Systematic structure in the K-edge photoabsorption spectra of the $4d$ transition metals

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K-edge photoabsorption measurements of the $4d$ transition metals (Y, Zr, Nb, Mo, Ru, Rh, Pd, and Ag) using synchrotron radiation from the 12-GeV electron synchrotron at the Wilson Synchrotron Laboratory at Cornell reveal considerable fine structure on or above ($\sim$150 eV) the edge. Systematics in the features closest to the absorption edge are attributed to structure in the "local-band-structure" density of states. This work points to the need for angular-momentum-resolved density-of-states calculations for energies far above the Fermi surface and for L-edge photoabsorption studies.

I. INTRODUCTION

We present the first systematic, high-resolution study of the fine structure in the K-edge photoabsorption spectra of the second-row ($4d$) transition metals. A synchrotron radiation source combined with a multibounce perfect-crystal diffraction element results in greatly improved resolution compared to that obtained with conventional x-ray sources and techniques. The improved resolution has in turn revealed a shoulder structure on the K edge itself of the first few members of the row, as well as details of the fine structure up to 150 eV above the edges of all the elements studied.

Although there exists no quantitative theory of the shape of the absorption edge that incorporates fine structure, we attribute the features closest to the edge to the "local-band-structure" density of states that the ejected photoelectron sees. At higher energies the scattering of the photoelectron by neighboring atoms becomes dominant. Plasmon satellites and multiple-electron excitations are ruled out as possible sources of observed fine structure.

II. EXPERIMENT

The 12-GeV electron synchrotron at the Wilson Synchrotron Laboratory at Cornell was used in a parasitic mode as a synchrotron radiation source. Radiation emitted by 11.3-GeV electrons, collimated horizontally to 0.015 mrad by a pair of slits 14 m apart, passed through the sample and was analyzed in the 17–26-keV range by a channel-cut silicon crystal spectrometer located 33 m from the tangent to the electron orbit. The small horizontal and vertical divergence (latter determined by the natural collimation of the synchrotron radiation beam at $\sim$0.05 mrad) help account for the high resolution ($\sim$1 eV) in this experiment. The transmitted radiation, diffracted in the electrons's orbit plane by the Si(220) plane, was detected by a 1-mm-thick NaI(Tl) detector. (Since the usable intensity from the Wilson Synchrotron extends well beyond 200 keV, unwanted higher Bragg orders present were eliminated by single-photon counting with electronic energy discrimination.)

A transmission ion chamber, located between the downstream collimating slit and sample, monitored the incident beam. Spectra were recorded by integrating the ion-chamber current for the time required to accumulate 10^4 counts by the NaI(Tl) detector, both for the sample in (I) and out (I_0) of the beam, corresponding to 1.4% standard deviation in I_0/I.

The samples were commercially available metal foils of 99.9% purity (except Y, which was rolled and then etched, and Ru, made from Ru power in an epoxy binder) whose thicknesses[1] were close to the thickness which maximizes contrast in the K-edge jump. To average out any thickness inhomogenieties in the foils, the samples were oscillated electromechanically when in the beam.

III. RESULTS AND DISCUSSION

The K absorption spectra are shown in Fig. 1, where $\mu x = \ln(I_0/I)$ is plotted against photon energy in excess of the K binding energy. A distinct shoulder appears on the absorption edges of Y, Zr, and Nb and to some extent of Mo, Ru, and Rh. No discernible shoulder appears in Pd and Ag. All the metals show a maximum just above the edge and further maxima separated by 20–50 eV. We label the maxima by A, B, C, ... and the shoulder by K'. The steps between data points (in eV) were determined from the K binding energy,[2] and the spectrometer incremental angle (0.0194 mrad). The energy separations of the various features which are summarized in Table I were obtained by subtracting an arctangent curve, computer fitted by eye, from the $\ln(I_0/I)$ of the data and then find-

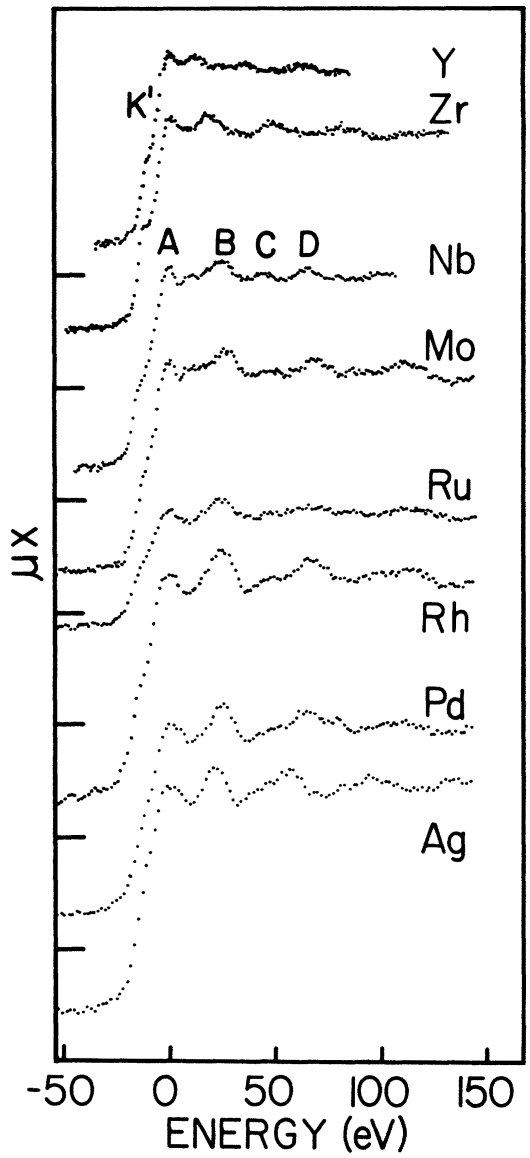

FIG. 1. K-edge photoabsorption spectra of second-transition-series ($4d$) metals with μx plotted vs photon energy in excess of the K binding energy with the energy zero arbitrarily chosen at peak A. The ordinate is in steps of 0.8, with each mark corresponding to the origin of μx for the spectrum immediately above (the scale for ruthenium is multiplied by 1.6).

ing the centroids of the remaining peaks. In fitting the arctangent curve, of the form $y = a[\frac{1}{2} + (1/\pi)\tan^{-1}(2\epsilon/\Gamma)]$, both the magnitude of the jump across the edge, a, and the $\frac{1}{4}a$ to $\frac{3}{4}a$ width of the curve, Γ, were varied until the steep rise of the curve, the low-energy side and the high-energy side, coincided with the data. Figure 2 shows the results of such an analysis performed on the molybdenum K absorption edge. The data and the fitted arctangent curve are shown in Fig. 2(a) and the result of subtraction of the two is shown in Fig. 2(b). The peaks are labeled for comparison. The width of the arctangent curve is 5.7 eV, which is fairly consistent with the calculated radiative width of 3.3 eV,[3] radiationless width of 1.2 eV,[4] and an instrumental width of ~1 eV. The zero of the energy scale was taken at the peak position A. (The peak to the left of A arises from the observed shoulder K' in the K photoabsorption data of the first few members of the series.)

The high resolution of this experiment has revealed the shoulder structure K' in Y, Zr, Nb, Mo, Ru, and Rh, previously observed only in Y. Earlier work[5] (which relied on conventional x-ray sources with most of the spectra recorded photographically) only partially dealt with the questions of resolution, sample thickness, and placement.[6] All of these tend to distort the spectra, and since they vary among investigations, it is difficult to compare unambiguously existing data with one another and our own. Our spectra were reproducible and showed the expected distortions with sample thickness and resolution (varied by changing collimating slit widths).

Existing theory gives the shape of the absorption edge of a metal as[7]

$$\mu(\omega) \propto \int_{\epsilon_k}^{\infty} \frac{d\epsilon\, N(\epsilon)\,|\langle \epsilon\,|\,H_I(\omega)\,|\,i\rangle|^2}{(\omega-\epsilon)^2 + (\Gamma/2)^2}, \qquad (1)$$

where $|i\rangle$ is the initial ground state, $|\epsilon\rangle$ the final state, $N(\epsilon)$ is the density of states whose Fermi level is ϵ_F, ϵ_K is the threshold energy for the transition, and $H_I(\omega)$ describes the photon-electron interaction. The width of the final state due to the filling of the core hole is Γ. For a constant density of states and matrix element, (1) yields the familiar arctangent formula[7]

$$\mu(\omega) \propto \tfrac{1}{2} + (1/\pi)\tan^{-1}[2(\omega-\epsilon_K)/\Gamma]$$

describing the gross shape of the edge, but exhibiting no fine structure.

An explanation of this fine structure necessitates

TABLE I. Summary of energy positions (relative to peak A) of features in Fig. 1 absorption spectra. Peaks obtained by subtracting an experimentally fitted arctangent curve and then finding the centroid of the remaining peaks.

Element	$K'-A$ (eV)	$B-A$ (eV)	$C-A$ (eV)
Y	−10	13	36
Zr	−13	18	46
Nb	−13	26	45
Mo	−12	27	70
Ru	−16	24	66
Rh	···	25	67
Pd	···	24	65
Ag	···	21	57

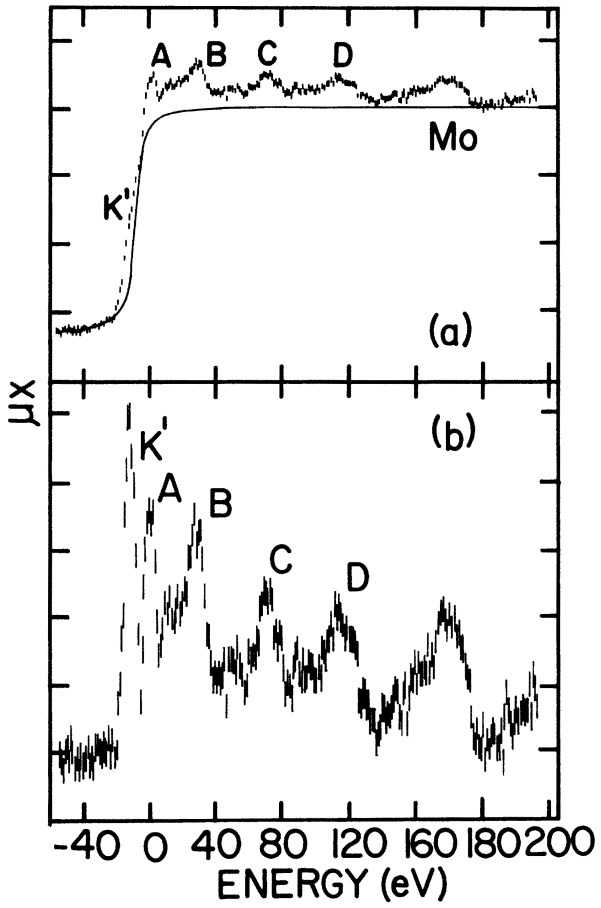

FIG. 2. (a) K photoabsorption spectrum of molybdenum showing $\mu x = \ln(I_0/I)$ of the data plotted vs energy (dots) and computer fitted by eye, arctangent curve (solid line). The difference between the arctangent curve and the $\ln(I_0/I)$ of the data is shown in (b). Bar height shows magnitude of error due to counting statistics.

two additional ingredients: (i) the "local band structure" in the vicinity of the core hole; (ii) the energy modulation of the matrix element due to scattering by the local environment. That the photoelectron sees only the local band structure arises from the short mean free path (mfp), ~10 Å,[8] of the electron with energy ≤ 100 eV; i.e., the electron sees the density of states for an atom cluster with mfp dimensions. Since density-of-states calculations for atom clusters give results similar to the bulk, only smeared out by an energy of the order $\hbar$(electron velocity)/(mfp),[9] we make use of existing band-structure calculations in which the density of states is smeared not only by the width of the 1s hole, but also by the width of the emitted electron.[10] At higher energies, the band potential perturbs only weakly the kinetic energy, and at sufficiently high energies one need only consider the (multiple) scattering of the emitted electron by neighboring atoms.[11]

The preceding discussion leads us to the following (speculative) interpretation of the absorption fine structure of the 4d transition metals. The K-edge dipole (1s–final-p) photoabsorption rate depends strongly on the p-wave projection of the density of available final states. A highly schematic plot of the density of states for the 4d series metals, shown in Fig. 3, exhibits some common features[12]: a broad d band of high density (containing some p-wave admixture)[13] followed by a sharp drop and then another band of high density with appreciable p-wave character about 10 eV above ϵ_F. The last feature has been calculated only for Mo and Rh,[12] and no calculations to even higher energies exist. The Fermi levels of Y, Zr, Nb, Mo, Ru, and Rh lie near the middle of the d band, resulting in a large density of unoccupied states for a few eV just above ϵ_F. Although transitions of a 1s electron to this primarily d band are suppressed, there could be enough p strength to give a peak, which, broadened by lifetime[14] (3–7 eV) and instrumental (1–2 eV) effects and superimposed on an arctangent curve, could lead to the observed shoulder K'. As the d band is filled going across the row, the shoulder structure should become progressively weaker, and disappear entirely for Ag with a filled d band. This is the trend we observe. The peak at A, we suggest, is a reflection of transitions to the second band of high density of states (dashed curve in Fig. 3). In the case of Mo this band lies 10–12 eV above the unoccupied d band, which agrees with the observed $A - K'$ difference of 12 eV. The higher peaks may reflect further (uncalculated) structure in the density of states, but in any case must soon merge into the region where the oscillatory amplitude of the final-state wave function due to scattering by neighboring atoms is dominant. The shift in the B peak to lower energy for Y (and to a lesser degree for Zr) may reflect Y's considerably larger (~30%) nearest-neighbor distance compared to the center of the row.

Finally, we discuss why some possible alternate explanations of the fine structure are not applicable.

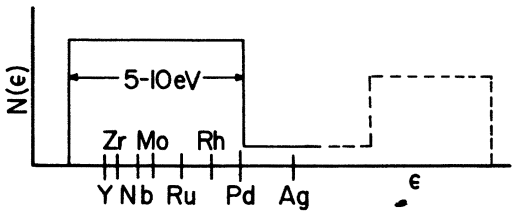

FIG. 3. Schematic density of states of the 4d transition metals showing the relative positions of the Fermi levels ϵ_F. The dashed portion at high energies has been calculated only for Mo and Rh.

Plasmon satellites. The shape of plasmon satellites, commonly mentioned as a source of x-ray structure,[15] would reflect the underlying photoabsorption process so that they would appear simply as scaled versions of the main edge displaced by the plasma frequency. Since the main edge is roughly a step function and only peaks are observed, we conclude that plasmon satellites are not important in our spectra. This is consistent with the observation that the x-ray transition does not involve a large distortion of the charge distribution and is thus unlikely to excite plasmons.[16]

X-ray singularity. For K absorption the conventional theory[17] predicts a rounded threshold and hence, if anything, this effect would tend to diminish the edge structure.

Multiple-electron excitations. The simplest example would involve the ejection of a $4p$ electron by the $1s$ electron (via the Coulomb interaction) during photoexcitation. The binding energies of the $4p$ electrons (26–62 eV across the row)[2] give a rough estimate of the additional energy required for double excitation. No such trend is observed. More important, one would again expect a step shape rather than a peak.

In conclusion, we note that extending band-structure calculations to higher energy and separating the density of states into s, p, d, ... contributions would be useful. On the experimental side, we would expect the L-absorption spectra of these metals to yield a strong peak on the edge (rather than the weak shoulder seen here) owing to both the narrower core-hole width and increased transition rate (atomic p to d band).[18]

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[1]Thicknesses in mg/cm^2: Y, 21.9; Zr, 21.9; Nb, 21.2; Mo, 25.2; Ru, ~20; Rh, 31.3; Pd, 31.4; and Ag, 42.8.

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