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Difference in the Cr L_3/L_2 Intensity Ratio Measured by Soft-X-Ray and Auger-Electron Appearance-Potential Spectroscopy*

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The L_3/L_2 radiative intensity ratio measured by soft-x-ray appearance-potential spectrum (SXAPS) techniques for a clean Cr surface is approximately unity. The Auger-electron appearance-potential spectrum data on the total Auger-electron yield show the expected statistical weighting ratio of 2. It is concluded that a radiative transition to a $2p_{1/2}$ hole is twice as likely as to a $2p_{3/2}$ hole. SXAPS L_3/L_2 ratios should provide a sensitive test for models of the electronic structure of surface atoms.

The total soft-x-ray emission of an electron-bombarded surface changes abruptly at potentials corresponding to core-electron binding energies of atoms in the surface region. These changes are essentially the core level excitation probabilities superimposed on a smoothly increasing bremsstrahlung background and can be sensitively detected in the derivative of the total x-ray emission.[1] However, while the shape of the differential excitation curves of the L_3 and L_2 levels of the $3d$ transition metals are in good qualitative agreement with a simple one-electron model of the excitation process,[2] the L_3/L_2 intensity ratios frequently deviate substantially from the expected ratio of 2 based on a statistical weighting of $2j+1$.

L_3/L_2 ratios greater than 2 have been observed in x-ray emission studies of Ti, V,[3] and Cr.[4] In each case the ratio decreased as the excitation energy was reduced. The effect has been attributed to self-absorption and to an $L_3 \rightarrow L_2$ Auger transition. Appearance-potential spectroscopy, however, is a threshold effect, and self-absorption can probably be neglected in this energy range.[5] Furthermore, the $L_3 \rightarrow L_2$ Auger transition should not in itself have any appreciable effect on the soft-x-ray appearance-potential spectrum (SXAPS) since the characteristic x rays are not dispersively analyzed. Thus, the radiative decay is simply used to signal an excitation and radiative transitions to the L_3 are indistinguishable from those to the L_2. In any case, these factors all tend to produce L_3/L_2 ratios greater than 2.

In the case of clean chromium, on the other hand, the L_3/L_2 ratio measured by soft-x-ray appearance-potential spectroscopy is *less* than 2, being approximately unity. This appears to require either that the excitation of these levels does not obey a weighting of $2j+1$ or that the $2p_{1/2}$ hole is twice as likely as the $2p_{3/2}$ hole to decay via a radiative transition.

This can be resolved in a straightforward way by comparing the SXAPS to the corresponding Auger-electron appearance-potential spectrum (AEAPS). The latter is essentially just the derivative of the secondary emission coefficient with respect to incident electron energy. The total decay probability of a core hole including both radiative and Auger processes is unity. Since nonradiative decays are of the order 10^3 times more probable than radiative decays for these levels, differences in their radiative transition probabilities will not appreciably affect the Auger rates. The L_3/L_2 intensity ratios measured by AEAPS should therefore accurately reflect the excitation probabilities.

The apparatus used in this comparison is shown schematically in Fig. 1. The system is cylindrically symmetric, with the axis of the cylinder lying vertically in the plane of the figure. The grids g maintain a field-free region for the scattered electrons. Those electrons emerging at nearly grazing angles pass through a slit in the shield surrounding the sample S and are collected on the electrode E. The collector is biased to re-

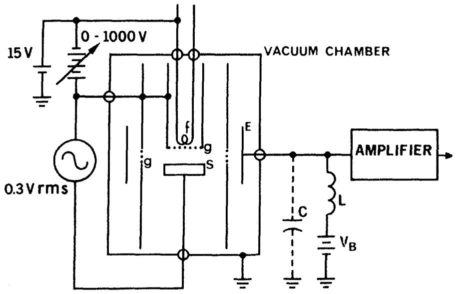

FIG. 1. Schematic diagram of the Auger appearance-potential spectrometer. f is a pure tungsten filament; the grids g maintain a field-free region around the sample S; secondary electrons are collected by the electrode E. A high-Q inductor L in parallel with the distributed capacitance C forms a resonant circuit at the oscillation frequency of 6 kHz. The bias V_B (≈ 200 V) is reversed for the soft-x-ray measurements.

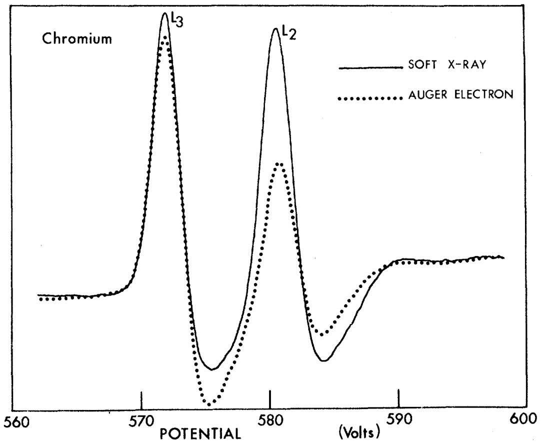

FIG. 2. Comparison of the L_3, L_2 spectrum of clean chromium by SXAPS and AEAPS. The plots were approximately normalized to the L_3 peak-to-peak amplitude.

ject the so-called "true" secondary peak. To obtain the derivative of the collector current, a small oscillation is superimposed on the sample potential. That portion of the collector current varying at the oscillator frequency (≈ 6 kHz) is selected by a tuned circuit consisting of a high-Q inductor L in parallel with the distributed capacitance C. This provides sufficient frequency discrimination without the need for a lock-in amplifier since the signals are about 10^4 times larger than those typically observed in SXAPS. The principal disadvantage of the AEAPS as compared to SXAPS is that the background is not well behaved. At energies below about 200 eV, strong diffraction effects are observed as diffraction maxima are swept across the slit. In addition, secondary emission does not exhibit the nearly linear dependence on incident energy observed for the bremsstrahlung background in SXAPS.[2] In the results reported here the bias on the collector V_B was adjusted until the secondary emission variation of the collector just offset that of the sample over the region of interest.

To obtain the SXAPS, the bias V_B on the collector was simply reversed. The collector then becomes a photocathode.

The results obtained by the two methods for a clean polycrystalline chromium surface are compared in Fig. 2. The SXAPS is identical to that previously reported for clean Cr.[2] The shape of the spectrum for a single level is qualitatively what one would expect on the basis of a simple band model.[2] However, whereas the shape of the spectrum for each level is nearly the same for the two techniques, in AEAPS the L_3/L_2 intensity ratio is almost exactly 2 as compared to approximately 1 for SXAPS.

We conclude that the excitation of $2p_{3/2}$ and $2p_{1/2}$ levels goes as $2j+1$ as expected. However, the $2p_{1/2}$ hole is twice as likely to decay via a radiative transition as the $2p_{3/2}$ hole. This is presumably a consequence of j-dependent selection rule for radiative transitions from the valance band to the $2p$ levels and should provide a sensitive test for models of the electronic structure of surface atoms.

ACKNOWLEDGMENTS

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