Autoionization Emission from Transition Metals by Electron Impact

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Intense gain satellites associated with the $M_{2,3}VV$ Auger transition have been observed for representative $3d$ transition metals. The satellites have line shapes and intensities that resemble those of the $M_{2,3}$ electron-energy-loss and resonant photon-excited spectra of these materials and are identified as being due to autoionization electron emission. This identification satisfies the expectation that the Fano effect should be manifest in both absorption *and* emission experiments, whether photon or electron excited.

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The $3d$-transition-metal series shows strong electron-energy-loss and photoabsorption peaks for energies corresponding to the resonant $3p$-to-$3d$ transition.[1,2] These peaks have been explained in terms of the resonant interaction between configurations that follow from the excitation to a quasidiscrete d level and to the continuum of f levels.[3,4] In atomic physics such a resonant interaction was first used by Fano[5] to explain the influence of autoionization levels on the electron loss spectra in He gas.[6] Mehlhorn[7] subsequently observed electron emission from autoionization levels of He. It has been established that the existence of autoionization levels should influence both the absorption *and* the emission spectra.[8] Since in the $3d$-transition metals the $3p \rightarrow 3d$ transition is an autoionization level leading to strong absorption, one should also expect to see strong autoionization emission in these materials. In fact, such an emission in the synchrotron-radiation–excited spectra has recently been reported in numerous publications[9-12] and there is little doubt that it should also be observable in electron-impact spectra.[12]

In this Letter we report intense high-energy satellites of the electron-excited $M_{2,3}VV$ Auger transitions of representative $3d$-transition metals, and identify them as the autoionization electron emission corresponding to the $3p$-to-$3d$ resonant transitions. The processes leading to this autoionization emission ϵf may be summarized as follows:

$$p^6d^n \rightarrow p^5d^n d^* \rightarrow p^6d^{n-1} + \epsilon f\,, \qquad (1)$$

where the first process is absorption and the second is emission, and d^* denotes that in the presence of the $3p$ core hole the originally unfilled d levels are renormalized and broadened by the Fano effect.

The experiments were performed in a UHV system (base pressure 4×10^{-11} Torr) equipped with an x-ray source (Mg $K\alpha$) and double-pass cylindrical-mirror analyzer with a coaxial electron gun. Undifferentiated Auger and electron-energy-loss spectroscopy (ELS) results were taken with no ac modulation of the outer cylinder, but with half-cycle blanking of the electron-gun emission and "analog pulse counting" using a lock-in amplifier. We used in the experiments polycrystalline V and Cr and single crystals of Ni and Cu, all $\sim 5\times5\times1$ mm^3. The samples were Ar^+ sputtered and annealed to eliminate trace oxygen, carbon, and sulfur contamination.

In Fig. 1 we show, taken simultaneously, both the loss and MVV Auger spectra for V, Cr, Ni, and Cu. A suitably low value of the primary beam energy (226 eV) was chosen to facilitate direct intensity comparisons of resonant absorption and emission features as outlined in Eq. (1) and described below. Four types of features (labeled a–d) are apparent in Fig. 1. At the high-

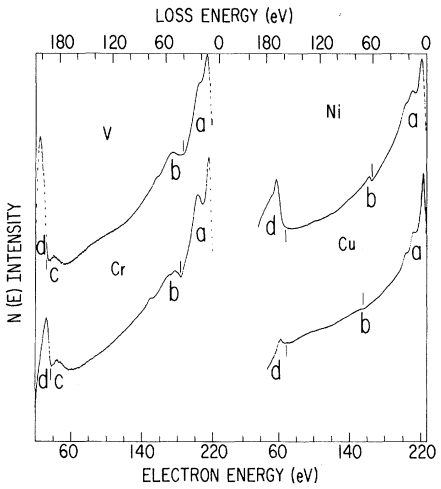

FIG. 1. Electron-energy-loss and emission spectra from V, Cr, Ni, and Cu by electron impact. a, Plasmon loss; b, $M_{2,3}$ loss; c, autoionization emission; d, $M_{2,3}VV$ Auger line.

est kinetic energies (lowest loss energies) are the plasma-type excitations (*a*), followed by the $M_{2,3}$ loss spectra (*b*), which decrease in relative intensity with increasing atomic number Z, as in Ref. 1. At the lowest kinetic energies are the $M_{2,3}VV$ Auger transitions (labeled *d*), followed by their gain satellites (*c*), which are of primary interest in the present study. Figure 2 illustrates a direct comparison of features *b* and *c* for V and Cr. (The Fe panel in Fig. 2 will be discussed later.) The striking similarities in thresholds, peak energies, and intensities found in Fig. 2 indicate that feature *c* is the ϵf emission counterpart to the Fano absorption process[3,4] observed in $M_{2,3}$ loss spectra and outlined in Eq. (1). Full identity between the absorption and emission spectra (regions *b* and *c*, respectively, of Fig. 1) is not expected[8] since narrow collection angles ($43° \pm 3°$) are necessarily employed, approximate ($\propto E$) transmission-function corrections are used, etc.

We believe that our autoionization emission assignment is definitive in that we can rule out earlier interpretations of region *c* in Fig. 1. Firstly, the satellites (*c*) mask the weak M_1VV Auger transitions, but cannot possibly stem from M_1 initial states. This is because the satellites are both too intense (in V and Cr by factors of $\sim 10^1$) and too wide (greater than twice the occupied bandwidth), as we show in detail elsewhere.[14] For example, an M_1VV Auger transition appears in Fig. 3, curve *b*, to be discussed below. Secondly, we rule out an $M_{2,3}M_{2,3}$ doubly ionized initial-state basis for the satellite (*c*). Such an $M_{2,3}VV$ double-ionization satellite should be located energetically closer to the $M_{2,3}$ threshold (by factors of ~3–5). The basis for this estimate is the difference in $M_{2,3}$ binding energies of neighboring elements, well known to core-level spectroscopists as the $Z+1$ rule. Thirdly, possible plasmon-gain satellites are energetically mispositioned, based on our inversion of standard loss-stripping procedures to compute such features.[14] Finally, double-ionization and plasmon-gain mechanisms cannot plausibly explain the high intensities, nor the intensity variation with Z.[15]

We further scrutinized our autoionization-emission interpretation in a variety of ways. Experiments were performed to verify that the autoionization satellite persists on compound formation. In Fig. 3 we show results for $V_3Si(100)$, where the vanadium ϵf emission satellite persists, as expected. Also, oxidation of vanadium (not shown) resulted in a somewhat increased satellite intensity. This is consistent with the Z-dependent intensity behavior, since charge transfer to oxygen gives rise to an increased number of *d* holes. In addition to the intensity trend with Z,

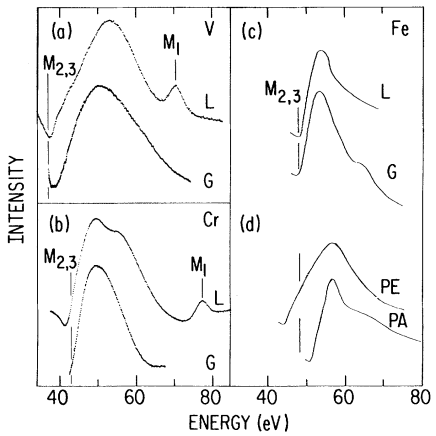

FIG. 2. $M_{2,3}$ core-level absorption and emission spectra. (a) and (b) Electron energy loss (L) and $M_{2,3}VV$ gain satellite (G) for V and Cr, correspondingly (our experimental results). (c) Same as in (a) and (b) for Fe; curve L from Ref. 1 and curve G from Ref. 13. (d) Resonant photoemission (PE) (Ref. 9) and photoabsorption (PA) (Ref. 2) curves for Fe.

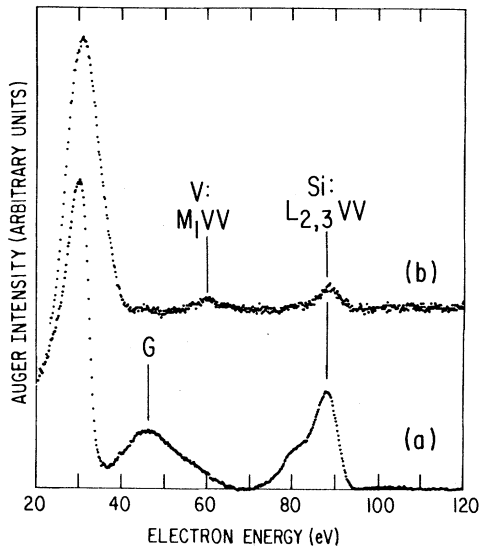

FIG. 3. Vanadium Auger $M_{2,3}VV$ and M_1VV for V_3Si. Curve *a*, electron-excited spectrum ($E_p = 2$ keV) with G being the intense gain satellite (autoionization emission). Curve *b*, x-ray–excited ($h\nu = 1253.5$ eV) spectrum with no gain satellite and with an observable M_1VV line. The peak on the right-hand side is Si $L_{2,3}VV$.

the width of the autoionization at the beginning of the d series is broad, as a result of strong multiplet splittings of the initially quasidiscrete levels, and narrower toward the end of the d series, as a result of filling of the d band.[3,4] Note also (Fig. 2) that the emission line shapes for V and Cr exhibit a small asymmetry with a steeper falloff toward lower kinetic energies, a well-known signature of Fano lines. In addition, we found (Fig. 3, curve b) that the satellite is not x-ray stimulated with a Mg $K\alpha$ source, again as expected, since such x-ray absorption will cause the $3p$ electron to be removed from the solid, while inelastic electron scattering permits excitation of a broad spectrum of the resonant $3p \rightarrow 3d$ transitions. Finally, no readily discernible gain satellites were observed in Ni and Cu, in agreement with the general autoionization process, since in these materials one observed only antiresonant behavior of the main valence-band photoemission.[10,11]

Very recently an $M_{2,3}VV$ gain satellite was detected, but not assigned, in a pioneering spin-polarized Auger study of Fe.[13] This Fe satellite is plotted in Fig. 2(c), where it is compared with the loss spectrum of Ref. 1 arbitrarily normalized at their peak maxima. Using the comparison of Fig. 2(c) we identify the gain satellite of Ref. 13 as being due to autoionization as in V and Cr. Figures 2(c) and 2(d) give a graphical demonstration that the four different experiments —electron loss (from Ref. 1), electron-excited autoionization (from Ref. 13), resonant photoabsorption (from Ref. 2), and photoemission (from Ref. 9)—all stem from the same autoionization levels associated with the $3p$-to-$3d$ transition.

The results of Ref. 9 for Mn, Fe, and Co show a falloff with Z in the valence-band resonant photoemission, which is in agreement with the ELS study of Ref. 1, and with our autoionization results. They also show a visible resonant effect for Mn and Fe, while for Co the effect is mainly antiresonant in nature. Accordingly, one should expect to see autoionization emission by electron impact from Mn and Fe, as we observed from V and Cr (our intense Cr autoionization emission should be compared with the strong valence-band photoemission enhancement of Barth *et al.*, Ref. 16) while in Co the situation should be similar to our results for Ni and Cu, with no detectable autoionization emission. In Ref. 13 an intense (with respect to the main $M_{2,3}VV$ Auger line) gain satellite was observed only by polarization detection, indicating that most of the resonant emission comes from the lower part of the valence band of Fe which is predominantly majority spin. This is in accord with the preferred resonant enhancement of the bottom of the valence band in $3d$-transition metals.[9-11,16] The $M_{2,3}VV$ Auger line of Fe comes from the full d-band density of states below the Fermi energy, and will therefore be less polarized than the gain satellite which orginates mainly from the positively polarized bottom of the band. This explains the unusually high polarization of the gain satellite relative to the Fe main Auger line in Ref. 13. We believe that the nonappearance of a visible Fe $M_{2,3}VV$ gain satellite in the unpolarized mode of Ref. 13 was mainly due to a strong sloping background that masked it.

In summary, we observe broad, intense gain satellites above the $M_{2,3}VV$ Auger transitions for $3d$-transition metals, and identify them as being autoionization emission that accompanies $3p \rightarrow 3d$ resonant inelastic electron scattering. We base our conclusions on intensity, threshold, and peak-position comparisons with $M_{2,3}$ electron-energy-loss spectra taken simultaneously with the emission spectra. Also, literature comparisons for Fe (Ref. 13) and oxidation results for V support our finding as does the nondetection of these satellites in Mg-$K\alpha$ x-ray–stimulated spectra. The clear identification of autoionization emission in $3d$ metals by electron impact finally satisfies the expectation that the Fano effect should be manifest in both absorption *and* emission experiments, whether photon or electron stimulated.

As a concluding remark we point out that autoionization gain satellites should also be observable in the Auger spectra of other transition metals, lanthanides, and actinides, since Fano resonances are known to exist in their electron loss, photoabsorption, and photoemission spectra.[17,18]

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