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BRIDGE-STACKED POLYMERIC STRUCTURE OF A FLUORINATED Ga(III) PORPHYRIN DEDUCED FROM A PERTURBED DIFFERENCE FOURIER ANALYSIS OF EXAFS SPECTRA

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The aim of the present paper is to check if EXAFS spectroscopy can afford a rapid discrimination between a purely molecular or a bridge-stacked polymeric structure of a fluoro-octamethylporphyrinato–gallium(III) complex (OMP):GaF. A new method, i.e. the perturbed difference Fourier analysis (PDFA), combining the structural information of two independent experiments carried out on (OMP):GaF and (OMP)·GaOH was developed and proved to be most appropriate for solving this problem Consistent results are indeed obtained for the distances Ga...Ga (3.9_4 Å), Ga ..F (1.97 Å) and Ga. .N (2.04 Å) in (OMP).GaF. Also derived is the axial shift of the metal $\Delta h = 0.3_8$ Å in the penta-coordinated reference compound (OMP):GaOH.

1. Introduction

It has been shown recently by Wynne and co-workers [1,2] that iodine oxidation of fluoroaluminium or fluorogallium phthalocyanines yields highly conducting organometallic materials. The bridge-stacked polymeric structure of these compounds was also shown to pre-exist before oxidation by a single-crystal X-ray structure determination performed on fluorogallium phthalocyanine [3]. A parallel study of similar systems is being developed at the University of Dijon (France), the large phthalocyanine ring being replaced by selected, substituted porphyrins [4]: it was then essential to know if a polymeric structure of such gallium porphyrins was still preserved. On the other hand, extended X-ray absorption fine structure (EXAFS) appeared recently as a valuable new tool for structural analyses of chemical systems where only the local arrangement of atoms surrounding an absorbing element is to be determined [5]. It was thus attracting to check if this technique could discriminate between a polymeric or non-polymeric structure. In a fairly different optics, the recent discovery that trace amounts of gallium porphyrins were present in coal [6], prompted us to record as well the EXAFS spectra of a number of other gallium(III) porphyrinic derivatives. This paper will show that a direct comparison of the hydroxo- and fluorogallium (III)–2,3,7,8,12,13,17,18-octamethylporphyrins ((OMP):GaOH and (OMP):GaF) already can afford some evidence for the polymeric structure of the latter complex, but a more spectacular demonstration can be given by a refined subtraction of spectra. Difference Fourier analysis of EXAFS

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was first used by Cramer et al. [7] while comparing the EXAFS spectra of the oxy- and deoxy-picket fence porphyrins. We have also shown recently that subtraction of EXAFS spectra could be a useful way to restitute structural information lost by destructive interference of EXAFS oscillations featuring opposite phases [8,9]. For the present study we have developed a perturbed difference Fourier analysis, taking into account the axial displacement of the metal out of the mean porphyrinic plane, for the non-polymeric hydroxo compound.

2. Materials and methods

2.1. *Materials*

The porphyrin free base was prepared and characterized by standard methods [10].

(i) *Chloro-(octamethylporphyrinato) Ga(III)*: The chlorogallium complex, used as a precursor for the preparation of (OMP):GaF and (OMP):GaOH, was synthesized following the same procedure reported elsewhere for the indium complexes [11]. Porphyrin (15 mmol) and $GaCl_3$ (23 mmol) were refluxed in 500 ml of acetic acid containing sodium acetate (0.22 mol). When the reaction was completed (24 h), the resulting solution was cooled down to 0°C and the precipitate obtained was recrystallized from a methylene chloride–heptane (1:1) mixture. (Yield: 67%; ^{1}H NMR (25°C, DMSO-d_6): meso-H = 10.25, singlet, $-CH_3 = 3.67$, singlet; IR (Nujol mull) ν Ga–Cl = 370 cm^{-1}; visible spectrum (nm, ϵ): 375 (16.1), 396 (115.9), 494 (0.8), 529 (4.0), 567 (5.1); analysis: calculated for $C_{28}H_{28}N_4GaCl$, C = 63.97, H = 5.37, N = 10.66, Ga = 13.26, Cl = 6.74; found: C = 63.8, H = 5.4, N = 10.0, Ga = 13.2, Cl = 6.5.)

(ii) *Fluoro-(octamethylporphyrinato) Ga(III)*: The chloro compound (OMP):GaCl was dissolved in 200 ml of methanol. After addition of an aqueous solution of hydrofluoric acid (40%), the mixture was allowed to repose without stirring for 16 h. The excess hydrofluoric acid was removed by vacuum distillation and the solution was evaporated to dryness. The residual was washed with heptane and cooled methanol and recrystallized from methanol. (Yield: 72%; ^{1}H NMR (25°C, DMSO-d_6): meso-H = 10.25, singlet, $-CH_3 = 3.67$, singlet; IR (Nujol mull) ν Ga–F = 562 cm^{-1}; visible spectrum (nm, ϵ): 375 (80.1), 396 (560.2), 494 (3.9), 529 (20.9), 567 (27.2); analysis: calculated for $C_{28}H_{28}N_4GaF$, C = 66.04, H = 5.54, N = 11.00, Ga = 13.69, F = 3.73; found: C = 65.5, H = 5.6, N = 10.8, Ga = 12.8, F = 3.7.)

(iii) *Hydroxo-(octamethylporphyrinato) Ga(III)*: The hydroxy compound (OMP):GaOH was prepared by chromatography on hydrated alumina. A concentrated solution in toluene of (OMP):GaCl (3.94 mmol in 80 ml of toluene) was injected into an alumina column and was elutriated with toluene. Recrystallization was from toluene and the crystals were dried at 340°C under vacuum (10^{-3} mm Hg). (Yield: 78%; ^{1}H NMR (25°C, pyridine-d_5). meso-H = 10.53, singlet, $-CH_3 = 3.59$, singlet, OH = 5.67 (broad line); IR (Nujol mull) ν GaOH = 550 cm^{-1}; visible spectrum (nm, ϵ): 375 (10.1), 395 (105.3), 494 (0.3), 530 (3.7), 568 (5.1); analysis: calculated for $C_{28}H_{29}N_4GaO$, C = 64.29, H = 5.76, N = 11.05, Ga = 13.74; found: C = 64.3, H = 5.7, N = 10.9, Ga = 13.0.)

2.2. *X-ray absorption spectroscopy measurements*

Our EXAFS spectra were recorded at L.U.R.E. (the French national synchrotron radiation facility) using the X-ray emission of a positron beam (1.8 GeV, 250 mA) in the storage ring DCI. The new EXAFS-II spectrometer has already been described elsewhere [12]. Its key component is a two separated crystal monochromator equipped with a pair of Si (311) monocrystals. For the present study we had not to worry about harmonics, because the second-order harmonics are structurally forbidden for the reflecting planes considered, whereas the level of third harmonics is rather poor, because of the low-lying cutoff energy of the DCI machine. The detectors used were two gas-filled ion chambers incorporating home-made ultra-low noise preamplifiers.

2.3. *Basic reduction of the EXAFS data*

The basic analysis (e.g. background subtraction, normalization, FFT, etc.) followed now standard numerical procedures already detailed elsewhere [13,14]. As in our previous papers [9,14,15], the Fourier-transformed (FT) radial distributions $\tilde{\chi}(R)$ displayed below were all corrected according to

$$\tilde{\chi}_N(R)=\int_0^\infty \mathrm{d}k\, g(k)\chi(k)\frac{kR_N^2}{N_N|F_N|A_N} \times \exp\left[2\sigma^2_{Ga-N}k^2-2ikR-i\psi_{Ga-N}(k)\right], \quad (1)$$

where the backscattering amplitude function $F_N(k)$ and the total phase shift $\psi_{Ga-N}(k)$ obviously refer here to the major scattering contribution of the $N_N=4$ equivalent nitrogen atoms of the porphyrinic ring, located at a short distance R_N from the absorbing atom (Ga*). For the numerical evaluation of these functions, we used the parameterization proposed by Teo et al. [16] which proved to be reliable in a number of cases as long as one is keeping slightly adjustable the energy offset E_0 involved in the definition of the photoelectron wavevector: $k=[2m\hbar^{-2}(E-E_0)]^{1/2}$. This additional degree of freedom makes it possible to compensate for some of the imperfections of the theory (e.g. plane-wave propagation of the photoelectron, crudeness of the model potential, neglect of the chemical bonding effects, etc. [17]).

As we are interested here in the comparison of two porphyrinic derivatives, which both exhibit a white line at nearly the same energy ($E_{WL}\approx 10376 \pm 0.5$ eV), the analysis of the two sets of data had to be carried out with the same value of E_0 (10384 eV). Indeed, for the sake of maximum consistency within such comparison, identical standard values were given to the additional amplitude parameters required in eq. (1), e.g. to the Debye–Waller second moment $\sigma^2_{Ga-N}=(R_N-\bar{R}_N)^2$ of the Ga*...N shell, or the pseudo-self-energy Γ_{Ga-N} and the parameters of $S_N^2(k)$ involved in the semi-empirical and rather crude correction [5,14]:

$$A_N(k)=S_N^2(k)\exp(-2R_N\Gamma_{Ga-N}/k), \quad (2)$$

accounting for inelastic effects [18,19]. Of course, both calculations were performed with identical Kaiser window functions $g(k)$ required for minimizing the well-known side-lobe effects in truncated spectra.

Refinement of selected amplitude or phase parameters is always possible by fitting out in the R-space the signal of a single or composite shell j, backtransforming it into the k-space and fitting it against the standard formulation:

$$\chi(k)=\sum_j N_jA_j(k)\exp\left(-2\sigma_j^2k^2\right)|F_j(k)| \times\sin\left[2kR_j+\psi_j(k)\right]. \quad (3)$$

A package of quite efficient non-linear least-squares fitting FORTRAN programs was developed for this task, delivering for each calculation the residual factor of the fit together with the correlation matrix of the fitted parameters. Due to these correlations, only a restricted number of parameters can be refined from such a fit: the others have to be preset to standard, self-consistent values obtained from a large number of previous calculations carried out on model compounds, or from reasonable structural assumptions.

2.4. Perturbed difference Fourier analysis

The principle of the method is summarized in the block-diagram shown in fig. 1. The perturbation accounting for a shift Δh of the metal back to the plane of the four nitrogens (e.g. in (OMP):Ga–OH) was produced in the R-space by the simple transform: $(R')^2=R^2_{real}-\Delta h^2$, while a sophisticated interpolation procedure resulted in $\tilde{\chi}(R')$ spectra featuring a linear sampling of the R' scale. The difference between the two sets of experimental data was then carried out in the k-space, in order to minimize imperfect cancellation of side-lobe signatures. These calculations were reproduced in an automatic optimization loop, until optimal cancellation occurred in the perturbed difference Fourier spectrum $|\tilde{\chi}_{GaF-GaOH}(R)|$ for the most typical signature of the C_a carbons of the porphyrinic ring. A fast convergence was achieved in less than 10 steps with the present minimization algorithm.

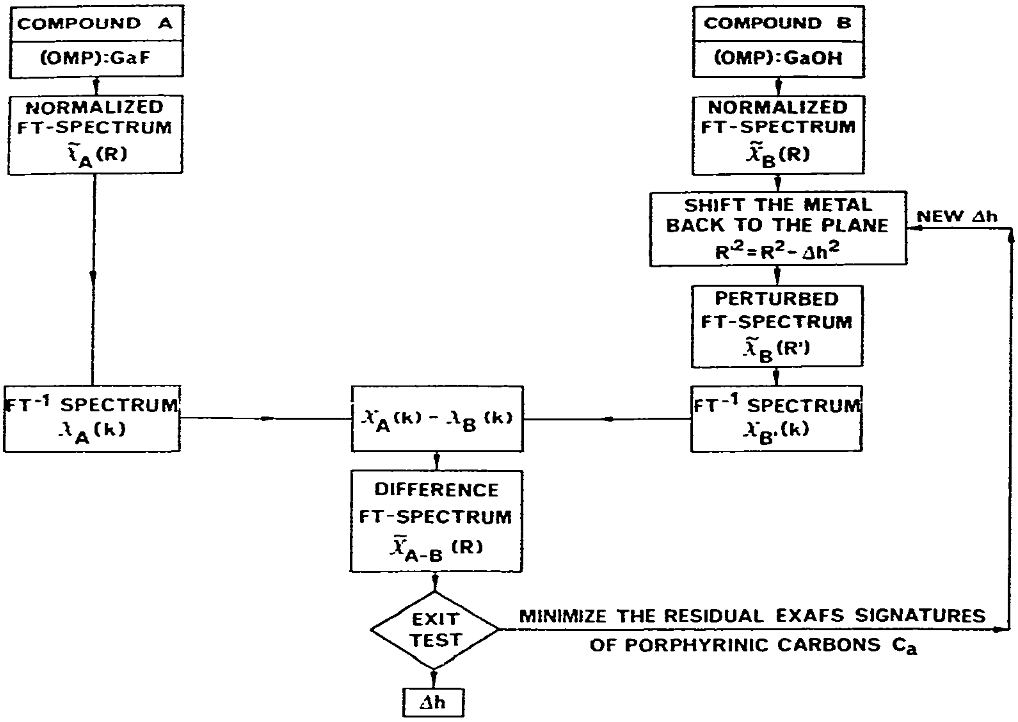

Fig. 1. Block diagram of the perturbed difference Fourier analysis carried out on (OMP):GaF–(OMP).GaOH

3. Results

The magnitude $|\tilde{\chi}(R)|$ and imaginary part Im $\tilde{\chi}(R)$ of the FT EXAFS spectra of the two gallium derivatives are compared in figs. 2a and 2b respectively. The dominant signal peaking at $R < 2.1$ Å is to be assigned to the scattering contribution of the whole coordination shell including the four nitrogen atoms of the porphyrin and the axial ligands (F, OH). The typical signatures [15] of the three successive metal...carbon shells of the porphyrinic ring: Ga...C_a, Ga...C_{meso}, Ga...C_b are indeed apparent in the spectra of both compounds. However the only direct evidence of a polymeric structure of (OMP):Ga–F seems to be the stronger intensity of its first peak (fig. 2a), thus suggesting a probable hexa-coordination of the metal involving two fluorine atoms, while penta-coordination only is expected for the hydroxo derivative (OMP):Ga–OH. A more subtle indication is also to be found in the lack of superimposition of the two EXAFS patterns of the porphyrinic ring, as shown on an expanded scale by fig. 3: this observation was related to the classical displacement of the metal out of the mean porphyrinic plane for penta-coordinated derivatives, and led us to develop the abovementioned perturbed difference Fourier analysis.

Figs. 4a and 4b show the difference spectra $|\tilde{\chi}(R)|$ obtained respectively with and without the compensation accounting for this axial shift of the gallium atom. Obviously at the optimal value $\Delta h = 0.38 \pm 0.05$ Å, the cancellation of the porphyrinic patterns becomes nearly perfect (fig. 4a) and makes apparent a clean contribution of the Ga...Ga signal at nearby twice the distance of the first peak resulting from the difference: $(2\text{Ga...F}) - (\text{Ga...OH})_{\text{perturbed}}$. One should however keep in mind that this apparent Ga...Ga signal needs to be corrected (i) for the phase shift difference: $\Delta\psi(k) = \psi_{\text{Ga-Ga}} - \psi_{\text{Ga-N}}$, (ii) for the additional phase shift associated with the multiple scattering effect expected for a linear sequence Ga...F...Ga [5,20] and resulting in an approxi-

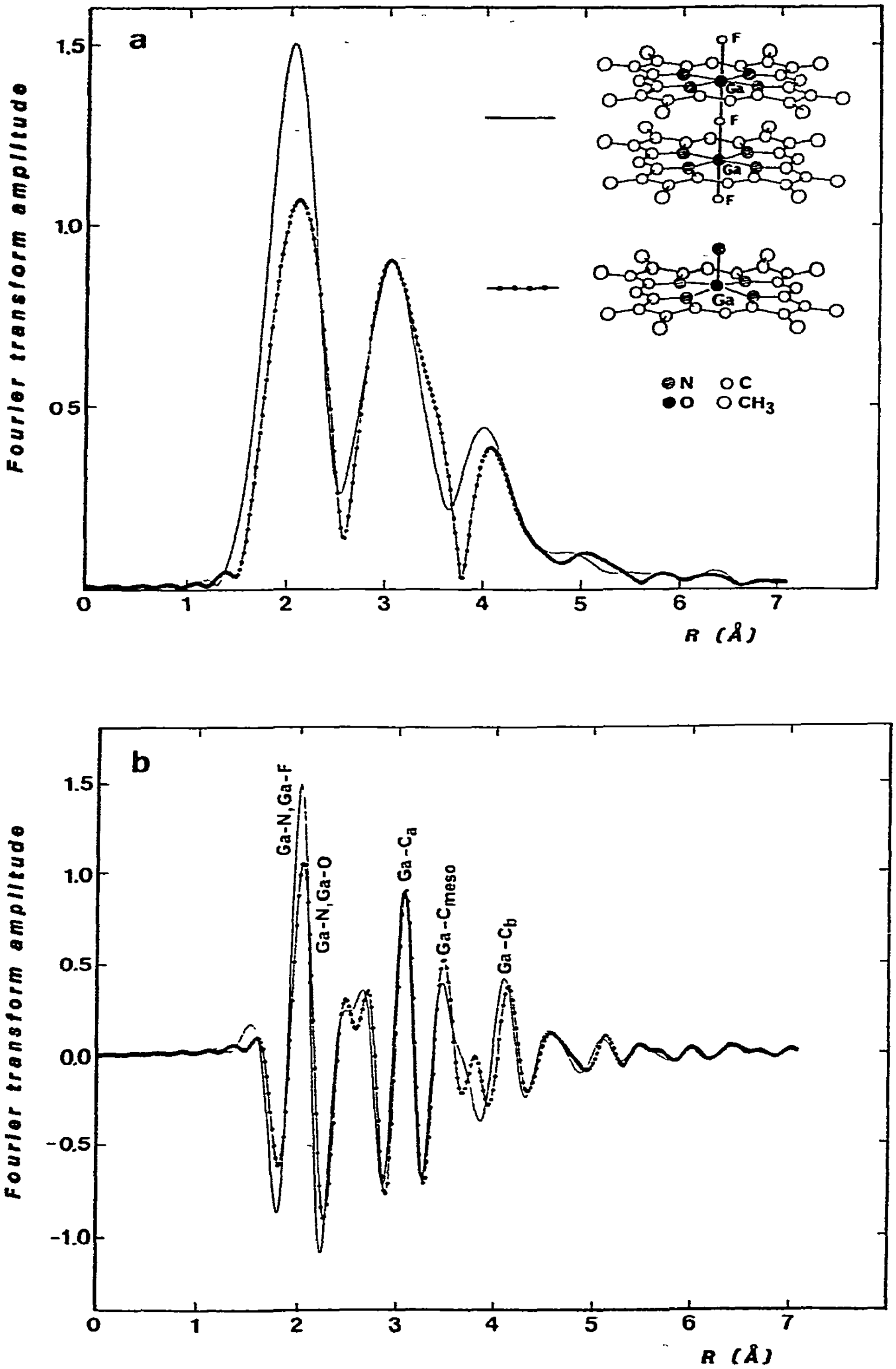

Fig. 2. Comparison of the FT spectra obtained respectively for (OMP):GaF (full line) and (OMP):GaOH (dotted line) at room temperature 298 K. (a) $|\tilde{\chi}_N(R)|$ versus R, (b) Im $\tilde{\chi}(R)$ versus R.

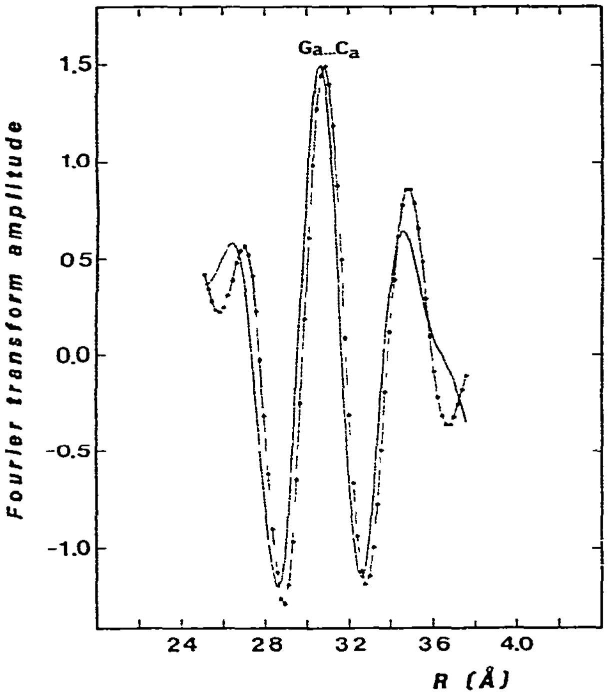

Fig 3. Expanded-scale comparison of the FT spectra Im $\tilde{\chi}(R)$ of (OMP).GaF (full line) and (OMP).GaOH (dotted line) in the range of the Ga*...C_a and Ga*...C_{meso} signatures. Note the small but significant shift of the Ga*. C_a signal accounting for the "in-plane" metal location in the polymeric structure.

mate distance correction of ≈ 0.08 Å. From this spectrum, the R(Ga...Ga) distance could be estimated: R(Ga–Ga) = 3.94 ± 0.06 Å while a reasonable distance R(Ga...F) = 1.97 ± 0.03 Å [3] was implicitly obtained.

At this stage of our analysis we tried to check the self-consistency of the various structural data extracted from these EXAFS spectra. For each compound, the first peak was filtered out, back-transformed to the k-space and fitted against a "degenerated" two-shell model accounting for the different distances, phase shifts and amplitudes of the Ga...N, Ga...F/Ga...OH signals: however in order to minimize the number of free parameters ($N_{max} = 3$), the relevant distances R(Ga...F) = 1.97 Å and R(Ga...O) = 1.99 Å were fixed while a unique Debye–Waller second moment σ_I^2 and a unique normalization factor a_I (thus assuming the implicit coordinations 4N + 2F, 4N + O) were optimized, together with the distance R(Ga...N). The quality of the fits reproduced in figs. 5a and 5b is encouraging. The Ga...N distances found respectively for (OMP): GaF (R_N = 2.04 ± 0.02 Å) and (OMP): GaOH (R_N = 2.08 ± 0.02 Å) are, within the error bars consistent with the optimal value of Δh. For (OMP): GaF (I), R_N is also basically consistent with the location of the gallium well in the porphyrinic plane, and with the radius of the macrocyclic cavity ($R_c \approx 2.043$ Å [21,22]) For (OMP): GaOH (II), the axial shift of the metal $\Delta h = 0.38$ is of the order of the known displacements reported for other d_{10} penta-coordinated porphyrinic complexes [21]. On the other hand the difference $\sigma_{II}^2 - \sigma_I^2 = 0.0002$ Å^2 and the ratio $a_{II}/a_I = 1.0_2$ are definitively supporting the hexa-coordination of the fluorinated derivative. Finally quite reasonable Ga...carbon distances are also available:

$R_I(Ga...C_a) = 3.06 \pm 0.02$ Å,
$R_I(Ga...C_m) = 3.45 \pm 0.05$ Å,
$R_I(Ga...C_b) > 4.10$ Å,
$R_{II}(Ga...C_a) = 3.09 \pm 0.02$ Å,
$R_{II}(Ga...C_m) = 3.48 \pm 0.05$ Å,
$R_{II}(Ga...C_b) > 4.16$ Å,

the latter Ga...C_b distances being classically found underestimated by ≈ 0.15 Å as a consequence of the neglect of multiple scattering paths [20] and possibly other phase effects [23].

4. Conclusion

The aim of the present study was to check if EXAFS spectroscopy could afford a rapid discrimination between a purely molecular or a bridge-stacked polymeric structure of (OMP): GaF. The above developed perturbed difference Fourier analysis (PDFA) which combined the structural information of two independent experiments carried out on (OMP) : GaF and (OMP): GaOH proved to be most appropriate for answering positively such a question. The method, however, does not tell us whether the pyrrole rings are stacked in perfectly eclipsed situation with respect to each other or not. On the other hand, the reliability of this method requires also the two systems to be compared to feature enough chemi-

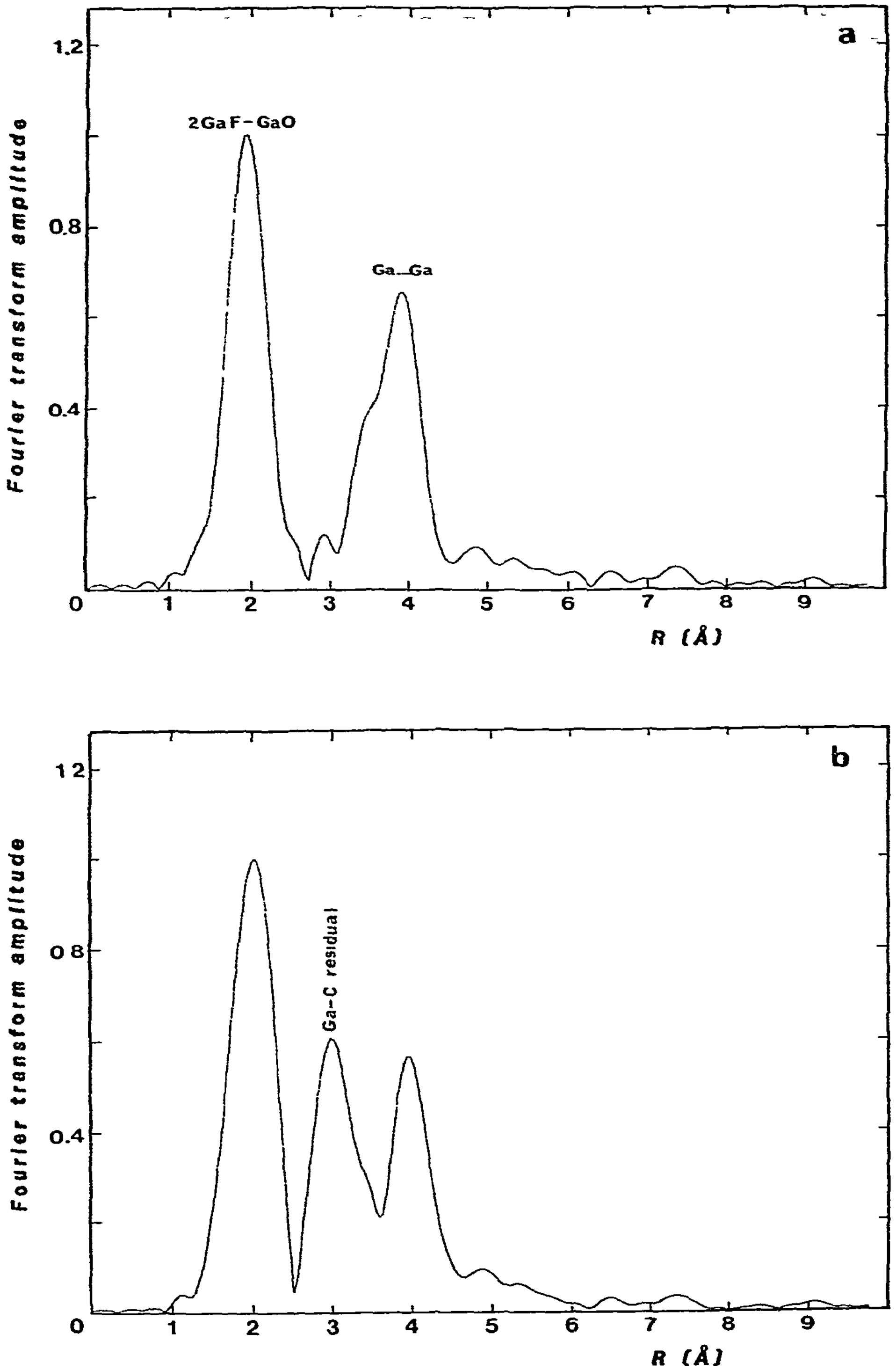

Fig. 4 Fourier difference spectra $|\tilde{\chi}(R)|$ obtained with (a) or without (b) the perturbation accounting for the axial displacement of the gallium atom.

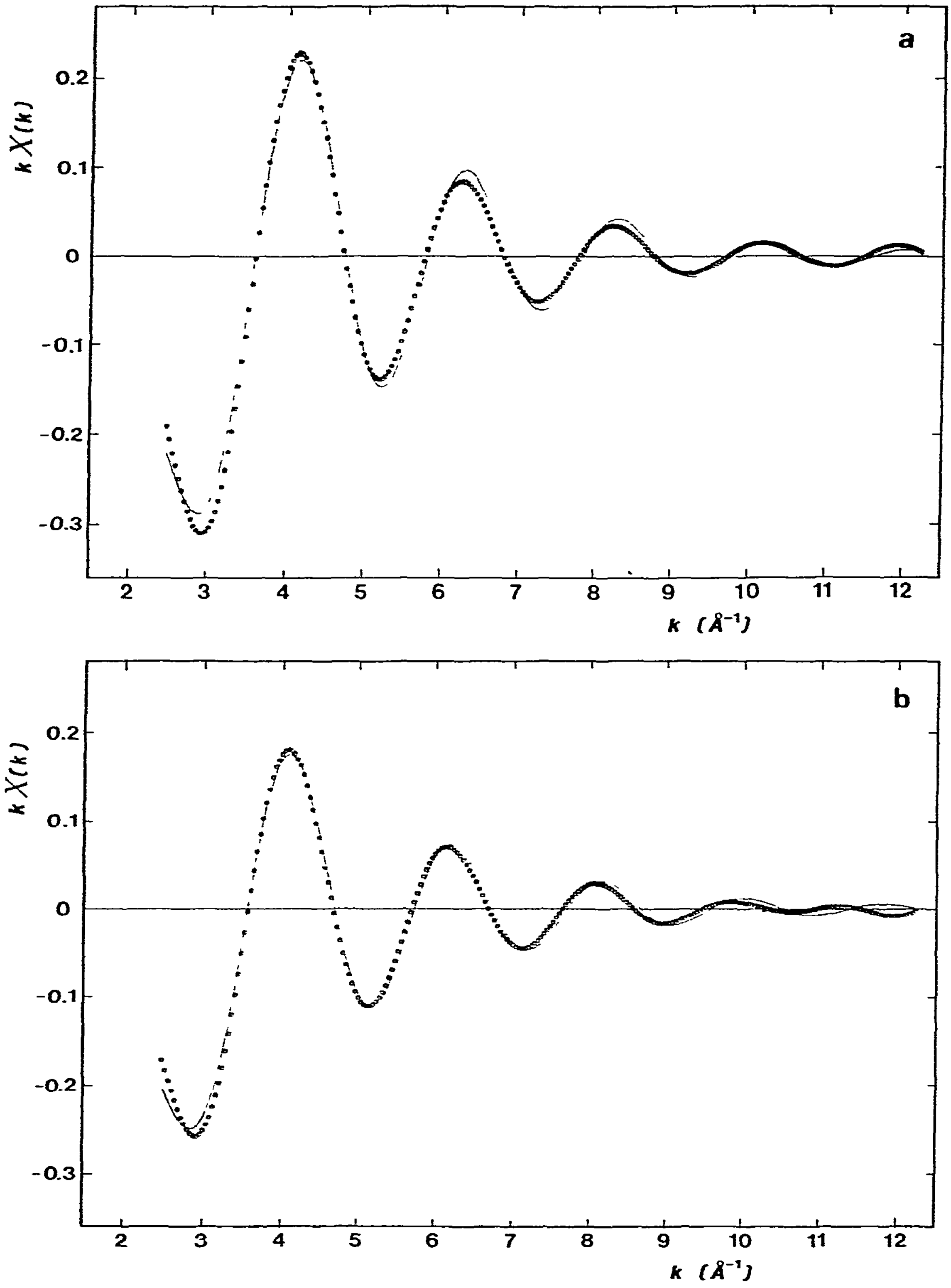

Fig 5. Fourier filtered EXAFS oscillations $k\chi(k)$ of the whole coordination shell (dots) and the least-squares fit (full line) obtained for: (a) (OMP):GaF, (b) (OMP):GaOH.

cal similarity in order to minimize possible but small variations of the energy offset E_0 (or of the phase shifts $\psi(k)$) thus aliasing the phase information of the EXAFS oscillations. We are now investigating further extensions of this difference method combining the respective advantages of a numerical analysis in both k- and R-space.

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