11] (3) *Dynamically screened intermediate states* proposed by Kanski and Wendin[12] may explain the appearance of the 41–44-eV peak in the Cr $3p$-loss spectra at low E_p. (4) *Exchange scattering effects*[3] can induce optically forbidden, new loss peaks such as the Cr 41–44-eV peak to appear for near-threshold E_p. (5) $3p \rightarrow \epsilon s, \epsilon d$ *transitions* may explain the Fermi-edge-like feature at 41–44 eV in the Cr spectra (Fig. 1), as described previously.[1] The above factors (3)–(5) can explain the intensity change

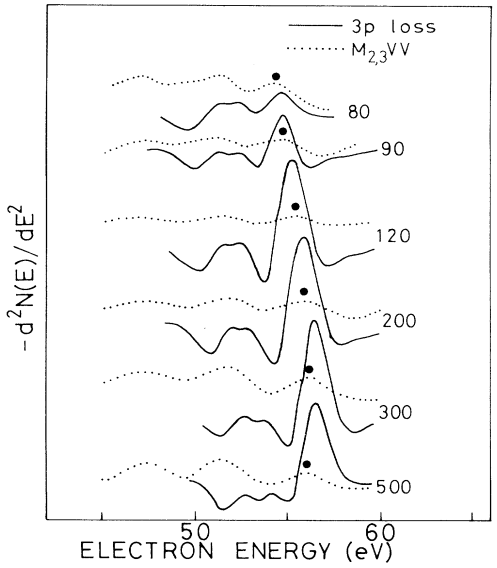

FIG. 4. Same as in Fig. 2 except the sample is now FeO(111)/Fe(110) prepared by 100-L O_2 exposure at 300 K.

of the loss peaks with E_p, but have difficulty in explaining the equal shifts for all loss features except for the near-threshold ones. Therefore, (6) *post-collision interaction (PCI)*[13] comparable to the same interaction found in the Auger and autoionization spectra of free atoms can be considered to be the other important factor for explaining such shifts. When the inner-shell ionization (excitation) is caused by electron impact near threshold, there are two slow electrons, i.e., an inelastically scattered electron and an ionized (excited) electron. The slower electron partially screens the ionic field and therefore the faster electron sees a smaller attractive potential, resulting in an available energy transferred to the faster electron. It leads to an energy gain for the faster electron balanced by an equal loss in energy for the slower electron from the excitation process in the present case.

The classical PCI theory[13] gives the relationship $\epsilon_W = (2\tau)^{-1}(2\Delta E)^{-1/2}$, for $\epsilon_W \ll \Delta E$, where ϵ_W is the peak energy shift, ΔE the excess energy above the threshold without PCI, and τ the lifetime of the inner-shell hole (Auger emission case) or an adjustable parameter. The measured shifts $(-\epsilon_W)$ of the $3p$-loss features and the $M_{2,3}VV$ satellite as a function of ΔE are compared with the classical PCI theory (the solid lines) in Figs. 5 and 6, respectively, for Cr and Fe. Although metallic screening effects (response time $\sim 10^{-16}$–10^{-15} sec) would be expected to reduce the PCI effects, the experimental points and the theoretical lines are in qualitative agreement. Classically, there is a correlation between the shift ϵ_W and the distance traveled by the scattered electron during τ. We might expect the presence of a scattered elec-

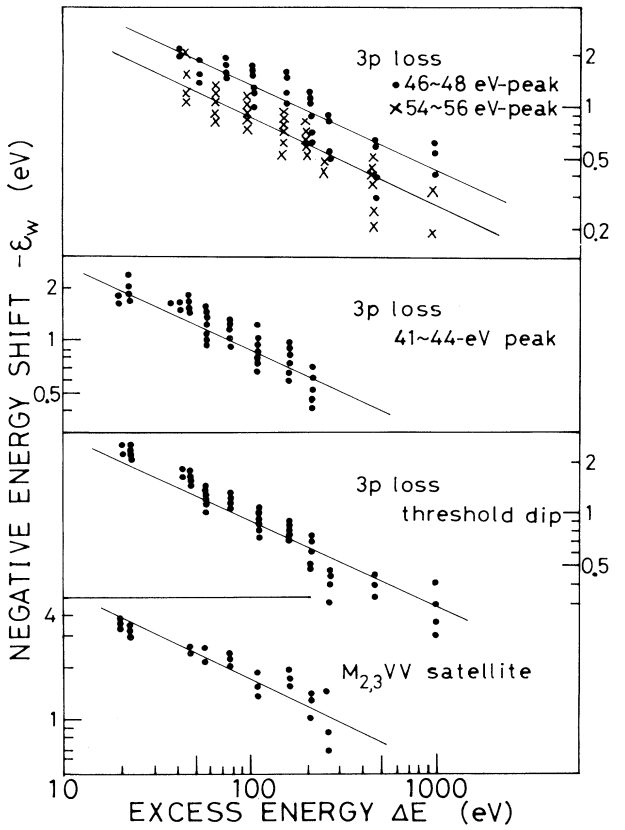

FIG. 5. Negative energy shifts of the $3p$-loss features and the $M_{2,3}VV$ satellite for Cr(110) as a function of excess energy. The solid lines are the classical PCI results.

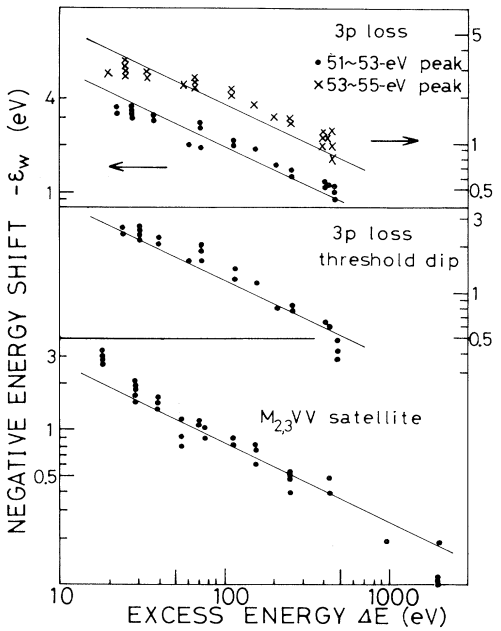

FIG. 6. Same as in Fig. 5 except the sample is now Fe(110).

tron in the vicinity of the excited atom at the instance of the $3p \rightarrow 3d$ excitation to enhance greatly the PCI mechanism, if the slow primary electron is assumed to penetrate into the atom. From Figs. 5 and 6, the typical value of ϵ_W for the $3p$-loss features of Cr and Fe is 2–3 eV at $\Delta E = 30$ eV. The resulting value of τ is $\sim 10^{-17}$–10^{-16} sec which is approximately compatible with the typical time scale in the $3p$-excitation process $[\hbar/(\sim 50\ \text{eV})]$. In the case of Auger emission by electron impact, the Auger electron can interact with two electrons, i.e., the scattered electron and the ionized one from the inner shell. The two electrons are expected to be far away from the ion when the Auger emission occurs and therefore the resulting PCI shift should be smaller. The net PCI effects will depend on the probability distribution of sharing the excess energy between the two slow electrons. The $M_{2,3}VV$ Auger peak shifts ϵ_W for Cr and Fe obtained in the present experiment are ~ 0.15 eV at $\Delta E = 20$ eV. The resulting mean value of τ is $\sim 3 \times 10^{-15}$ sec. This value is approximately in agreement with that of the Fe $M_{2,3}$-hole lifetime obtained from the x-ray photoemission-spectroscopic $M_{2,3}$-level width which is almost entirely due to Auger decay.[14]

In summary, the positions of both $3p$-loss features and the $M_{2,3}VV$ satellite for Cr and Fe shift in parallel to lower energies by 2–3 eV, when E_p is lowered. We suggest that the loss-peak shifts are possibly due to PCI effects.

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