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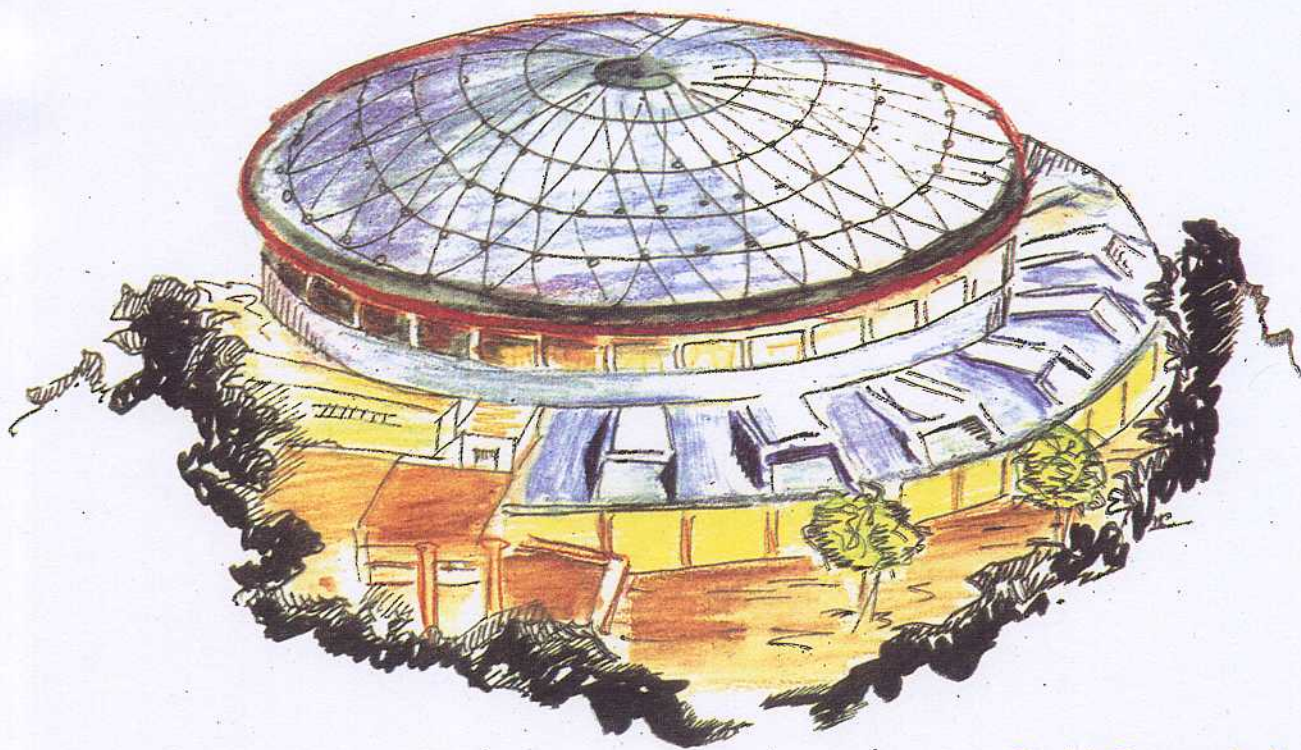
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**NEW METHOD FOR COMPARISON OF EXAFS SPECTRA AT THE L EDGES:
APPLICATION TO THE THEORETICAL AND EXPERIMENTAL L₁ AND L_{2,3}
EDGES OF BARIUM IN BaF₂**

J. Chaboy, J. Garcia* and A. Marcelli
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Abstract

In this paper we discuss a new method for direct comparison between L_{2,3} and L₁ EXAFS spectra. A detailed analysis of the basic EXAFS formula leads to a simple relationship between the EXAFS signals at the L₃ and L₁ edges that includes the total phase-shift difference for the two absorption processes. This relation has been successfully used to perform the comparison of theoretical and experimental data of barium in the cubic BaF₂ system.

INTRODUCTION

X-ray absorption spectroscopy (XAS) has large applications as a technique for investigation of the structural and electronic properties of materials. Impressive progress of XAS investigations are not only due to the significant development of the synchrotron radiation sources and the experimental apparatus, but also to the accuracy of theoretical models and computer simulations in accounting for the photo-absorption process. In fact, the use of an exact curved wave one-electron formalism together with the inclusion of multiple scattering contributions⁽¹⁻³⁾ leads to accurate EXAFS (Extended X-Ray Absorption Fine Structure) data analysis. In this way EXAFS is today competitive with diffraction experiments and in the cases of disordered and amorphous systems it allows the determination of the local geometry via the determination of complex structural

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parameters such as bond angles.⁽⁴⁾ However, one of the most attracting properties of XAS lies on the possibility to extract details of the electronic configuration of the system under analysis. The photo-absorption process probes the partial and local densities of the empty states above the Fermi level. In particular, complementary information can be obtained by comparison of the absorption spectra at the L edges of the same atom according to the different symmetry of the final states involved in the absorption process, i.e. $2s \rightarrow \epsilon p$ for the L_1 edge and $2p \rightarrow \epsilon d$ and $2p \rightarrow \epsilon s$ for the $L_{2,3}$ edges via the dipole selection rules. However, in spite of this unique possibility few published works have made the comparisons of the L-edges. Most of these investigations concern rare earths systems where the L-edges comparison is used:

- i) to determine the valence state of the rare earth ion and its electronic configuration;⁽⁵⁾
- ii) to identify the features of the near edge as multiple scattering resonances or final state effects due to the mixed valence nature of the system;⁽⁶⁾
- iii) as a rule for the normalization procedure of the absorption coefficient.^(6,7)

Very recently the comparison has been also used as an attempt to "illustrate the join" between the x-ray absorption near edge structure (XANES) and the extended x-ray absorption fine structure (EXAFS).⁽⁸⁾

These investigations have been performed using a method (that we refer to below as the " π approach"⁽⁹⁾) which is based on the existence of a value of π for the phase shift difference between the $L_{2,3}$ and the L_1 signals. The validity of this approach would lead to the exact correspondence between maxima and minima of the EXAFS oscillations, i. e. each peak in the L_3 (L_2) edge spectrum would exactly correspond to a valley in the L_1 spectrum and vice versa.

Until now theoretical support for the " π approach" has been obtained looking at the difference between the symmetry of the initial state wave functions, $2s$ versus $2p$, because the $2s$ (L_1 edge) does not have a node at the origin while the $2p$ electron does ($L_{2,3}$ edge). As a consequence, an exact π difference between the phase dependence of the EXAFS spectra at the L_1 and $L_{2,3}$ edges would exist, as claimed by several authors,⁽⁵⁻⁸⁾ who address this interpretation in two pioneering papers on x-ray absorption spectroscopy.^(10,11) We have recently shown the invalidity of this approach⁽⁹⁾ and then a strong criticism concerns all the conclusions derived in the past when applying this comparison scheme.

The aim of this work is to clarify the state of the art of the comparison procedure of the EXAFS at the L-edges. In fact, an exhaustive analysis of the EXAFS theory clearly shows the failure of the " π approach" and leads us to propose a new method for the comparison of the EXAFS spectra at the L edges. Using this method it is possible to generate from the experimental spectrum at the L_3 (L_2) edge the spectrum at the L_1 edge and vice versa. This new comparison scheme may be of fundamental interest to discuss the presence of multi-electron excitations. As it has been addressed^(12,13), such multi-electron excitations introduce specific problems in the conventional EXAFS data analysis. Their presence has to be carefully taken into account to avoid errors in the determination of structural parameters.

In the following we first review the basic equation of the EXAFS theory, looking for the details of the phase dependence of the signals both at L_1 and $L_{2,3}$ edges. Our analysis will demonstrate the failure of the " π approach" and will introduce a model to take into account the

theory. This model is then used to obtain a comparison of the XAS spectra at the L_1 and $L_{2,3}$ edges. An example employing both methods made on the L -edges of barium in BaF_2 system is given.

THEORETICAL BACKGROUND

In the plane wave approach (PWA) the absorption coefficient for the excitation from an s level (K or L_1 edge), normalized to the background μ_0 , is described by the well known formula

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0} = - \sum_j 3 \cos^2 \theta_j \frac{N_j}{kr_j^2} |F_j(k)| \sin(2kr_j + \psi_j(k)) e^{-2k^2 \sigma_j^2} e^{-2r_j/\lambda(k)} \quad [1]$$

where $F_j(k)$ is the backscattering amplitude from each of the N_j neighbouring atoms of the j^{th} type, placed at a distance r_j from the central (absorber) atom and characterized by a Debye-Waller factor σ_j , which is introduced to account for the thermal vibrations and the static disorder. ψ_j is the total phase shift probed by the photoelectron in the scattering path and is given by the relation

$$\psi_j(k) = \phi_a^{\ell=1}(k) + \phi_b(k) \quad [2]$$

where $\phi_b(k)$ is the phase of the backscattering amplitude of the neighbour, while $\phi_a^{\ell=1}(k)$ equals to $2\delta_1$, δ_1 being the phase shift of the central atom. Because the position vector of the j^{th} neighbour describes an angle θ_j , respect to the polarization vector of the x -ray, the factor $(3 \cos^2 \theta_j)$ averages to one for polycrystalline samples. The overall minus sign which appear in Eq. [1] comes from the $(-1)^\ell$ factor, where ℓ is the angular momentum of the final state. It can be introduced in Eq. [2] as an additional equivalent π factor

$$\psi_j(k) = \phi_a^{\ell=1}(k) + \phi_b(k) - \pi \quad [3]$$

which in fact removes the minus sign in the Eq.[1]. The exponential term $e^{-2r_j/\lambda(k)}$ is introduced to account for the inelastic scattering losses, λ being the electron mean free path. Finally, k is the photoelectron wave vector defined as

$$k = \sqrt{\frac{2m}{\hbar} (E - E_0)} \quad [4]$$

where E is the photon energy and E_0 is the threshold energy of the absorption edge under consideration. One shall note that in the EXAFS formula, while the backscattering amplitude is a function of the scatterer only, the phase shift depends on both the central (absorber) and the backscatterer (neighbour) atoms. This consideration will be important for the following discussion.

For an excitation from a p level ($L_{2,3}$ edges), the EXAFS formula becomes more complicated because, following the dipole selection rules, the photoelectron ejected from an initial p state, has

two possible final states with s or d symmetry. Then, in the case polycrystalline materials the simple formula of Eq.[1] is replaced by

$$\chi(k) = \sum_j \frac{N_j}{kr_j^2} |F_j(k)| e^{-2k^2\sigma_j^2} e^{-2r_j/\lambda(k)} \frac{\left\{ M_{21}^2 \sin(2kr_j + \phi_{2j}) + \frac{1}{2} M_{01}^2 \sin(2kr_j + \phi_{0j}) \right\}}{\left(M_{21}^2 + \frac{1}{2} M_{01}^2 \right)} \quad [5]$$

where M_{01} and M_{21} are respectively the radial dipole matrix elements of the 2p ($\ell=1$) atomic wave function and of the ($\ell=0$) and ($\ell=2$) final states. For the j^{th} atom the phase functions which appear in Eq. [5] are

$$\phi_0(k) = \phi_a^{\ell=0}(k) + \phi_b(k) = 2\delta_0(k) + \phi_b(k) \quad [6]$$

$$\phi_2(k) = \phi_a^{\ell=2}(k) + \phi_b(k) = 2\delta_2(k) + \phi_b(k) \quad [7]$$

The resulting Eq. [5] is still a complicated expression with two sets of central atom phase shifts and the ratio between the dipole matrix elements M_{01} and M_{21} . Estimates of the ratio (M_{21}/M_{01}) for different elements like Ti, Zr or W, yield a value of five.⁽¹⁴⁾ Subsequently, the transition to the d final states is favoured by a factor of ~ 50 when compared to the transition to the s final states. As a consequence, $L_{2,3}$ spectra can be analyzed as due to transitions from the 2p initial state to d-symmetry final states only.⁽¹⁵⁾ We have verified these results for the $L_{2,3}$ edges of barium obtaining a factor of ~ 100 for the ($2p \rightarrow \epsilon d$) / ($2p \rightarrow \epsilon s$) transition ratio. Then, neglecting contribution of the s part to $\chi(k)$ Eq. [5] may be rewritten as:

$$\chi(k) = \sum_j \frac{N_j}{kr_j^2} |F_j(k)| \sin(2kr_j + \psi_j(k)) e^{-2k^2\sigma_j^2} e^{-2r_j/\lambda(k)} \quad [8]$$

where

$$\psi_j(k) = \phi_a^{\ell=2}(k) + \phi_b(k) \quad [9]$$

Now, comparison of expressions [1] and [8], excluding the averaged $3 \cos^2\theta_j$ term, clarifies the ambiguous role of the minus sign that factorizes Eq.[1], which is not present in the $L_{2,3}$ edge description given by Eq. [8]. This factor, as Eq. [3] clearly shows, corresponds to a π phase shift difference between the L_1 and the $L_{2,3}$ EXAFS signals and is at the origin of the " π approach". This approximation leads to the simple relation between the different signals :

$$\chi_{L_3}(k, \phi) = - \chi_{L_1}(k, \phi) \quad [10]$$

However, a detailed analysis of the two expressions for the normalized absorption coefficient both at the L_1 edge (Eqs. [1] and [2]) and at the $L_{2,3}$ edge (Eqs. [8] and [9]) shows the existence of a second contribution which can not be neglected. This last is related to the different central atom phase shift associated with the different symmetry of the final state and is explicitly expressed by

$\phi_a^{\ell=2}(k)$ and $\phi_a^{\ell=1}(k)$ in equations [2] and [9]. As a consequence, the relationship between the normalized absorption coefficients for the excitation of one electron from a core level 2p ($L_{2,3}$ edge) and from a level 2s (L_1 edge) may be now expressed as :

$$\chi_{L_3}(k, \phi) = -\chi_{L_1}(k, \phi) \cos(\Delta\delta) + \chi_{L_1}(k, \phi - \frac{\pi}{2}) \sin(\Delta\delta) \quad [11]$$

where

$$\Delta\delta = \phi_a^{\ell=2}(k) - \phi_a^{\ell=1}(k) \quad [12]$$

is the difference of the central atom phase shift for the two excitations.

These equations clearly show the dependence of the EXAFS signal on the different phase shift associated to the central atom and address the question of the inadequacy of the assumptions based on the " π approach".

To clarify the critical role of the central atom phase-shift difference we have applied both the equation [11] and the π approach (Eq. [10]) to the comparison of the barium L-edges in BaF_2 compound using both theoretical simulation and experimental data.

COMPARISON OF BA L-EXAFS IN BaF_2 : DISCUSSION OF THE THEORETICAL SIMULATIONS

The previous analytical derivation has been developed in the framework of the plane-wave approximation (PWA) which provides all the basic theoretical ingredients to carry out comparison of the EXAFS spectra at the L-edges. In the PWA formalism the equation [11] is exact, indeed, the only fingerprint of the initial state symmetry is the different partial-wave shift, δ_ℓ , in the final state potential of the absorbing atom. However, as the importance of curved wave corrections in XAFS has been clearly addressed by several authors,^(16,17) we have investigated the validity of our equation for the comparison using theoretical EXAFS signals calculated via the exact spherical wave formulation.

Theoretical EXAFS signals at the barium L edges in BaF_2 were generated using the multiple scattering codes MSCALC and PROGC.⁽¹⁸⁻²⁰⁾ For the initial state, neutral potentials at the crystallographic positions were superimposed. For the excited state, the potential was calculated in the Z+1 approximation, i.e. the orbitals for the absorbing barium atom were the orbitals of lanthanum with the proper core-hole. The superimposed potentials were spherically averaged around each centre, in a sphere whose muffin tin radius was determined according to Norman's criterion.⁽²¹⁾ The charge density obtained was then used to generate the local density exchange correlation potentials. For this calculation several cluster sizes as well as different exchange potentials were used: X_α exchange potential,⁽²²⁾ Dirac-Hara exchange potential⁽²³⁾ and Hedin-Lundqvist exchange and correlation complex potential.⁽²⁴⁾

In our system best agreement with the experimental data was obtained using a cluster of eleven coordinations shells constituted by 239 atoms, with Hedin-Lundqvist complex potential and

only when multiple scattering contributions were included. An extensive discussion of these results exceeds the nature of the present paper and it is given in reference 13. However, it is important to stress that the successful reproduction of the experimental EXAFS spectra using these theoretical signals is a strong support for the validity of the comparison method discussed in this paper.

Figure 1 reports (upper part) the comparison, using expression [11], between the theoretical EXAFS signal at the barium L_1 -edge for the BaF_2 cluster, including only the single scattering contribution of the first six coordination shells around the absorber, and that generated by the theoretical signal of the Ba L_3 -edge. Using this procedure the central atom phase shift difference $\Delta\delta$ can be directly obtained from the code output and its value is in agreement with experimental result. However, we have preferred in this example to follow the same procedure as for the experimental data analysis. Thus, the theoretical signals were Fourier transformed in the same k -space range, using identical windows, and the first shell contribution was backtransformed. This procedure leads to the decomposition of both L_1 and L_3 EXAFS signals, coming from the photoelectron single scattering processes with the eight fluorine atoms of the first coordination shell, into phase and amplitude functions. Starting from the basic assumption that structural information, like coordination numbers, interatomic distances and disorder effect, carried out by the EXAFS at the two edges must be identical, the subtraction of the phase functions obtained have to give directly the central atom phase difference $\Delta\delta$ of the expression [12]. One time $\Delta\delta$ has been calculated, the Fourier transform of the whole spectrum was backtransformed to obtain the decomposition $\{A(k)\sin(k,\phi)\}$ of the EXAFS signal. A $\pi/2$ factor was then subtracted from the effective phase ϕ obtained prior to rebuild the signal giving the $\chi_L(k,\phi-\pi/2)$ term of Eq. [11].

This procedure shows in fact a very good agreement, (set top of Figure 1) while the comparison of the same theoretical signals using the " π approach" does not give the same agreement (bottom part of Figure 1). Although the ab initio calculation provides the exact correspondence between the energy reference for both L_1 and L_3 theoretical signals, one might have the impression that a shift of E_0 yields a similar good agreement also for the " π approach". Thus, we applied several E_0 shifts obtaining the best agreement when an E_0 shift of 9 eV is introduced, as showed in Figure 1. As expected, see expressions [11] and [12], any "unphysical" shift can give the whole spectra agreement.

There is also another arbitrary procedure associated with the " π approach" method which consists, prior to compare the spectra in multiplying by an arbitrary factor the k -scale of one of the two signals^(5,8). From the discussion above it is now clear that such a factor is used as an attempt to compensate the difference of the central atom phase shifts between the L_1 and L_3 EXAFS spectra.

The Fourier transform technique that we have used to extract the phase difference between the L_1 and $L_{2,3}$ EXAFS spectra returns the total difference of the photoelectron phase shift in the two absorption processes. Moreover, the difference in the backscattering amplitude, that is exactly zero in a PWA formalism, can be obtained looking at the difference in amplitude of the backtransformed signals. At this point it is important to note that in the framework of the plane-wave approach this method is exact. When considering spherical-wave corrections small differences in the amplitude of the two signals can be observed but only in the low energy region of the spectra. (see Figure 1 between 2 and 4 \AA^{-1}).

COMPARISON OF BA L-EXAFS IN BaF_2 : DISCUSSION OF THE EXPERIMENTAL DATA ANALYSIS

To confirm the validity of our method, we performed also the comparison using the experimental EXAFS data of barium. Several samples of BaF_2 were measured in different experimental runs at the PULS Synchrotron Facility of Frascati. Materials were powdered and samples were prepared, optimizing thickness and spreading fine powders on a Kapton tape. This was clamped on a thick aluminium film to assure thermal homogeneity at low temperature. The absorption spectra at the Ba L-edges (L_1 and $L_{2,3}$) were recorded both at room temperature and at $T=10$ K in the transmission mode; using a Si(111) double crystal monochromator. The background subtraction of the experimental EXAFS signals was performed according to the standard methods.

The first step of our experimental comparison procedure was to generate the L_3 EXAFS signal starting from the experimental L_1 spectrum recorded at low and room temperature, via Eq. [11]. We applied the same procedure as previously described for the simulation of the theoretical signals. The phase-shift difference obtained from the experimental signals included in Eq. [12], to generate the corresponding L_3 EXAFS signals at the two temperatures, does not differ from that extracted from the theoretical signals. The upper part of Figure 2 shows the good agreement between the experimental and the generated signals. In the same figure (bottom part) the failure of the " π approach" also for the experimental data is reported. As shown for the theoretical comparison, the experimental frequency dependence of the signals is well reproduced by a calculation taking into account the phase-shift difference according to the expressions [11] and [12].

Beyond the improvements which can be obtained, this comparison provides a useful way to align the spectra of the L_3 and of the L_1 edges of the same atom. This opens the possibility for a clear investigation of the near edges regions of the spectra at the L edges, after the E_0 position is uniquely defined. In fact, the achievement of the phase correspondence between the experimental and the calculated, using Eq. 11, signals implies the validity of the phase function used and, as a consequence, the determination of a unique threshold energy for the two signals. In fact, it is important to emphasize that the use of arbitrary energy scales, i.e. arbitrary E_0 , implies that after the subtraction of the phase functions obtained from the Fourier transformed spectra, as previously discussed, we would obtain an effective phase difference $\Delta\phi_{\text{eff}} = 2\Delta kr_1 + \Delta\delta$ instead of just the exact central atom phase difference $\Delta\delta$. The introduction of this arbitrary phase difference $\Delta\phi_{\text{eff}}$ in Eq. 11 yields a perfect agreement in the comparison between the first shell contribution to the L_1 and L_3 EXAFS signals. However, when applied to further shells it is not possible to reproduce the frequency of the experimental signals because the correction to apply must to be $\Delta\phi_{\text{eff},j} = 2\Delta kr_j + \Delta\delta$, i.e. different for each of the shells placed at a distance r_j from the central atom. Thus, only in the case of an exact determination of the energy thresholds for each edge it would be possible to obtain the good agreement between the experimental and the generated, using Eqs. 11–12, signals.

In our case, the energy reference for the experimental spectra was shifted from the usual choice at the maximum of the first derivative of the spectra by $\Delta E_0 = 5$ eV and 15 eV for the L_1 and L_3 respectively, in good agreement with the values obtained by fitting the theoretical spectra. Figure 3 reports the comparison between the normalized spectra at the L_1 and at the L_3 edges of barium in

BaF₂ according to the determination of the threshold at the maximum of their derivatives and using the method discussed above to determine the E_0 values. It is possible to recognize that in the L₃ edge, the threshold energy usually associated to the inflection point of the edge, is located beyond the white line. This result can be of help in locating the Fermi level in the spectrum of metallic systems.

To conclude, it is important to underline that in the procedure that we have developed no free parameters have been introduced, both in Eq. [11] and [12], to obtain the right phase dependence of the calculated L₃ EXAFS signal. However, although no parameter has been introduced to modify the frequency of the generated signals, to match the calculated and experimental signals it is still necessary to multiply the experimental amplitude of the generated spectrum by a constant value of 0.6 which has no clear physical meaning.

Coming back to Eq. [11] we have to include another term $e^{-\Gamma R/k}$ to take into account of the different core-hole lifetime for the excitation of 2p and 2s electrons, which are respectively $\Gamma = 4.5$ eV and $\Gamma = 3.2$ eV for the L₁ and the L₃ edges. These terms lead to a factor greater than one for the comparison shown in figure 2, because the different core-hole relaxation effect gives a larger damping effect for the L₁ than for the L₃, while the factor that we need to get the agreement of the experimental EXAFS signals is less than one. The observed experimental behaviour is just the opposite than that produced by the core hole relaxation terms.

In general, the experimental amplitude of the EXAFS signal at the L₃ edge is always less than the one at the L₂ edge and both are lower than the one at the L₁ edge. This trend can be observed in previous published investigation of L edges of Au and rare earths compounds^(12,25) in full agreement with our analysis. In addition, we show that the factor needed to match the amplitude of the signals, is constant in the k-space and does not seem to have any functional dependence. This result is illustrated in figure 4 where on the left it is reported the comparison between the experimental L₂ and L₃ EXAFS signals and the weak, but observable, mismatch of the amplitude. On the right we show the same comparison when the L₂ signal has been multiplied by 0.81.

Accurate analysis of the unexpected different amplitudes which are experimentally observed is still in progress. However, the origin of the amplitude difference is physical. We should assign it to the contribution of relativistic effects in the EXAFS of high Z elements. In fact, "ab initio" calculation of the atomic cross section for the L-edges absorption processes, including relativistic effects on the core initial state, shows for the L₂ over L₃ edge a constant ratio of 0.89 and 0.8, respectively for Ba and Au atoms. These preliminary calculations lead to a estimation between 10 to 20% for the difference of the total cross section at the L₂ over L₃ edges, due to relativistic effects, in agreement with our data.

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BaF₂

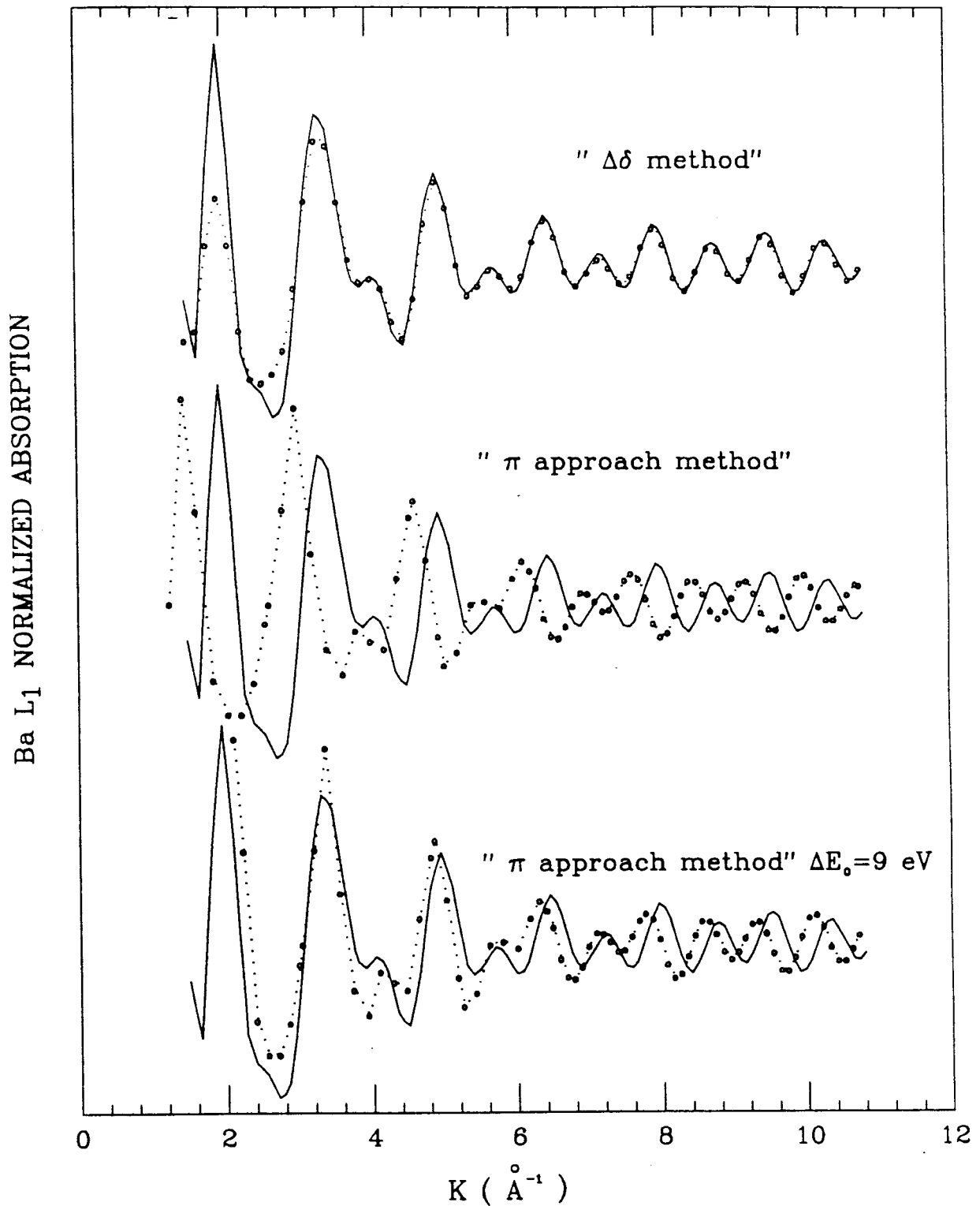


FIG. 1 – The top line shows the comparison, obtained using the expression [12] in the text, between the theoretical EXAFS signal at the barium L₁-edge (continuous line), for a BaF₂ cluster of the first six coordination shells around barium, and that generated by the theoretical signal of the L₃-edge (dotted line). The comparison of the same theoretical signals obtained by the " π approach" method is reported in the middle (without any shift) and in the bottom (applying the best shift, $E_0 = 9$ eV) of the figure.

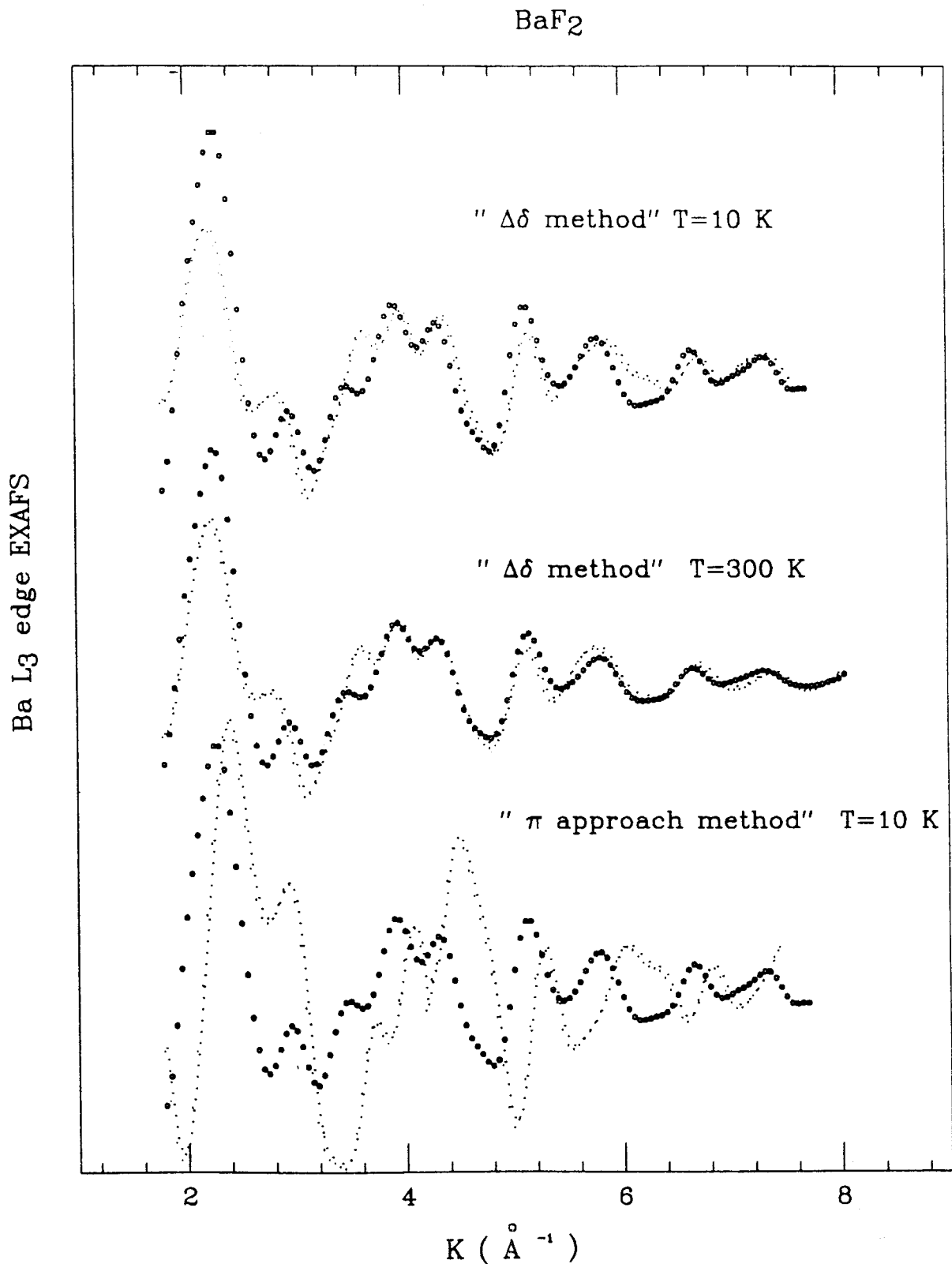


FIG. 2 – The upper part of this figure shows the agreement, between the experimental Ba-L₃ signals at the two measured temperatures (points) and those generated (dotted line) with the method discussed in the text. In the bottom panel, the failure of the " π approach" also for the experimental data is clearly shown.

BaF₂

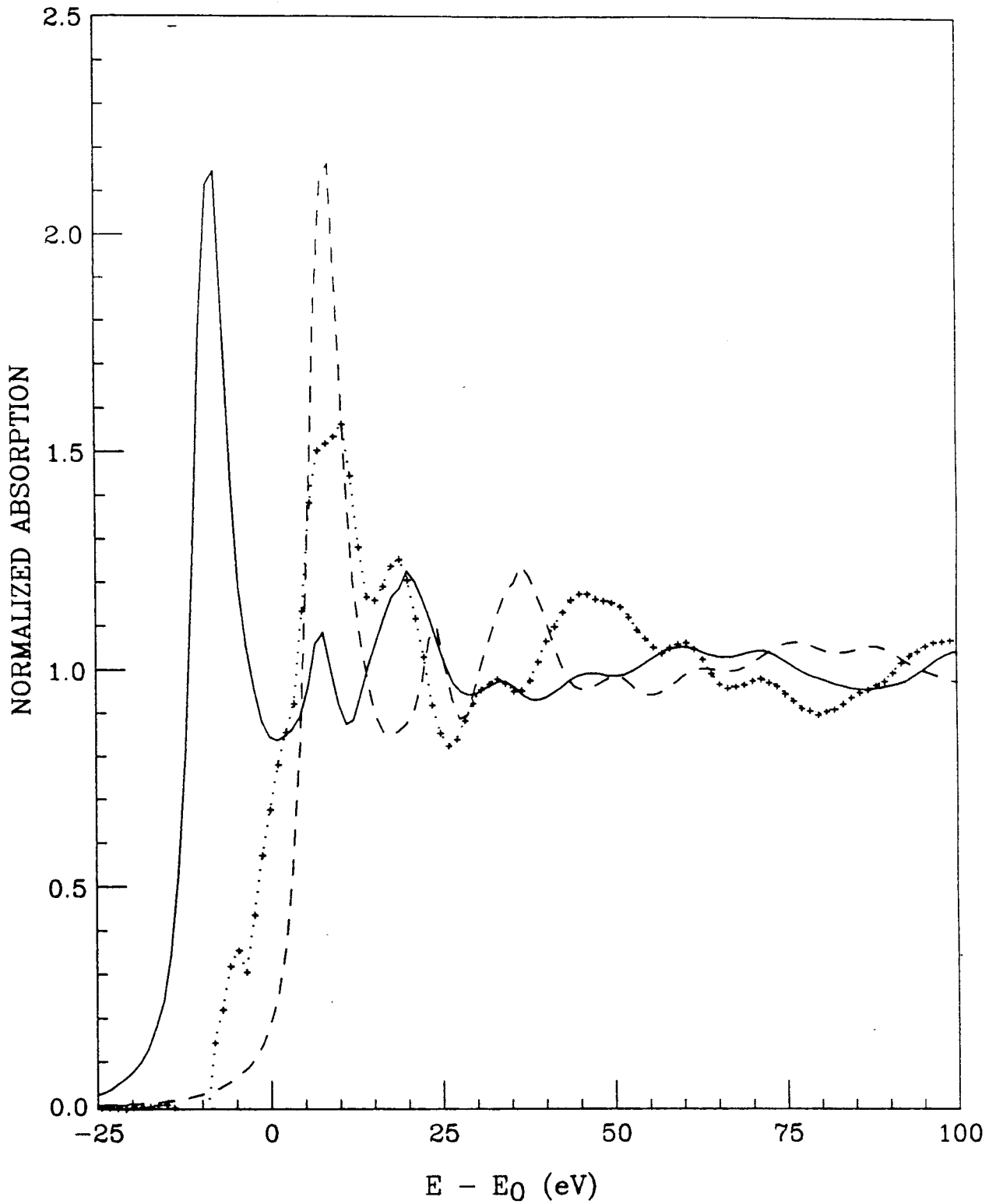


FIG. 3 – Comparison between the normalized spectra at the L₁ (+) and at the L₃ edges of barium in BaF₂ : a) (L₃ dotted line) according to the determination of the threshold at the maximum of the derivatives; b) (L₃ continuous line) using the method discussed in the text to determine the E₀ values. The maximum of the L₃ edge white line is related to the shoulder of the L₁ edge.

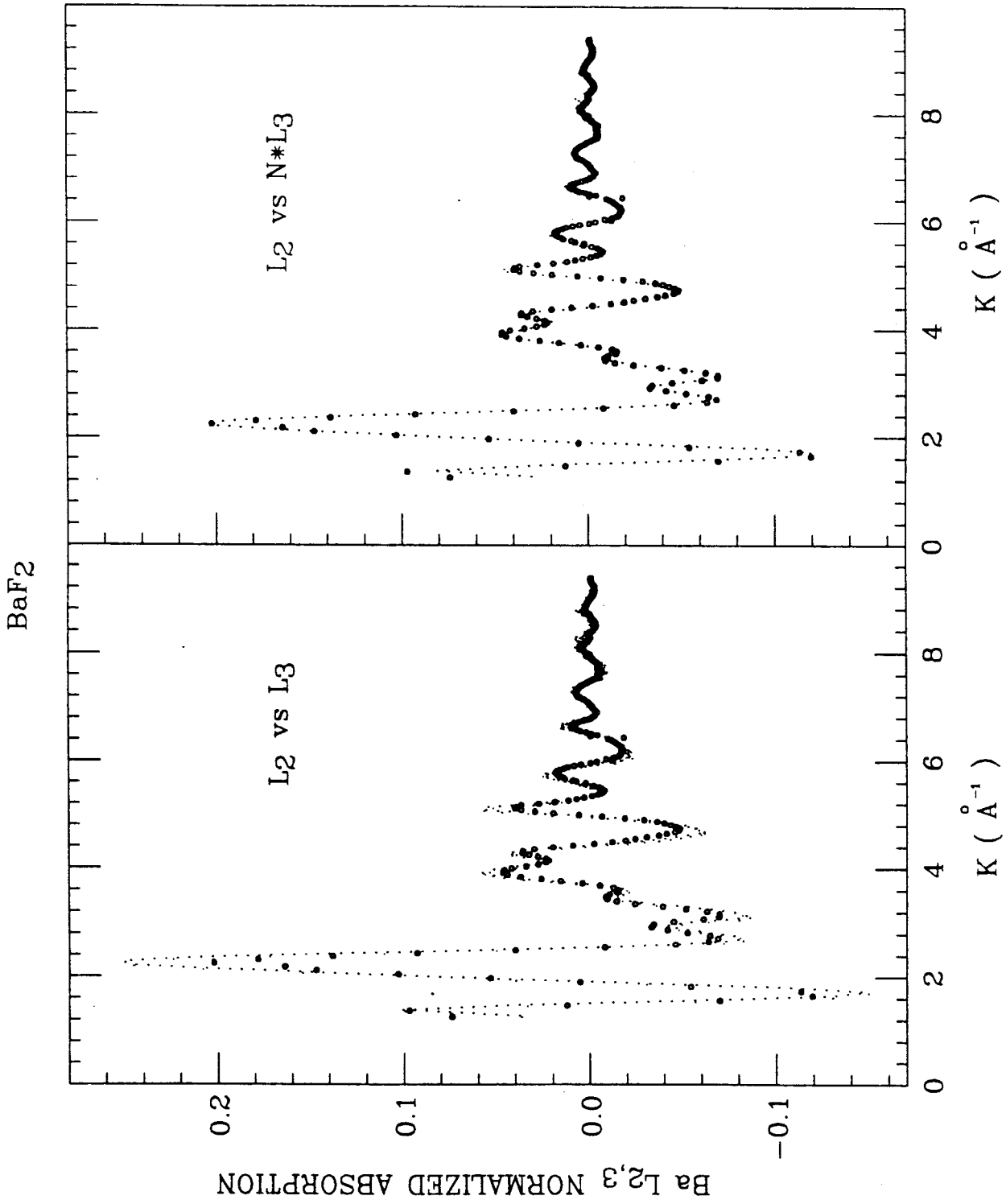


FIG. 4 - On the left it is reported the comparison between the experimental L₂ (dotted line) and L₃ (o) EXAFS signals. On the right the same comparison but when the L₂ signal has been factorized by 0.81 to match the amplitude of both signals.