Observation of the Transition from the Adiabatic to the Sudden Regime for the $M_3M_{4,5}M_{4,5}(^1G)$ Auger Excitation in Zinc

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It has been observed that the photoexcited $M_3M_{4,5}M_{4,5}(^1G)$ Auger line in Zn asymmetrically broadens to lower energy with increasing photon energy. The broadening can be described by a change in the asymmetry parameter $\Delta\alpha = 0.09$ in a Doniach-Sunjic line shape. This is the first evidence for the transition from the adiabatic to the sudden regime in a solid. The onset of this change ~14 eV above threshold is related to $3d$ screening electron excitations which are seen as $3p$ core-level satellites.

Relaxation effects accompanying the creation of a core hole in a metal are of basic importance in understanding the photoemission process. There are several phenomena associated with the response of the conduction electrons to the creation of a core hole, e.g., relaxation energy shifts between atom and solid and asymmetric line shapes. Photoexcitation also creates a photoelectron and the response of the conduction electrons to the photoelectron can affect the relaxation of the hole. Depending on the kinetic energy of the photoelectron, an adiabatic and a sudden regime have been distinguished.[1] For photoemission from a core level, the adiabatic regime is characterized by full screening of the core hole by conduction electrons resulting in a symmetric line. In the sudden limit, i.e., with fast photoelectrons, the conduction electrons cannot respond quickly enough to screen the hole completely. In this case, the core hole is left in an excited state via creation of electron-hole pairs, plasmons, interband transitions, etc. and the predicted photoelectron spectrum is characterized by an asymmetric line shape with a tailing of the adiabatic peak towards lower kinetic energy (produced by electron-hole pair excitations) and by intrinsic energy loss features (e.g., plasmon satellites).[1] The transition between the adiabatic and sudden limits has been estimated[1] to occur when the photoelectron leaves the atom faster than a characteristic response time τ given roughly by $\tau \sim \hbar/E_x$, where E_x is a characteristic excitation energy of the core hole. In a unified picture of photoemission and Auger-electron emission, the photoemission line shape is related to the Auger line shape via the spectral function of the core hole.[2] However, the details of this relation are not clear close to the photothreshold.

Experimental evidence for these effects is scarce. The asymmetric core-level photoemission line shape has been seen in the sudden limit by x-ray photoemission spectra (XPS).[3-5] Efforts to observe the transition to the adiabatic limit at lower photon energies[6] have been indeterminant for core levels. For Auger emission lines of atomic Xe and Kr, a line-shape asymmetry and a shift to higher kinetic energy (~100 meV) has been reported within a few electron volts of the ionization threshold. This is attribuuted to Coulomb interaction of the Auger electron with the outgoing slow photoelectron (post-collision interaction).[7,8,9] Our results cannot be explained by this effect which increases monotically towards threshold. The intensity of intrinsic plasmon losses is related to the sudden switching on of the hole potential. The photon energy dependence of plasmon loss intensities has been measured,[10] but intrinsic losses could not be separated out in these experiments, because extrinsic losses dominate.[11] The $M_{4,5}M_{4,5}$ super Coster-Kronig transition in zinc is well known from earlier experimental[12] and theoretical[13] work. Individual Auger multiplet lines can be distinguished which have the same width as the corresponding core-level photoemission peak.

We have found that the line shape of the photoexcited $M_3M_{4,5}M_{4,5}(^1G)$ Auger transition in zinc metal changes at a photon energy $h\nu$ of ~14 eV above threshold. Namely, the low-kinetic-energy tail shifts down by 140 meV. This line-shape change can be described by a change of the asymmetry parameter $\Delta\alpha = 0.09$ in a Doniach-Sunjic line shape.[5] A further increase in line shape asymmetry is observed at higher energies when the Auger transition is excited by 2-keV electrons ($\Delta\alpha = 0.21$ with respect to the low-energy limit). This is comparable to typical line-shape asymmetries in XPS.

The observed onset of the adiabatic-to-sudden transition at ~14 eV above photothreshold is equivalent to a response time of the electrons of $\tau \sim \hbar/14\ \text{eV} = 5\times10^{-17}$s. This corresponds quite well to a characteristic satellite structure observed at ~13 eV below the $3p$ core-level photoemission peak in XPS.[14] This structure is related to $3d$ to conduction band excitations and has a larger energy than the plasmon excitation energy of 9.6 eV.

Experimentally, the detection of Auger-electron energy shifts has avoided several problems associated with the observation of core-level photoelectron line shapes. Since the kinetic energy of Auger electrons is constant to first order in photon energy $h\nu$, the escape depth remains constant (i.e., surface effects[6] can be excluded). Also, the secondary electron background is relatively smooth in the region of the Auger peaks in contrast to that encountered for core-level photoemission near threshold. Moreover, the photon energy resolution and the calibration of the monochromator and the electron spectrometer do not affect the results. We have used synchrotron radiation from the 240-MeV storage ring Tantalus I monochromatized by a toroidal grating monochromator (set to a resolution of ~1 eV). The electron spectrometer was a display-type spectrometer[15] integrating over a solid angle of 1.8 sr with an energy resolution setting of ~0.3 eV and count rates of $\sim10^6$/s in this experiment. A Zn(0001) surface was prepared by sputter-etching and annealing in a vacuum in the 10^{-11}-Torr range and characterized by low-energy electron diffraction (LEED), Auger spectroscopy, and photoemission.

Figure 1 gives an overview photoelectron spectrum of Zn(0001) at a photon energy $h\nu = 100$ eV (12 eV above the $3p_{3/2}$ threshold). A strong $3d$-emission peak is seen centered at 9.9 eV below the Fermi level E_F, with two energy loss features ~9.6 and ~14.2 eV below the $3d$ peak. The energy loss of 9.6 eV is due to the bulk plasmon of zinc.[16,17] We attribute the loss of 14.2 eV to $3d$ conduction-band excitations [see optical constants of Zn (Ref. 17)]. Also, the $M_{2,3}M_{4,5}M_{4,5}(3p\,3d\,3d)$ Auger doublet is seen. It consists of two $3d^8$ multiplets[12] split by the spin-orbit splitting of the $3p$ holes [$E_B(3p_{3/2}) = 88.1$ eV, $E_B(3p_{1/2}) = 91.0$ eV below E_F]. For this experiment we consider only the lower energy peak of the $M_{2,3}M_{4,5}M_{4,5}$ doublet which is associated exclusively with the

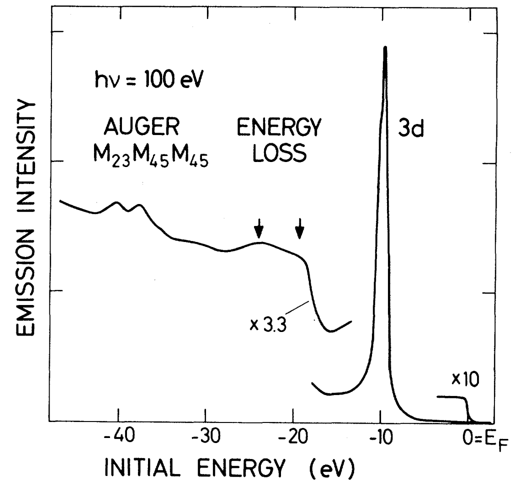

FIG. 1. Photoelectron energy distribution curve of a Zn(0001) single crystal. Emission is seen from the $4s$, $4p$ valence band (near the Fermi level E_F), from the $3d$ levels, from the $M_{2,3}M_{4,5}M_{4,5}$ ($3p$ $3d$ $3d$) Auger transition, and from energy loss features ($\Delta E = 9.2$ and 14.2 eV below the $3d$ level, see arrows).

$3p_{3/2}$ hole [essentially the $3d^8$ (^1G) configuration].[12]

As a measure of the change in the Auger line shape, the energy positions of the leading and the trailing edge of the $M_3M_{4,5}M_{4,5}(^1G)$ Auger peak are plotted versus photon energy $h\nu$ in Fig. 2. In addition to photon excitation, we have measured the Auger spectrum excited with 2-keV electrons in the same spectrometer (see full dots in Fig. 2). To determine shifts of the tails of the Auger peak we have consistently used the same background subtraction procedure for all $h\nu$ values as shown in the inset of Fig. 2. Using different background subtraction methods (e.g., the background shown in Fig. 2 for the leading edge applied to determine the trailing edge), we have ascertained that systematical errors associated with the background subtraction are smaller than the statistical errors given by the scatter of the data points (~±20 meV).[18]

The low-kinetic-energy edge shifts down rather abruptly by 140±10 meV between $h\nu = 100$ and $h\nu = 104$ eV. For the 2-keV electron-excited Auger spectrum a further shift downwards of ~200 meV is observed for the lower edge. A line-shape analysis shows that a Doniach-Sunjic function[5] fits the $M_3M_{4,5}M_{4,5}(^1G)$ Auger peak quite well with use of a width parameter ($2\gamma = 2.2$ eV) which corresponds to the $3p_{3/2}$core-level width (we measure 2.1±0.2 eV full width at half maximum for the $3p_{3/2}$ core level at $h\nu = 120$ eV). This fit yields an increase in the asymmetry parameter of $\Delta\alpha$

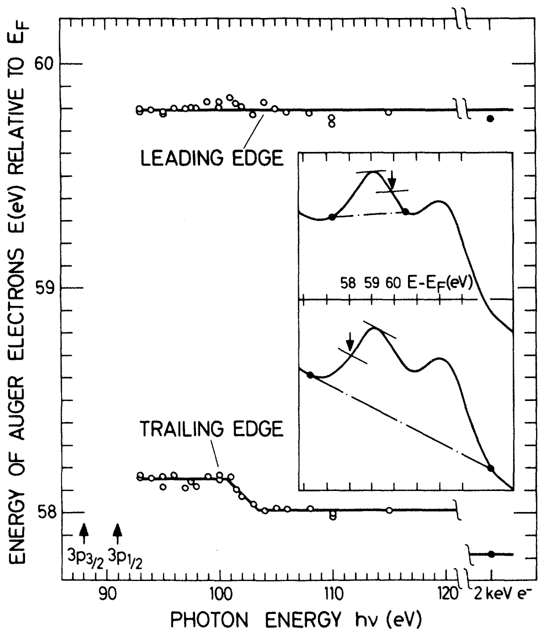

FIG. 2. Energies E of the leading and trailing edges of the $M_3M_{4,5}M_{4,5}$ ($3p_{3/2}$ $3d$ $3d$) Auger peak are plotted vs photon energy. The edges are defined according to the inset drawing. Full dots are for Auger transitions excited by a 2-keV electron beam.

$= 0.09 \pm 0.02$ between $h\nu < 100$ eV and $h\nu > 104$ eV and of $\Delta\alpha = 0.21 \pm 0.04$ between $h\nu < 100$ eV and 2-keV electron excitation.[19] This asymmetric broadening of the ^1G Auger multiplet peak appears to reflect the asymmetric tailing of the core-level photoelectron spectra calculated[5] and observed[3,4] in XPS. The larger asymmetry observed with electron excitation could be due in part to the different excitation mechanism (one more electron is present compared with photoexcitation). In the gas-phase experiments, larger shifts have been seen for electron excitation compared with photo excitation.[7,8] Thus, the 2-keV electron-excited data cannot be compared with XPS data as reliably as the photoexcited data, although the average excitation energy is closer.

The transition from the adiabatic to the sudden regime is tied to the response of the screening electrons. Using linear response theory, the dynamically screened charge density is given by[20]

$$\tilde{n}(q,\omega) = n(q,\omega)/\epsilon(q,\omega),$$

where $\tilde{n}$ and n are the Fourier transforms of the total charge density and the bare-core-hole plus photoelectron charge density, respectively, and ϵ is the Fourier transform of the dielectric constant. The dielectric constant of Zn has been measured optically and via electron energy loss.[17] The loss function $\mathrm{Im}(1/\epsilon)$ exhibits two main structures with roughly equal area at $\hbar\omega = 9.6$ eV (due to plasmon excitation[16]) and between $\hbar\omega \sim 10$ eV and $\hbar\omega \sim 17$ eV (due to $3d$ conduction-band excitations). These structures are related to satellites seen ~ 9 and ~ 14 eV below the $2p$ core-level photoemission peaks in XPS[14] and below the $3d$-level photoemission peak in ultraviolet photoelectron spectroscopy (see Fig. 1). For the $3p$ level in question, these satellites seem to have merged into a broad structure ~ 12–13 eV below the center of gravity of the $3p_{1/2}$ and $3p_{3/2}$ emission.[14] Energy position and width of the 14-eV satellite (see Fig. 1) agree very well with position (14 eV above threshold) and width (~ 4 eV) observed for the adiabatic to sudden transition (see Fig. 2). The fact that the 9.6-eV plasmon loss structure is not reflected in the Auger peak asymmetry can be due to at least two reasons: One is that the ten localized d electrons are much more effective in the dielectric response to the creation of the core hole than the two s,p electrons which account for the 9.6 eV plasmon excitation in zinc. Secondly, using a recent calculation for a jellium model[20] of the plasmon excitation, the transition from a symmetric to an asymmetric line shape proceeds smoothly between $\hbar\omega_p/20$ and $\hbar\omega_p$ above photothreshold. This conclusion is based on the switching-time parameter η calculated in Ref. 20 and the relation between η and the line-shape asymmetry given in Ref. 1. Such an effect cannot be observed in our experiment, because there is a strong perturbation of the Auger peak by resonant satellites[21] in most of the energy region where this transition is predicted.

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[18]The experimental accuracy was limited by minor abrupt changes in the light intensity of the storage ring. The dash-dotted background lines shown in Fig. 2 do not represent the actual background, in particular not for the leading edge. Compared with a full line-shape analysis of the whole Auger multiplet, the high-energy tail determined as in Fig. 2 exhibits only 60% of a possible shift, while the low-energy tail exhibits more than 90% of the shift.

[19]Our fit is not sensitive enough to determine absolute values of α. The change in the asymmetry parameter $\Delta\alpha$ can be determined accurately and $\Delta\alpha$ is insensitive to the values of α and γ chosen for the "adiabatic" case $h\nu < 100$ eV ($<10\%$ uncertainty in $\Delta\alpha$). Also, there is negligible influence of a varying tail of the second Auger peak on the line-shape analysis.

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