



High-energy resonant photoemission and resonant Auger spectroscopy in Ce-Rh compounds

P. Le Fèvre, H. Magnan, D. Chandesris, J. Vogel, V. Formoso, F. Comin

► To cite this version:

P. Le Fèvre, H. Magnan, D. Chandesris, J. Vogel, V. Formoso, et al.. High-energy resonant photoemission and resonant Auger spectroscopy in Ce-Rh compounds. *Physical Review B*, 1998, 58 (3), pp.1080-1083. <10.1103/PhysRevB.58.1080>. <hal-04196565>

HAL Id: hal-04196565

<https://hal.science/hal-04196565v1>

Submitted on 5 Sep 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

High-energy resonant photoemission and resonant Auger spectroscopy in Ce-Rh compounds

P. Le Fèvre, H. Magnan, and D. Chandesris

*Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, 91405 Orsay, France
and Commissariat à l'Energie Atomique, SRSIM, 91191 Gif sur Yvette, France*

J. Vogel

Laboratoire Louis Neel, BP 166X, 38042 Grenoble, France

V. Formoso and F. Comin

ESRF, BP 220, 38043 Grenoble, France

(Received 9 February 1998)

Strong resonant effects are observed at the Ce L_3 absorption edge in Ce-Rh compounds, both for the Ce $3d$ photoemission peaks and the $L_3M_{4,5}N_{4,5}$ Auger lines. These resonances show unambiguously that interference effects exist in core-level spectroscopies. In mixed-valent compounds, they occur at different photon energies making it possible to unravel the x-ray-absorption profiles. Moreover resonant $L_3M_{4,5}N_{4,5}$ Raman Auger lines are observed up to 10 eV above the L_3 absorption-edge jump, showing the strong localization of the core excited state. [S0163-1829(98)06527-8]

In the description of the physical properties of transition-metal, lanthanide and actinide compounds, electronic correlations play an important role: the quite high localization of the d or f orbitals leads to an intermediate situation where it is not clear whether the band-like or atomic-like model is more appropriate. For these d or f states, the intra-atomic Coulomb interaction is important, but the direct overlap of the orbitals on different sites and their hybridization with the other bands have also to be considered. High-energy spectroscopies such as x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) applied to the electronic structure of matter are powerful techniques, but due to the presence of multielectronic effects, the interpretation of the experimental results is not straightforward. Many studies have been devoted to this question recently, and a new impetus has been given to this domain by the development of experimental techniques such as resonant photoemission^{1,2} and resonant inelastic x-ray scattering.³ Both techniques need the high brilliance of new synchrotron radiation sources.

In mixed-valent cerium compounds, spectroscopic data have been interpreted in terms of band-like⁴ or localized⁵⁻⁷ models. We present here the results of core-level resonant photoemission and Auger spectroscopy in various Ce-Rh compounds, which support the localized many-body approach for the description of L_3 edge XAS spectra.

The unusual physical properties of cerium compounds are connected to the cerium electronic structure: the high density of $4f$ states at the Fermi level can lead to a partial delocalization of the $4f$ electrons, which gives an intermediate-valent ground state. XAS at the $L_{2,3}$ edges has been widely performed to study the electronic properties of intermediate-valent compounds, since it is not surface sensitive and does not need an ultrahigh-vacuum environment. From absorption data, one has deduced the $4f$ occupancy of Ce, using phenomenological interpretation of the edge profiles.⁸ On the other hand, with circularly polarized light [x-ray magnetic

circular dichroism (XMCD)], absorption thresholds give also access to the magnetic properties of Ce.⁹ $L_{2,3}$ edges contain therefore a lot of information, but their interpretation is complicated: the interaction in the final state between the photoelectron and the excited atom cannot be neglected.¹⁰ Resonance experiments are a new way to assign the main structure of the absorption edge to precise final electronic configurations, for relatively localized states. In a classical absorption experiment, one simply measures the total absorption cross section, which represents all the transition probabilities from an initial state to different final states, leading to different decay processes. In a resonance experiment, one selects only one decay process, corresponding to a well-defined final state, and the intensity of this decay is monitored across the absorption edge. Thus, fluorescence decay has allowed to detail the understanding of the L_3 edge and the XMCD of Gd.¹¹ In this paper, Ce $3d$ photoemission and $L_3M_{4,5}N_{4,5}$ Auger lines are used to study the Ce L_3 edge in mixed-valent compounds. In these compounds, Ce $3d$ photoemission spectra exhibit well-defined satellites: they have been described assigning the different peaks to the relaxation of the $4f$ electrons in the core-hole potential.¹² Then, each peak can be attributed to a precise electronic final state. We show here that strong resonances occur for all these peaks when varying the energy of the excitative photons across the L_3 edge. The energy positions of the resonances provide new elements for the understanding of the absorption profiles. With the resonant Auger measurements, the experiment gives a quite complete description of the electronic structure of the excited atom, i.e., in the presence of the core hole. Our resonant photoemission and Auger data support an atomic-like model for the description of the L_3 edge XAS data of cerium in mixed-valent Ce-Rh compounds. They allow us to assign the main structures in the XAS spectra to the different $4f^2$, $4f^1$, and $4f^0$ configurations. These measurements also demonstrate that the photoelectron created in the absorption process, even 10 eV above

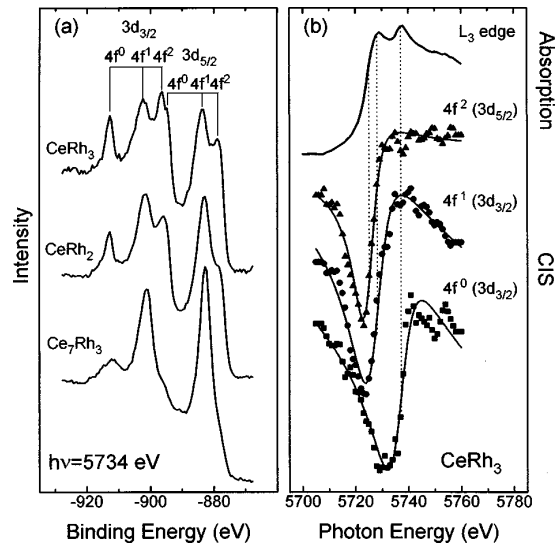


FIG. 1. (a) Photoemission spectra for Ce_7Rh_3 , CeRh_2 , and CeRh_3 at a photon energy of 5734 eV. (b) Ce L_3 absorption edge (top part), and different CIS spectra of CeRh_3 for three photoemission lines: $3d_{5/2}4f^2$ configuration (triangles), $3d_{3/2}4f^1$ (circles), and $3d_{3/2}4f^0$ (squares). The solid lines are fits with the Fano function, and the vertical dotted lines show the positions of the resonance energies E_0 determined by the fits (respectively, 5725 ± 1 , 5728 ± 1 , and 5737 ± 1 eV).

the L_3 edge jump, is localized on the absorbing atom. The understanding of the Ce L edge profiles and the atomic character of the $2p \rightarrow 5d$ transitions are the subjects of a long-standing debate. Our results confirm that, in these compounds, attempts should be made to calculate the XMCD signals in an atomic formalism, as theoretically predicted for $L_{2,3}$ edges of rare-earth compounds.¹³

We performed experiments on three different Ce-Rh compounds: Ce_7Rh_3 , where the Ce atoms are purely trivalent [with a $4f^1(5d6s)^3$ electronic configuration], and CeRh_2 and CeRh_3 , where Ce has a ground state consisting of a mixture of $4f^1(5d6s)^3$ and $4f^0(5d6s)^4$ electronic configurations. We measured the $3d$ photoemission of Ce with photon energies around the Ce L_3 absorption edge [Fig. 1(a)]. The spectra presented here were obtained at the ESRF, on the ID32 beamline using a Si(111) double-crystal monochromator. The good energy resolution available on this beamline, even at this high energy (better than 1 eV at 5 keV), allowed us to isolate, in the CeRh_3 and CeRh_2 photoemission spectra, the peaks corresponding to mainly $4f^0$, $4f^1$, and $4f^2$ character of the final state.¹² In Ce_7Rh_3 , the XPS spectrum shows a classical shape, with mainly $3d_{3/2}$ and $3d_{5/2}$ peaks; the high-binding energy structure is due to the plasmon, as shown by Fuggle *et al.*¹²

Due to the small escape depth of the electrons in matter, classical Ce $3d$ XPS with photons around 1500 eV is a surface-sensitive technique. The lowering of the coordination number for surface atoms leads to a narrowing of the electronic bands. In Ce compounds, this effect should decrease the hybridization between the $4f$ states and the valence band, and give a more localized character to the $4f$ electron. If one is interested in the bulk electronic structure, one has to evaluate the relative bulk and surface contributions. Several groups have tried this, varying the escape depth of the photoelectrons by varying the energy of the photon

excitation.^{14,15} The mean free path is of the order of 10 Å, the surface contribution cannot be neglected and has been estimated by the authors. The estimation is difficult and inaccurate results can lead to a wrong determination of the bulk ground-state parameters. In our study, the $3d$ photoemission spectra were recorded with photon energies around the L_3 absorption edge of Ce (5723 eV). The kinetic energy of the photoelectrons is then around 4800 eV, and their mean free path is larger than 50 Å. The surface contribution can be neglected therefore, which is an important advantage of this very high-energy spectroscopy to procure a real probe of the Ce bulk atoms. In our CeRh_3 photoemission spectrum recorded at 5710 eV, the relative intensities of the $4f^1$ and the $4f^2$ contributions have an intermediate value, between those determined for the bulk in Refs. 14 and 15. A recent work confirms that, at this photon energy, the intensities of the photoemission peaks are similar to those expected in a purely bulk sensitive spectrum.¹⁶

Next, the experiment consisted in measuring the intensities of the Ce $3d$ photoemission peaks while sweeping the photon energy across the Ce L_3 absorption edge [constant initial state spectra (CIS)]. Around the L_3 edge, the direct photoemission process interferes with a resonant process (autoionization) which leads to the same final state. The two processes are

$$2p^6 3d^{10} 4f^n (5d6s)^{4-n} + h\nu \rightarrow 2p^6 3d^9 4f^n (5d6s)^{4-n} + e^-,$$

$$2p^6 3d^{10} 4f^n (5d6s)^{4-n} + h\nu \rightarrow 2p^5 3d^{10} 4f^n (5d6s)^{5-n} \rightarrow 2p^6 3d^9 4f^n (5d6s)^{4-n} + e^-.$$

These interferences were described by Fano,¹⁷ and can give rise to strong variations in the photoemission cross section for relatively localized electronic states. The CIS spectra are presented on Fig. 1(b) for CeRh_3 (where Ce has an intermediate ground state), together with the Ce L_3 absorption edge. For Ce_7Rh_3 (where Ce is purely trivalent) the $3d_{3/2}$ and $3d_{5/2}$ CIS spectra display a typical Fano profile, and the two resonances occur at 5728 eV, at the maximum of the Ce absorption white line. For the CeRh_3 mixed-valent compound, the CIS spectra were recorded for three lines of the XPS spectrum, due to final states of the Ce atoms with zero, one, or two $4f$ electrons (labeled $4f^0$, $4f^1$, and $4f^2$). The results show different resonance energies for the contributions of the different final states.

Much information is to be found in these results. Along with observations on other La and Ce compounds,¹⁸ to our knowledge, these are the first observations of resonances for deep core levels. It is the first evidence of the existence of coupling between core levels; it reveals the existence of the interaction between the $3d$ and $5d6s$ levels of Ce in the presence of the $2p$ hole. The questions, how does this coupling influence the L -edge profiles and how should it be taken into account for the theoretical calculations, must be asked. The resonances are quite intense, of the order of 30%. They are true Fano resonances, since they are measured on direct photoemission lines, at kinetic energies where there is no superposition with the appearance of Auger lines, as it occurs in valence-band resonant XPS.² These resonances are proof that, in this energy range, the excitation and decay must be considered in terms of a one-step model; they are

truly coherent processes. They also show that the $5d$ states of rare-earth compounds, which are less localized than the $4f$, can give rise to resonant effects.

In Fig. 1(b), the CIS spectra of the $3d_{5/2}4f^2$, $3d_{5/2}4f^1$, and $3d_{3/2}4f^0$ photoemission peaks of Ce in CeRh_3 are reported, together with fits to a Fano function.¹⁷ A clear result that comes out directly of the raw experimental data is a different resonance energy for each line. In Fig. 1(b) straight lines correspond to the resonance energies E_0 of the Fano fits. The photoemission line due to $4f^2$ final state resonates at 5725 eV, slightly before the first structure of the L_3 edge, the $4f^1$ contribution resonates at 5728 eV, on the first hump of the L_3 edge, whereas the $4f^0$ satellite resonates at 5737 eV, on the second hump of the L_3 edge. The results obtained on CeRh_2 , another intermediate valent compound, are similar. So, in the intermediate valent compounds, the position of the resonances makes it possible to assign unambiguously the two main lines in the XAS profile to mainly $2p^54f^1$ and $2p^54f^0$ final states, and the shoulder in the rise at the absorption edge to a $2p^54f^2$ final state, as already suggested by Bianconi *et al.*¹⁹ Although this has been suspected for a long time⁸ (the relative intensities of the two lines have even been used to determine the Ce $4f$ occupation in the compounds), this simple atomiclike interpretation of the shape of the XAS profiles of cerium compounds remained controversial. In the same way, the understanding of the XMCD signal at the cerium L_3 edge is not yet completed. Giorgetti *et al.*⁹ suggest that an atomiclike picture is most suited, with a $4f^1$ contribution at the edge, and $4f^0$ and $4f^2$ contributions at, respectively, +9.6 and -3 eV, in full agreement with the energy positions we have observed in our resonant photoemission experiment.

The high-resolution resonant photoemission experiment described here has shown that a one-step treatment of the excitation and deexcitation processes must be considered for an accurate description of the Ce L_3 edge absorption profile. On the other hand, it is correctly assumed that far above the edge, the normal treatment of Auger decay is a two-step process: the absorption and the Auger decay are treated as independent incoherent processes. However, for photon energies near the core-level binding energy, Raman-Augere resonant effects are expected, if the d orbitals in the intermediate state are localized. So, for a better understanding of the absorption edges, we have performed resonant Auger on the two samples with different Ce $4f$ occupancy: Ce_7Rh_3 and CeRh_3 . The study is done on the $L_3M_{4,5}N_{4,5}$ Ce Auger lines, and the spectra, obtained at different photon energies across the Ce L_3 edge are presented on Fig. 2.

For the compound Ce_7Rh_3 , characterized by a highly localized $4f^1$ state, above the edge, the Auger spectrum consists of a doublet corresponding to the $L_3M_4N_{4,5}$ and $L_3M_5N_{4,5}$ lines appearing at constant kinetic energy. Before the L_3 edge, the energy of the main doublet follows the varying excitation energy, arguing in favor of a coherent one-step Raman-Augere process. The solid lines in the figure indicate the position of this double line appearing at constant binding energy. As the figure shows, the peaks are sharper in the Raman regime than in the Auger regime; this narrowing is expected in a coherent event, where the width of the $2p$ hole does not contribute to the process. The intensity of the Raman doublet increases when the photon energy ap-

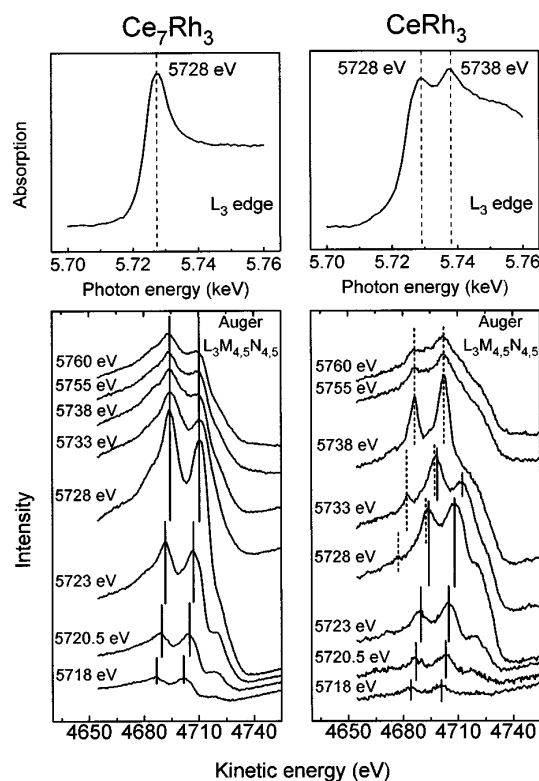


FIG. 2. $L_3M_{4,5}N_{4,5}$ Auger spectra of Ce_7Rh_3 (left panel) and CeRh_3 (right panel) for photon energies across the Ce L_3 edge. Solid (dotted) line: position of the $4f^1$ ($4f^0$) Raman and Auger doublet (see text). Ce L_3 absorption edge is shown in the top two panels.

proaches the L_3 threshold, resonates at the maximum of the white line of the XAS spectrum (5728 eV), and afterwards becomes the normal Auger process (at constant kinetic energy). This behavior is that expected in a metal where, above the edge, the $2p$ core electrons are excited to delocalized orbitals of d and s symmetry.

On the other hand, the same measurements done on the CeRh_3 , highly correlated $4f$ compound, are more complex. Up to 5728 eV (and the maximum of the first structure of the XAS spectrum), the spectra are very similar to those measured on the Ce_7Rh_3 compound. We observe a double peak (marked by solid lines on Fig. 2) at a kinetic energy that disperses with the photon energy; this behavior is typical of a Raman Auger process ($L_3M_4N_{4,5}$ and $L_3M_5N_{4,5}$ lines). This doublet appears at the same kinetic energy as in the Ce_7Rh_3 compound, which allows us to attribute it to a $4f^1$ configuration. As expected, the intensity of this doublet increases when the photon energy approaches the L_3 edge, and resonates at 5728 eV, the first maximum of the XAS spectrum. What is surprising is that this double line still disperses to higher kinetic energies for photon energies between 5728 and 5738 eV. The fact that the energy of the $4f^1$ Auger doublet follows the varying excitation energy shows that the photoelectron created in this energy range (more than 10 eV above the edge jump) is still located on the absorbing atom.

Between 5728 and 5738 eV, a second double line appears at varying kinetic energy, resonates at 5738 eV (at the maximum of the second structure of the XAS spectrum) and afterwards becomes the classical Auger process at constant kinetic energy. This second doublet, having a kinetic energy of 15 eV lower than the $4f^1$ doublet, can be attributed to a $4f^0$

configuration of cerium: the energy difference between the $4f^0$ and $4f^1$ Auger doublet is due to a better screening of the core holes by f as compared to valence electrons. Moreover, it is consistent with the previous resonant photoemission results, that the doublet, which corresponds to $4f^1$ and $4f^0$ final states resonate, respectively, at 5728 and 5737 eV. So this second doublet exhibits a Raman-like regime up to the second maximum of the XAS spectrum. At higher energy, the CeRh_3 Auger spectra are dominated by the $4f^0$ doublet, while in the $3d$ photoemission spectra (Fig. 1), the $4f^1$ doublet is the most intense: the screening process of the core holes is obviously strongly different in the two spectroscopies. On this sample also, in the Raman regime, the doublets are sharper than in the Auger regime. It is particularly clear at the 5738-eV resonance of the $4f^0$ doublet where the lines can be fitted with two Lorentzian profiles of 5 eV for the $L_3M_4N_{4,5}$ line and 7 eV for the $L_3M_5N_{4,5}$ line. In the Auger regime, the width of these two lines are, respectively, 15 and 16 eV.

One of the main results of this Auger study is to provide evidence for an intense Raman-Auger regime where sharp lines can be measured. This opens new possibilities for the identification of well-defined decay processes around absorption edges. The second important result is to show that in a mixed-valent cerium compound like CeRh_3 , the transitions occurring in the L_3 XAS spectrum are dominated by transitions to localized states up to 10 eV above the edge jump. This result supports the use of atomiclike models to interpret both XAS profiles and XMCD spectra of mixed-valent cerium compounds.

In conclusion, taking advantage of the high brilliance of beamline ID32 at ESRF, we have performed high-energy resonant photoemission experiments. First of all, high-energy XPS provides a real probe of the bulk cerium atoms, by deleting the surface contribution via an increase in the photoelectron mean free path. Moreover, resonant core-level photoemission, unlike valence-band photoemission, provides resonances purely due to coherent processes, i.e., with no incoherent contribution of Auger lines superimposed to the photoemission at the same kinetic energies. On various Ce-Rh compounds, both trivalent and mixed valent, we have measured the intensities of the $3d$ photoemission peaks, with photon energies varying across the L_3 absorption edge of

cerium, and brought out important resonances for deep core levels. The occurrence of a resonant profile is evidence of a strong autoionization process involving core levels ($2p$ and $3d$). These decay processes have to be considered for a detailed description of the XAS profiles of cerium compounds. The good energy resolution of the ESRF setup made it possible, in mixed-valent compounds, to isolate the different photoemission satellites and revealed that the resonances occur at different photon energies for the different final electronic configurations of cerium. Therefore, we can assign unambiguously the main structure of the absorption threshold to precise cerium atomic final states and support the localized description of the absorption process. Finally, we have performed resonant $L_3M_{4,5}N_{4,5}$ Raman-Auger spectroscopy, which informs directly on the localization of the core-excited states above threshold. Before the L_3 edge, the spectra are characteristic of a coherent Raman-like regime: the energy of the spectral features corresponding to a $2p^63d^94d^9$ final state follows the varying excitation energy. Well above the edge, the Auger peaks are at fixed kinetic energy, as expected for an incoherent two-step Auger process. In the trivalent compound, Ce_7Rh_3 , the transition between these two regimes is abrupt at the $2p$ threshold energy, while in the intermediate valent compound CeRh_3 , the transition occurs more than 10 eV above threshold. This persistence of an atomiclike coherent process above the edge is clear evidence of the strong localization of the first excited electron in the intermediate valent compounds. The energy position of the real ionization threshold appears to be at higher photon energy than it was previously supposed.

Obviously, these spectroscopies provide new elements for a global knowledge of the electronic structure in these strongly correlated systems. The atomic character of the $2p \rightarrow 5d$ transitions is clearly demonstrated and argues in favor of atomic models for the description of XAS profiles and XMCD signals.

We thank G. Krill, J. P. Kappler, F. Bertran, D. Malterre, and C. Giorgetti for fruitful discussions prior to and after the experiment and G. Schmerber for providing us the Ce-Rh samples. We acknowledge C. Hague for a critical reading of the manuscript. We are also grateful to all the ESRF staff, especially on beamline ID32. J.V. acknowledges the European Union for Grant No. ERBCHBGCT 941817.

¹W. Drube, R. Treusch, and G. Materlik, Phys. Rev. Lett. **74**, 42 (1995); O. Karis *et al.*, *ibid.* **76**, 1380 (1996).

²M. Weinelt *et al.*, Phys. Rev. Lett. **78**, 967 (1997).

³S. M. Butorin *et al.*, Phys. Rev. Lett. **77**, 574 (1996).

⁴E. Weschke *et al.*, Phys. Rev. Lett. **69**, 1792 (1992).

⁵M. Grioni *et al.*, Phys. Rev. B **55**, 2056 (1997).

⁶C. O. Almbladh and L. Hedin, in *Handbook on Synchrotron Radiation*, edited by E. E. Koch (North-Holland, Amsterdam, 1983), Vol. 1.

⁷N. Witkowski, F. Bertran, and D. Malterre, Phys. Rev. B **56**, 15 040 (1997).

⁸J. Röhler, in *Handbook on Physics and Chemistry of Rare Earths*, edited by K. A. Gschneider and J. Hüfner (North-Holland, Amsterdam, 1987), Vol. 10.

⁹C. Giorgetti *et al.*, Phys. Rev. B **48**, 12 732 (1993).

¹⁰D. Malterre, Phys. Rev. B **43**, 1391 (1991).

¹¹M. H. Krisch *et al.*, Phys. Rev. Lett. **74**, 4931 (1995); Phys. Rev. B **54**, R12 673 (1996).

¹²J. C. Fuggle *et al.*, Phys. Rev. B **27**, 7330 (1983).

¹³M. Van Veenendaal *et al.*, Phys. Rev. Lett. **78**, 1162 (1997).

¹⁴C. Laubschat *et al.*, Phys. Rev. Lett. **65**, 1639 (1990).

¹⁵L. Braicovich *et al.*, Surf. Sci. **331-333**, 782 (1995).

¹⁶L. Braicovich *et al.*, Phys. Rev. B **56**, 15 047 (1997).

¹⁷U. Fano, Phys. Rev. **124**, 1866 (1961).

¹⁸J. Vogel *et al.*, J. Electron Spectrosc. Relat. Phenom. **76**, 735 (1995).

¹⁹A. Bianconi *et al.*, Solid State Commun. **49**, 409 (1984).