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# Observations of the Mo emission band satellite obtained by incident electrons of near-threshold energy

P. Jonnard,\* C. Bonnelle, and I. Jarrige

*Laboratoire de Chimie Physique - Matière et Rayonnement,  
Université Pierre et Marie Curie, UMR-CNRS 7614,  
11 rue Pierre et Marie Curie, F-75231 Paris Cedex 05, France*

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The satellite of the Mo  $L\beta_2$  valence emission band ( $4d \rightarrow 2p_{3/2}$  transition) is excited by bombarding a molybdenum target with electrons having energy around the  $2p_{3/2}$  ionization threshold. This satellite, whose intensity is higher than that of the parent transition, is observed about 8 eV above it. This energy interval is well accounted by theoretical calculations that take into account the correlations between the various decay processes. New light is shed on the dynamics of the  $4d - 4d$  excitation process in the transition metals.

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X-ray emissions are generally accompanied by satellite emissions, clearly less intense than their parent line [1]. By using, as probe particles, electrons of energy varying from a fifteen of electronvolts above the  $2p_{3/2}$  ionization threshold up to more twice the threshold, we have observed the  $4d \rightarrow 2p_{3/2}$  ( $L\beta_2$ ) emission band of the metal molybdenum and evidenced a resonant-like behaviour for the satellite emission located towards the higher energies of this band. Indeed, close to the threshold, the intensity of the satellite is higher than that of the parent emission. We discuss this result in connection with the excitation dynamics between the occupied and unoccupied valence states of the  $4d$  transition metals, which play a key role in the observation of this satellite.

When an  $nlj$  core sub-shell is ionized by incident electrons whose energy  $E_i$  is much higher than the ionization threshold, a  $nlj$  electron is thrown rapidly out in the continuum. The atom adjusts to the perturbed potential and a second electron is ejected, either to unoccupied bound states (shakeup) or into the continuum (shakeoff) [2]. These multiple ionization processes have been treated in the sudden perturbation model. The subsequent decays are independent of the initial process and a clear separation exists between the competing channels [3]. The x-ray emission can be described in a one-electron framework.

In contrast, when  $E_i$  is of the order of the ionization threshold, the  $nlj$  atomic electron is removed slowly. Breakdown of the one-electron model occurs and correlation effects can be noticeable [4]. Consequently, the emission intensity is governed by the presence of strong configuration interactions between the states involved in the various transitions. At a double-excitation threshold, the probability of the shake processes go to zero. When the incident energy increases, the shake-up satellite strength reaches rapidly its limit if the energy to create the shake-up excitation is low, and the intensity of the satellite is always clearly weaker than that of the parent emission [5–7]. However, in a solid, when the core-ionization

is accompanied by very probable intraband excitations, a satellite is expected near the threshold, whatever are the conditions of initial ionization. Such a satellite strongly depends on the  $d$  correlations and it is characteristic of the transition metals.

For a transition metal, a band-like picture is appropriate to describe the  $d$  electronic distribution. If the emission is induced by incident electrons, whose energy  $E_i$  is much above the core hole ionization energy, the emission band can be interpreted in a single-particle model and gives a good description of the density of  $d$  states. X-ray satellite emissions of weak intensity are observed towards the higher energies of the parent line and are interpreted as transitions in multiply-excited, or ionized, atoms. Their intensity varies with  $E_i$  as predicted by the sudden approximation.

If the  $nlj$  core hole is created by an incident electron of energy close to the monoionization threshold, both core and incident electrons are present in unoccupied states of low energy. The excess energy above the threshold is distributed between both electrons. No selection rule exists in the characteristic energy loss process of the electrons and, consequently, all the empty states can accept the incident electron. However, if a high density of unoccupied  $nl$  states exists in a narrow range of energy just above the threshold, the probability that an electron be present in this energy range is large. This is the case for the transition elements, where a high density of unoccupied  $d$  states exists above the Fermi level.

In the case of molybdenum, for energy of the incident electrons just above its first double-excitation threshold, two electrons can simultaneously be ejected to conduction states, where the incident electron can also be present. Among the doubly-excited configurations of Mo with a  $2p_{3/2}$  core hole, the  $2p_{3/2}^{-1}4d^{n-1}cded$  configuration is strongly populated because of the high density of occupied and unoccupied Mo  $4d$  states [8], and because the transition from the ground state satisfies to the optical selection rules [9]. Then, the final state of the  $L\beta_2$  satel-

lite has the  $4d^{n-2}e\delta e\delta$  configuration, i.e. two holes in the  $4d$  sub-shell [10]. The strong coupling expected between the pair of  $d$  holes significantly affects the intensity of the satellite.

We present an experimental study of the behaviour of the Mo  $L\beta_2$  high energy satellite for incident electron energies from 15 eV above the threshold, up to 2.4 times this threshold ( $\approx 6000$  eV). The Mo sample is either a 99.9% purity plate, or a 1  $\mu\text{m}$  thick film deposited by magnetron sputtering on a silicon substrate. The x-ray emission experiments are described elsewhere [11]. Electron irradiation is made under high vacuum ( $10^{-6}$  Pa or less) with a low electron current density (1 mA/cm<sup>2</sup>), which leaves the sample unaffected. For incident electron energies  $E_i$  as low as 3000 eV, the analyzed thickness is small (about 8 nm) and the reabsorption effect due to the strong variation of the absorption coefficient near the top of the valence band is negligible. Consequently, no distortion of the emission band shape occurs.

The Mo  $L\beta_2$  ( $4d \rightarrow 2p_{3/2}$  transition) emission obtained with  $E_i$  ranging from 2535 to 6015 eV is shown in Fig. 1. A background is subtracted as described in Ref. 11. The curves are normalized with respect to their maximum. The Mo  $2p_{3/2}$  binding energy is equal to 2520 eV [12]. For the experiments performed close to the threshold, the number of emitting atoms is small, and in addition the ionization cross sections are low, making the number of emitted photons small. In order to overcome this difficulty and facilitate the observations, the luminosity has been increased to the detriment of the resolution. Consequently, the spectral resolution is not the same for all the curves of the Fig. 1.

When  $E_i$  is higher than 2665 eV, the most intense peak is the  $L\beta_2$  normal emission at 2518 eV [13]. At an incident energy of 6015 eV, the  $L\beta_2$  emission band is rather symmetric. It describes the occupied  $4d$  density of states convoluted with the Lorentzian distribution due to broadening by the core hole lifetime and the instrumental function. At low values of  $E_i$ , the main peak is the satellite structure appearing about 8 eV above  $L\beta_2$ . For  $E_i$  lower than 2565 eV, the  $L\beta_2$  normal emission is not enough intense to rise up from the background or is observed only as a shoulder of the satellite structure.

The satellite structure is located well above the top of the emission band and cannot be related to a feature of the Mo density of states. In order to verify that this structure is not due to a superficial contamination, we have compared the Mo  $L\beta_2$  emissions observed for the metal and the MoO<sub>3</sub> oxide [11]. The energy of the maximum is the same for both emissions and no structure is present for the oxide in the 2525-2535 eV energy range. Then, the satellite structure cannot be due to an oxidation of the molybdenum. The same conclusions can be drawn for other Mo compounds [11].

The transition probabilities of the Mo  $2p_{3/2}^{-1}4d^n - 4d^{n-1}$

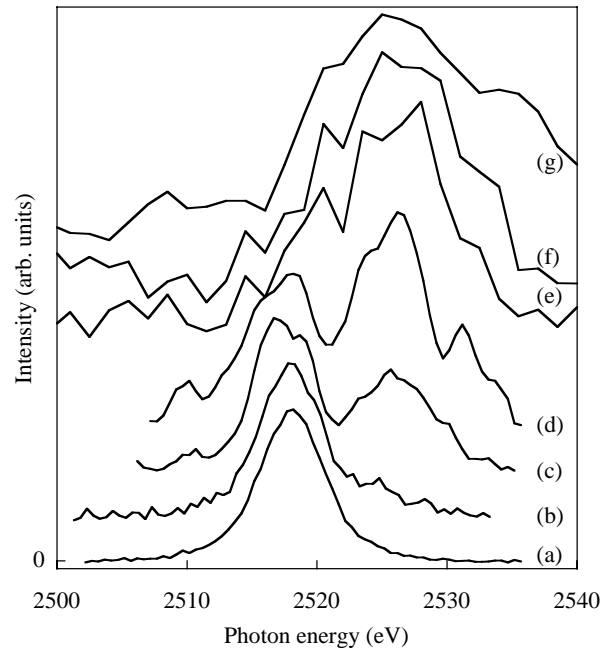


FIG. 1: Mo  $L\beta_2$  emission ( $4d \rightarrow 2p_{3/2}$  transition) of Mo metal for various electron energies : (a) 6015 eV; (b) 3015 eV; (c) 2665 eV; (d) 2630 eV; (e) 2565 eV; (f) 2555 eV; (g) 2535 eV. The resolution of spectra (e-g) is poorer to that of spectra (a-d) to improve the intensity.

emissions have been computed for  $n = 5$  and  $n = 4$  ions, using a multiconfiguration Dirac-Fock program (MCDHF) [14, 15]. When configuration interactions are included, the two emission curves are separated by about 7 eV (Fig. 2). The emission located towards the higher energies corresponds to the satellite with a supplementary  $4d$  hole. The simulated spectra have been adjusted to the experimental one by a shift of less than 0.6% of the energy.

It is known that the intensity of an x-ray emission increases with  $E_i$  following a law of the  $(E_i - E_{nlj})^{1.6}$  type [16], where the threshold energy  $E_{nlj}$  is here the Mo  $2p_{3/2}$  binding energy. We have verified that the intensity of the  $L\beta_2$  emission varies according to this law. The satellite intensity with respect to that of the parent line is shown in Fig. 3. From this figure, there is a large difference between the intensity behaviour of the  $L\beta_2$  emission and that of the satellite structure. For comparison, the Mo  $L\alpha$  ( $3d \rightarrow 2p_{3/2}$ ) emission of the metal observed at  $E_i$  equal to 6015 and 2715 eV is shown in Fig. 4. The spectra are normalized to their maximum and a linear background has been subtracted. This emission involves the same core level as the  $L\beta_2$  emission. The external level has the same symmetry but it is a core level and not the valence band. At high values of  $E_i$ , a satellite is clearly observed, about 10 eV towards the higher energies of  $L\alpha$  line. At 2715 eV, *i.e.* below the Mo  $2s$  threshold, this satellite almost disappears.

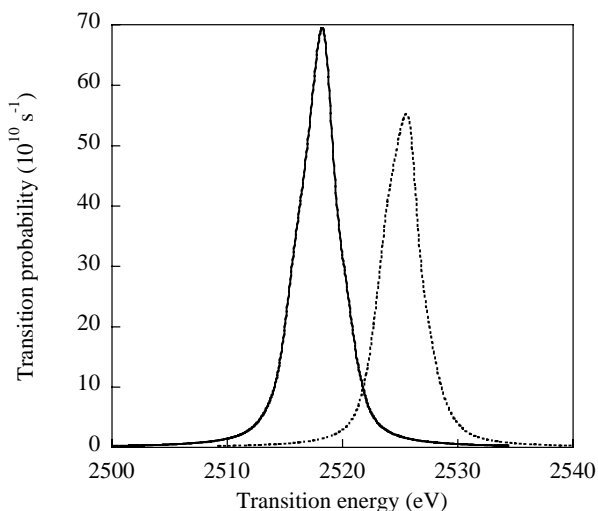


FIG. 2: Transition probabilities of the Mo  $2p_{3/2}^{-1}4d^n \rightarrow 4d^{n-1}$  emissions calculated with a multiconfiguration Dirac-Fock program (MCDF), for  $n = 5$  (normal emission, solid line) and  $n = 4$  (satellite emission, dotted line) ions.

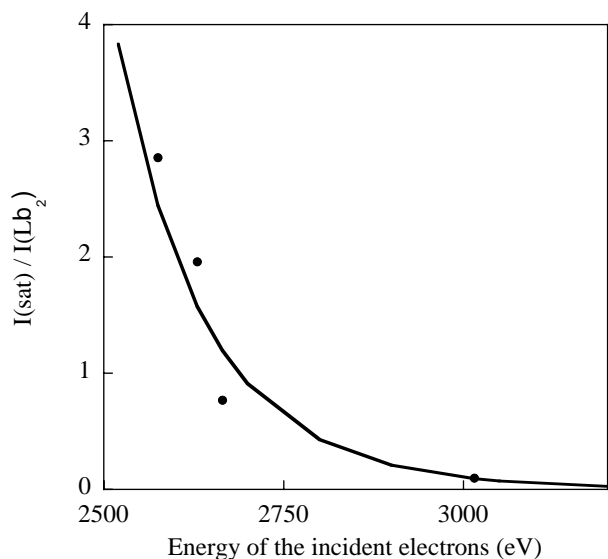


FIG. 3: Intensity of the Mo  $L\beta_2$  satellite with respect to that of the normal,  $I(\text{sat})/I(L\beta_2)$ , as a function of the incident electron energy. The line is to guide the eyes.

From our observations, the relative intensity of the satellite with respect to that of the  $L\beta_2$  emission band increases when  $E_i$  approaches to vicinity of the threshold. In the  $E_i$  energy range between 2535-2630 eV, *i.e.* between 15 to about 100 eV above the  $2p_{3/2}$  monoionisation threshold, the  $L\beta_2$  satellite is stronger than the parent line. Unlike the satellites of the  $L\alpha$  line, its relative intensity continues to increase when  $E_i$  becomes lower than the  $2s$  and  $2p_{1/2}$  ionization energies. Consequently, at low values of  $E_i$ , the possibility for the initial state of the  $L\beta_2$  satellite to be a doubly-excited, or -ionized

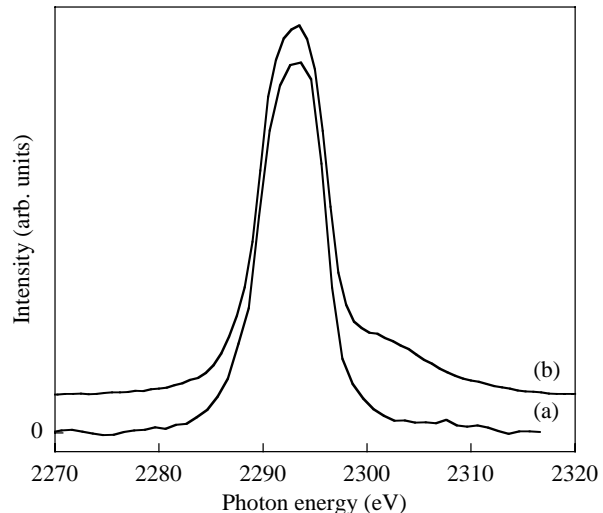


FIG. 4: Mo  $L\alpha$  emission ( $3d \rightarrow 2p_{3/2}$  transition) of Mo metal, obtained with 6015 (a), and 2715 eV (b) electrons.

state following a Coster-Kronig transition, is eliminated. The resonant-like behaviour of the satellite is observed on an electron energy range of about 100 eV. Indeed, incident electrons of initial energy higher than the double-excitation threshold are slowed down in the sample, in the course of very probable low energy inelastic collisions. Then, the electrons can get the energy convenient for induce the satellite line.

At 15 eV above the ionisation threshold, the double excitation involves valence states. As already underlined, this excitation is a  $d-d$  intraband transition and the shake model cannot explain the intensity variation observed at the threshold. In contrast, a collision between the ejected core electron of weak velocity and one of the  $4d$  valence electrons can contribute to the  $d-d$  excitation. On the other hand, when a  $L\beta_2$ -like transition is observed close to the threshold in the presence of  $d-d$  excitation, two  $4d$  electrons are transferred quasi-simultaneously. The coupling between  $4d$  electrons favorize the ejection of two  $4d$  electrons, one towards the  $2p_{3/2}$  core hole, another towards the high density of unoccupied  $d$  states, inducing strong correlations between the decay processes from the singly- and doubly-excited states. Indeed, to obtain a good agreement between the calculated and experimental positions of the parent and satellite lines, we have simulated the spectrum by taking into account the configuration interaction between all the  $J$ -levels of the initial and final states of both emissions. At the final state of the satellite emission, both  $4d$  holes present in the occupied states interact strongly. Therefore, the  $L\beta_2$  satellite can be considered as resulting from a one-site process, thus justifying a free atom approach for describing it. This atom-like character is responsible of the resonant-like behaviour of the satellite.

The characteristics of the satellite are governed by the

presence of the high density of the occupied and unoccupied  $4d$  states. The energy width of the unoccupied  $4d$  distribution does not exceed ten eV. Beyond, the states have essentially the  $s, p$  character and the density of the  $d$  states mixed with the continuum is weak. Moreover the transition probability to delocalized states in the continuum is weak. Consequently, it appears that the behaviour observed near the double-excitation threshold is widely dominated by the  $4d$  state distribution and the excitation dynamics between these states. Indeed, the same observations are observed for the  $nd$  ( $n = 3, 4, 5$ ) transition metals while they are absent for the noble metals [11].

Simultaneously with the core hole creation, an attachment of the incident electron could perturb the spectrum at the threshold. For conductor solids, this process has been observed only in the presence of strongly localized excited states of  $f$  character [17, 18]. Moreover, the corresponding satellite is located towards the lower energies of the parent line. This process is not observed here.

In summary, the observation of the Mo  $L\beta_2$  spectrum as a function of the incident electron energy  $E_i$  is a mean to determine the dynamical effects among low energy valence states. The resonant-like behaviour, observed for the first time with electrons as probe particles, strongly enhances the relative intensity of the satellite. It is due to the atomic-like character of the transitions involving two  $d$  electrons, and favors its observation. For values of  $E_i$  equal to the double-excitation threshold, the Mo  $L\beta_2$  emission appears to be shifted towards the higher energies and the shift corresponds to the mean  $d-d$  excitation energy in the presence of the core hole. Such a behaviour is characteristic of materials with a high density of interacting valence electrons and of quasi-bound empty states having the same symmetry.

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- \* Electronic address: jonnard@ccr.jussieu.fr
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