RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 10 1 APRIL 1987

# Extended fine structures in autoionization emission spectra of bulk chromium

G. Chiarello, V. Formoso, L. S. Caputi, and E. Colavita
*Dipartimento di Fisica, Università della Calabria, 87036 Arcavacata di Rende, Cosenza, Italy*

(Received 5 January 1987)

Extended fine structures have been observed in autoionization emission spectra of chromium. Their origin has been determined by a one-to-one comparison with the extended energy-loss fine structures above the $M_{23}$ energy absorption process. Similar to x-ray and electron-induced absorption spectra, both near-edge and extended fine features can be observed and distinguished in autoionization spectra.

Autoionization emission occurs at the high kinetic-energy side of $M_{23}VV$ Auger lines of $3d$ transition metals,[1,2] their oxides,[3] and silicides.[4,5] The process is associated with direct recombination of resonant $3p$-$3d$ transitions. A close correspondence in line shapes and intensities between the $3p$ electron-energy-loss (EEL) spectra and the autoionization near-edge structures (ANES) has been established[1] and studied for all the $3d$ transition metals.[6]

Chromium is expected to show a strong autoionization emission,[6] well separated from above the $3p$ threshold, and thus appears to be the best candidate for our purposes. The aim of the present work is to investigate the exsitence of fine structures above the autoionization near edge on the high kinetic-energy side and to compare them with the well-known oscillations[7,8] observed above the EEL $3p$ absorption edge on the high energy-loss side. The interpretation of the autoionization process would involve not only the near-edge features but also the structures which extend for several hundred eV from the $3p$ threshold. Moreover, the resonant $3p$-$3d$ transition would appear of fundamental importance for the Auger-satellite emission and also for its related fine structures.

It is well known that core-valence-valence Auger transitions are sensitive to the local density of occupied states at an atomic site and that autoionization emission of $3d$ transition metals gives further information on local electronic effects involving unoccupied levels.[4,9] Electron-induced emission is shown now to give surface structural properties through its extended fine structures.

Electron-energy-loss measurements[8] carried out above shallow $3p$ core levels exhibit extended oscillatory fine structures due to backscattering events of the $3p$ final-state electron wave in the potential of the surrounding atoms. These are termed extended-energy-loss fine structures (EELFS). Structural information in terms of the radial distribution function around the excited atom can be extracted using the same analysis procedure of the extended x-ray absorption fine structures (EXAFS) technique.[10] Similarly, the evidence of fine structures above the autoionization emission edge gives a structural EXAFS-like character to $3p$-$3d$ resonant spectroscopy.

Figure 1 shows the electron yield $Y(E)$ in the kinetic energy region of the Cr $M_{23}VV$ Auger line. Several features are clearly detected: the intense gain satellite, the $M_1VV$ Auger, and the autoionization extended fine structures (AEFS). The latter are visible in the enlarged scale and extend for several hundreds of eV toward high kinetic energy. Each feature is energy independent on the primary electron beam and a monotonic intensity decrease of the oscillatory part is observed.

The surface of the pure polycrystalline Cr sample was cleaned by argon-ion bombardment, annealed in ultrahigh vacuum (base pressure $10^{-8}$ Pa), and checked for cleanliness by Auger spectroscopy. The measurements were taken in both the first and second derivative detection mode by an hemispherical analyzer (EA 10:100) driven in the

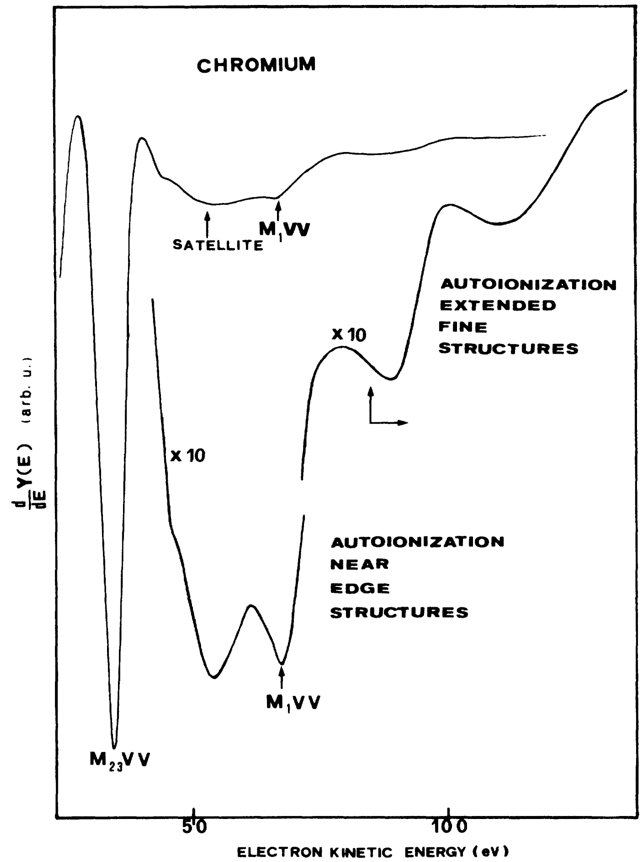

FIG. 1. Electron yield in the $M_{23}VV$ Auger energy region. Autoionization near-edge and extended fine structures are shown.

$\Delta E/E$ = const mode and by a glancing-angle electron gun. The modulation amplitude was varied from 2 to 5 $V_{pp}$ peak to peak and the electron beam current was 4 to 8 $\mu$A. The signal was recorded by an on-line Commodore computer which provided the necessary data-acquisition versatility to obtain a good signal-to-noise ratio.

In atomic notation the processes leading to the autoionization electron emission corresponding to the $3p$-$3d$ resonant transition can be depicted in two steps: The first one (absorption) is the electron-induced excitation of the $3p$ level into the empty $3d$ level

$$3p^63d^5 \rightarrow 3p^53d^6, \qquad (1)$$

and the second step (internal deexcitation) is the autoionization emission

$$3p^53d^6 \rightarrow 3p^63d^4 + \varepsilon f. \qquad (2)$$

The emission is significantly delayed above the $M_{23}$ threshold so that the $M_{23}VV$ and the autoionization emission is well separated in energy. The outcoming $3p$ electron would be lost among the secondaries if the subsequent direct recombination would not move the emission to higher kinetic energies. It carries information on the empty $d$ levels as well as on the free-electron-like band, and near-edge and extended fine structures are reproduced in the electron-induced emission. When the $3p$-$3d$ transition is observed instead, by the EEL technique both $3p$ near-edge features and extended fine structures of the absorption core spectrum are reproduced in the backscattering electron yield of the primary beam. Spectral features are in this case related to the elastic peak and occur at sensible higher kinetic energies with respect to autoionization structures. Thus, the same $3p$-$3d$ transition may give rise to $M_{23}$ EEL features or, via direct recombination, to autoionization emission.

Figure 2 shows the complete electron-induced backscattering yield of Cr from zero kinetic energy up to the elastic peak. In the low-energy side above the $M_{23}VV$ Auger line, the ANES and the first AEFS feature are shown. The high-energy side, instead, shows the $M_{23}$ absorption edge and the first EELFS oscillation. The two energy regions appear to be each the specular reflection of the other, and a one-to-one correspondence exists between the $M_{23}$ absorption edge and the autoionization near-edge emission, in agreement with previous findings.[1-4] The inset makes clear the suggested similarity of the two different parts of the electron yield. For this purpose the energy-loss spectrum has been reversed with respect to the kinetic energy axis and then moved till the $M_{23}$ edge was aligned to the $M_{23}$ x-ray value. The inset shows also that there is energy coincidence for the first oscillation detected in the autoionization emission and in the energy-loss mode.

A more complete comparison of the two spectra is accomplished in Fig. 3, where the extended oscillatory regions are shown. Each oscillation of the extended autoionization spectrum occurs at the same energy as the correspondent oscillation of the extended energy-loss spectrum; the fine structures of the autoionization emission, however, are broader than the $M_{23}$ EELFS, as expected because of the deexcitation mechanism.[11] This finding is evidence of the composite character of autoionization electron emission and, moreover, of its similarity with the ab-

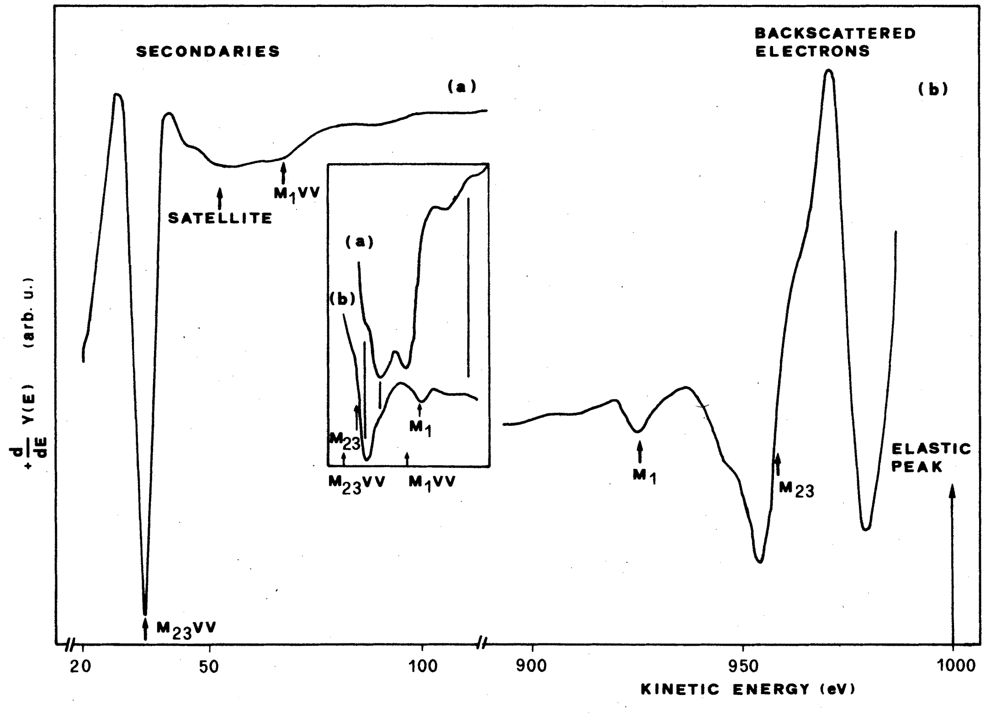

FIG. 2. Electron-induced backscattering yield of Cr. The inset shows the comparison between (a) the autoionization emission and (b) the $M_{23}$ EEL spectrum. The latter has been aligned with the x-ray photoemission spectroscopy binding energy position of the Cr $3p$ line by taking into account the work function.

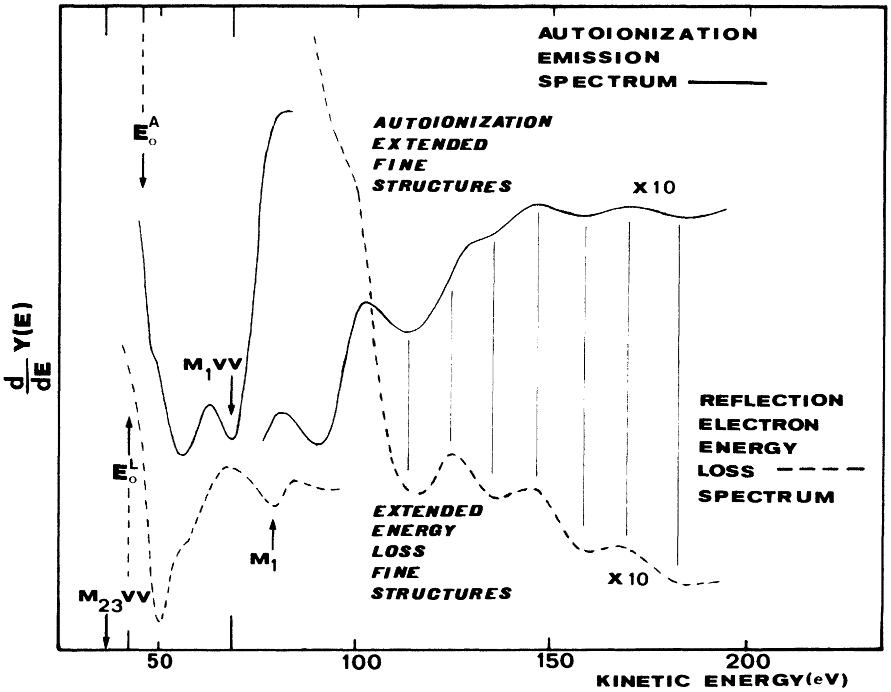

FIG. 3. Comparison between autoionization and energy-loss extended fine structures vs electron kinetic energy. Note the $M_{23}$ absorption threshold ($E_0^L$) and the $3p$-$3d$ autoionization emission onset ($E_0^A$).

sorption process, not only in the near edge but also in the structural EXAFS-like region. AEFS and EELFS oscillations have been compared again after the background subtraction and a one-to-one correspondence has still been observed especially for the third and fourth feature because of their much easier extraction from the static contribution.

Using the EXAFS procedure the two $X(E)$ signals have been turned into $X(k)$ spectra where $k$ is the wave vector of the excited electron in the free-electron-like plane wave above the edge, $k=[(2m/\hbar)(E-E_0)]^{1/2}$, and then Fourier transformed. The $E_0$ threshold energy has been chosen, respectively, at the $M_{23}$ EEL absorption and at the $3p$-$3d$ autoionization emission onset, which is about 3 eV higher because of the delayed maximum above the $3p$ threshold of the excitation cross section.[1] The obtained radial distribution functions are shown in Fig. 4 and peak at the same value of $R$ within 0.05 Å. Since the two signals are essentially due to the same $3p$-$3d$ absorption, the experimental peaks must be shifted for the same amount to find the real crystallographic distance.

At this stage of art, the meaning of AEFS oscillations seems established and, at the same time, any dependence[12] of the AEFS structures on the $M_{23}VV$ Auger process is ruled out, as verified also by a number of experiments. Both the autoionization near-edge features and the extended fine structures are absent above the $KVV$ Auger line of graphite (272 eV) and above the $L_{22}VV$ Auger line of Si (92 eV), for example. They are even absent above the $L_{23}VV$ Auger line of Cr, which involves deeper $p$-core levels. The occurrence of the $3p$-$3d$ resonant transition, instead, is necessary and appears to be the origin of autoion-

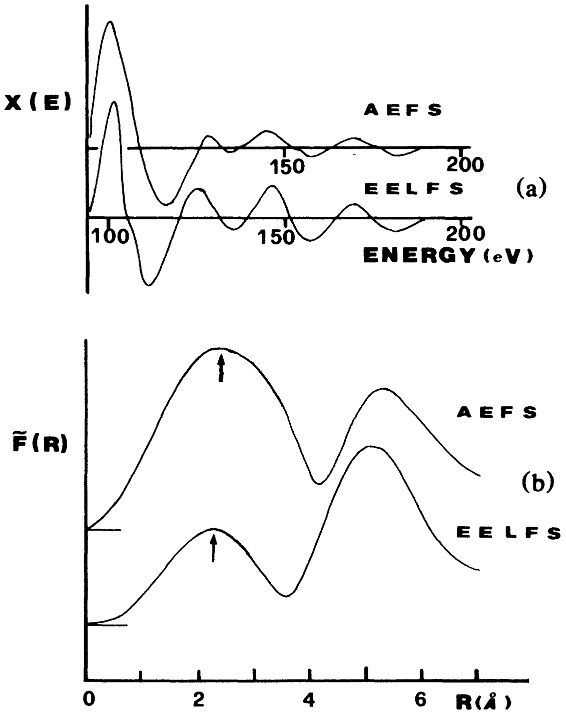

FIG. 4. (a) Comparison between AEFS and EELFS oscillations. (b) Fourier transforms of (a). Both $X(k)$ signals have been integrated between $k_{\min}=3.6$ Å$^{-1}$ and $k_{\max}=6.2$ Å$^{-1}$. The pseudoradial distribution functions peak at $R=2.35\pm0.05$ Å for the autoionization spectrum and at $R=2.25\pm0.05$ Å for the energy-loss spectrum.

ization oscillations. Finally, possible electron-electron scattering events may interfere with the autoionization signal but their uncorrelated nature is not expected to influence drastically the structural EXAFS-like character of the extended emission.

Together with speculations on the autoionization process, we have been motivated by possible applications in surface chemisorption studies on $3d$ transition metals.[13] The emitted electron is in this case coming from the very uppermost layer of the sample because of its low kinetic energy and may carry information on surface effects. Work is in progress to extend the above conclusions to all $3d$ transition metals because similar effects are expected.

We would like to thank Professor C. Calandra for stimulating discussions and encouragement. Particular thanks is due to E. Li Preti and V. Fabio for their invaluable technical support. This work was supported by Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche e Centro Interuniversitario di Struttura della Materia del Ministero della Pubblica Istruzione.

---

[1] S. D. Bader, G. Zajac, and J. Zac, Phys. Rev. Lett. **50**, 1211 (1983).

[2] S. D. Bader, G. Zajac, A. J. Arko, M. B. Brodsky, T. I. Morrison, N. Zaluzec, and J. Zac. Phys. Rev. B **33**, 3636 (1986).

[3] E. Bertel, R. Stockbauer, and T. Madey, Phys. Rev. B **27**, 1939 (1983).

[4] U. del Pennino, C. Calandra, L. Grandi, C. Mariani, and S. Valeri, Phys. Scr. (to be published).

[5] G. Zajac, J. Zac, and S. D. Bader, Phys. Rev. B **27**, 6649 (1983).

[6] G. Zajac, S. D. Bader, A. J. Arko, and J. Zac, Phys. Rev. B **29**, 5491 (1984).

[7] M. De Crescenzi, G. Chiarello, E. Colavita, and R. Memeo, Phys. Rev. B **29**, 3730 (1984).

[8] M. De Crescenzi and G. Chiarello, J. Phys. C **18**, 3595 (1985), and references therein.

[9] M. Polak and P. H. McBreen, Solid State Commun. **56**, 407 (1985).

[10] *EXAFS Spectroscopy: Technique and Application,* edited by B. K. Teo and D. C. Joy (Plenum, New York, 1981).

[11] J. A. D. Matthew and S. M. Girvin, Phys. Rev. B **24**, 2249 (1981).

[12] M. D Crescenzi, E. Choinet, and J. Derrien, Solid State Commun. **57**, 687 (1986).

[13] G. Chiarello (unpublished).