Large Final-State Effects in the Core-Level Electron Energy-Loss Spectra of Vanadium at Low Incident-Electron Energies

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Large final-state effects have been observed in the $3p$, $3s$, and $2p$ electron energy-loss spectra of vanadium as the incident-electron energy was reduced from 1500 eV to about 50 eV above the core threshold. Changes in the line shapes for the onset of $2p_{3/2}$ excitation and changes in measured threshold energies for $2p_{3/2}$, $3s$, and $3p$ excitation show the significance of the transition from sudden to adiabatic excitation. Strong excitations due to exchange effects are also observed in the $3p$ spectra at low incident energies.

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The nature of the electronic excitations, screening dynamics, and decay mechanisms in several different forms of electron spectroscopy of solids, particularly the core-level spectroscopy of metals, has been of considerable interest recently.[1] One area where little understanding and data for solids exist concerns effects which depend upon whether the initial core-level excitation is sudden or adiabatic.[2]

We have measured the $3p$, $3s$, and $2p$ electron energy-loss spectra of vanadium as the incident-electron energy E_0 was reduced from 1500 to about 50 eV above the threshold energy for core-level excitation. Changes have been observed in the threshold-region energy-loss line shape as the incident energy was varied. In the $3p$ loss spectra, intense and unexpected features were found for $E_0 < 300$ eV; these features are interpreted as arising from strong exchange effects. We have also observed systematic decreases, typically 0.5–1.0 eV, in the measured threshold energies for core-level excitation at low E_0 from the values found at high incident energies ($E_0 \approx 1500$ eV). These changes in energy-loss line shapes and threshold energies are associated with large final-state effects as the core-level excitations become more adiabatic at low E_0.

Experimental details are described elsewhere.[3,4] The energy-loss spectra were measured in two forms. First, the energy distribution $N(E)$ of electrons backscattered from a polycrystalline V foil was measured with a double-pass cylindrical mirror analyzer. Second, we measured the difference intensity $[\approx dN(E)/dE]$ corresponding to the difference of spectra acquired with and without a 1.35-eV bias voltage applied to the gun cathode. Auger-electron and other features of constant energy are eliminated from the latter data and line-shape changes can be conveniently observed.

Measured $N(E)$ spectra in the threshold region for $3p \rightarrow 3d$ excitation are shown in Fig. 1 for a number of incident energies. The data for $E_0 > 700$ eV are similar to earlier measurements at comparable energies.[5] Note that the onset of $3p$ excitation, at an energy loss ΔE of about 37 eV, is barely detectable for $500 < E_0 < 1000$ eV and that the maximum intensity for $3p$ excitation occurs at $\Delta E \approx 50$ eV. In this range of E_0, the loss spectra resemble x-ray absorption data.[6] For $E_0 < 300$ eV, structure at about 37.6 and 40 eV energy loss grow in intensity until, for $E_0 = 150$ eV, the 37.6-eV loss becomes of compar-

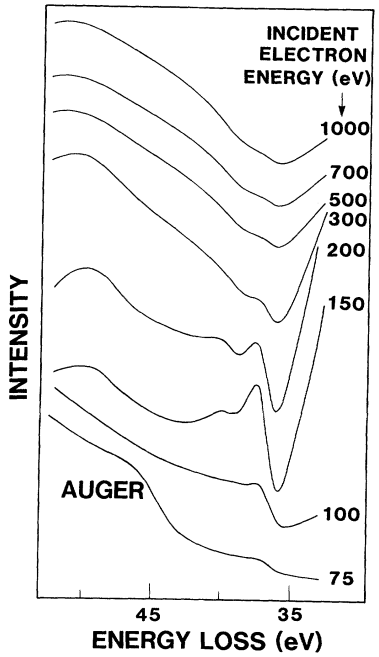

FIG. 1. V $3p$ energy-loss spectra $[N(E)]$ for the incident-electron energies indicated.

able intensity to the 50-eV peak. For $E_0 < 100$ eV, the $3p$ loss structure is superimposed on a background of low-energy secondary electrons; here, the 37.5-eV loss is strong and separate peaks at 40 and 50 eV are not discerned.

Figure 2 shows plots of the difference intensity $[\approx dN(E)/dE]$ for $3p$ excitation in V measured for various incident energies (note that the Auger peak seen in Fig. 1 for $E_0 = 75$ eV has been almost completely removed). The negative peaks for $\Delta E \approx 37$ eV correspond to the inflection points in the $N(E)$ data of Fig. 1 and provide a convenient measure of the threshold energy for $3p$ excitation at each E_0. There is a substantial change in the intensity of each threshold peak in Fig. 2 relative to other spectral features for the different incident energies. There are also systematic shifts in the positions of the threshold peak and the feature at $\Delta E \approx 40$ eV.

Figure 3 shows similar plots of the difference intensity for $2p \rightarrow 3d$ excitation in V at different incident energies; the feature for $\Delta E \approx 512$ eV corresponds to the $2p_{3/2}$ threshold while the 520-eV feature is the $2p_{1/2}$ threshold. The $2p_{3/2}$ negative peak is sharp for E_0 close to threshold but for $E_0 > 700$ eV another feature at $\Delta E \approx 514$ eV increases in intensity until, at $E_0 = 1500$ eV, only a broad composite is observed. Comparable changes are not observed, however, in the $2p_{1/2}$ component.

Similar measurements, not shown here, have been made of V $3s$ excitation. A threshold is found corresponding to the optically forbidden $3s \rightarrow 3d$ excitations[7] although the feature is broader than the $2p_{3/2}$ data in Fig. 3 due to the $3s$-hole lifetime being shorter than the $2p_{3/2}$-hole lifetime.

Figure 4 is a plot of the measured threshold energies for $3p$, $3s$, and $2p_{3/2}$ excitation in V as a function of incident energy. A systematic decrease is found in the threshold energies with decreasing E_0, i.e., as the excitations become more adiabatic. A comparison is made in Fig. 4 with the core-level binding energies (BE) determined on the same sample by x-ray photoelectron spectroscopy (XPS).[8] While an exact correspondence between the XPS BE data and the threshold energies measured for large E_0 is not expected,[9] there is close agreement for $3p$ excitation, good agreement for $2p_{3/2}$ excitation, and an apparently large disagreement for $3s$ excitation. The measured $3s$ loss spectra are dominated by $3s \rightarrow 3d$ excitations; that is, the final states are the same as for excitations from the $2p_{3/2}$ initial state. The apparent disagreement for the $3s$ data in Fig. 4 is believed due to the changing relative intensity with E_0 of the two final-state structures observed in the $2p_{3/2}$-loss data (Fig. 3) broadened by the $3s$ linewidth. The changing intensities lead to a large change in the measured threshold energy of the composite peak and change of linewidth. Thus, only for low E_0 is there an approximate corre-

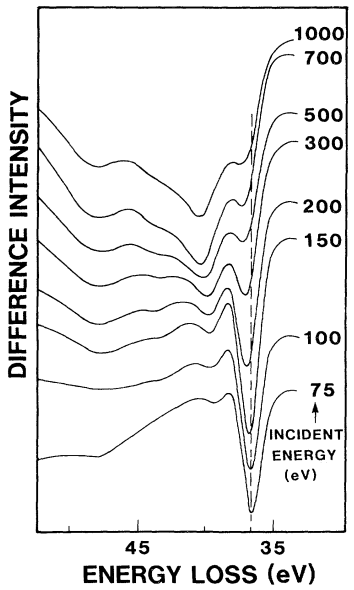

FIG. 2. Difference spectra $[\approx dN(E)/dE]$ for V $3p$ excitation at the indicated electron energies.

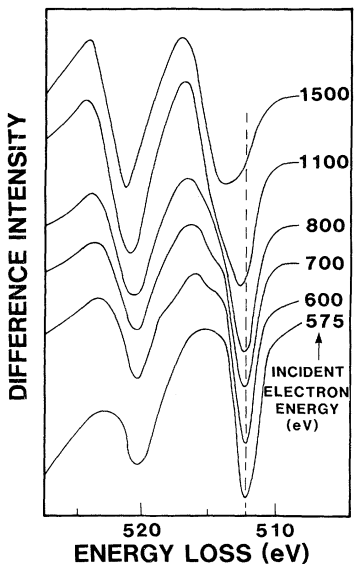

FIG. 3. Difference spectra for V $2p$ excitation at the indicated electron energies.

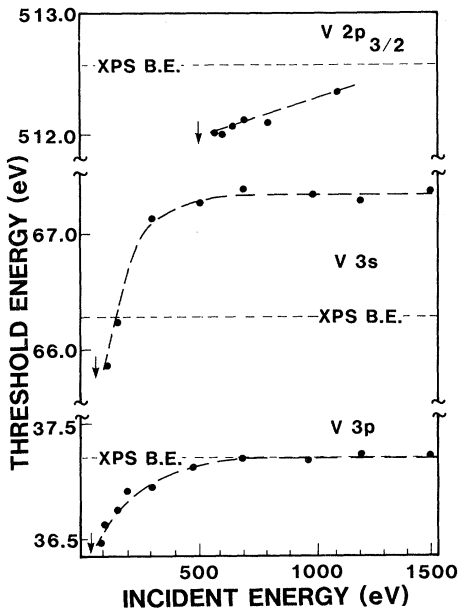

FIG. 4. Plots of the measured threshold energies for $3p$, $3s$, and $2p_{3/2}$ excitation in V as a function of incident-electron energy. A dashed line has been drawn through the points to guide the eye. The horizontal dashed lines represent measured values of XPS binding energies. The vertical arrows designate threshold energies on the incident-energy scale.

spondence between the measured $3s$ threshold energy and the XPS BE.

The observation of two final states with relative intensities depending on E_0 in the $2p_{3/2}$ loss data is similar to measurements of $3d$ excitation in Ba, La, and Ce by Kanski and Wendin.[1] These authors invoked a dynamic screening mechanism involving an intermediate, screened, quasilocalized state. An alternative explanation is that the $2p_{3/2}$-excitation threshold line shape is affected by an interference between the direct excitation $2p^63d^3 \rightarrow 2p^53d^4$ and the excitation $2p^63d^3 \rightarrow 2p^63d^2\epsilon f$ coupled via the $2p^53d^4 \rightarrow 2p^63d^2\epsilon f$ Auger transition. Such interference effects dominate the $3p$ x-ray absorption line shapes at threshold in Fe, Co, and Ni.[10] While the $2p^63d^3 \rightarrow 2p^53d^4$ direct excitation is strong and the interference in the $2p_{3/2}$ excitation is much weaker than for $3p$ excitation, it is believed that variations in the relative excitation probabilities for the $3d_{5/2}$ and $3d_{3/2}$ components with changing excitation energy, analogous to those found in the photoemission from the valence bands of the noble metals,[11] could explain the line-shape changes of Fig. 3. Results similar to Fig. 3 are found for Ti and Cr.[3,4] A systematic decrease is found in the separation of the two final states for $2p_{3/2}$ excitation in the sequence Ti, V, and Cr that appears to correlate with the decreasing widths of the unoccupied densities of states.

Effects similar to those just described could exist in the $3p$ excitation spectra although they are not observed because of the small $3p \rightarrow 3d$ cross section for $\Delta E < 40$ eV and $E_0 > 500$ eV (Fig. 1) and the emergence of new and intense features with increasing intensity as E_0 is reduced below 500 eV (Figs. 1 and 2). The rapid rise in intensity of these energy-loss features (observed also[3,4] in Ti and Cr) as E_0 is decreased below several times the minimum $3p$ excitation energy can be interpreted in terms of a strong exchange interaction. The existence of a strong exchange interaction in Ti $3p$ excitation has recently been demonstrated.[12] Energy losses due to exchange processes have not been observed previously in the $3d$ transition metals although analogous triplet excitations have been observed in He and other gases.[13]

The observed dependence of the $3p$ and $2p_{3/2}$ threshold energies on E_0 in Fig. 4 can be due to a number of factors.[3] The magnitude of the changes appears too large to be explained by BE differences of bulk and surface atoms or by effects due to changing minimum momentum transfer [Jach and Powell (second paper), Ref. 1]. The low-energy "loss" electron can interact, however, with the core hole, the "excited" electron, and the screening response of the solid. Effects of this type have been predicted for XPS line shapes as a function of photon energy[14] but no calculation has been made for the present experiment. The total changes in the threshold energies with E_0 could be the combination of these several effects. While a theory to describe the line-shape changes of Fig. 3 and the variation of threshold energies in Fig. 4 does not exist, the changes that occur over a range of incident energies of about 500 eV above the appropriate core-level BE indicate a transition from sudden-excitation conditions at high E_0 to more adiabatic excitation as E_0 is reduced to ≈ 50 eV above the excitation thresholds.

In summary, we have observed large changes in near-threshold energy-loss line shapes for $3p$, $3s$, and $2p$ excitation in vanadium as the incident-electron energy E_0 was varied within about 500 eV of the threshold for core ionization. In the same range of E_0, the threshold energies for core excitation changed by typically 0.5–1.0 eV. New structure due to a strong exchange interaction was found in the $3p$ loss spectra for $E_0 < 500$ eV.

These observations, together with similar results for Ti (Ref. 3) and Cr (Ref. 4), demonstrate the important effects of the transition from sudden to adiabatic excitation in determining electron dynamics in different types of core-level excitations.

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