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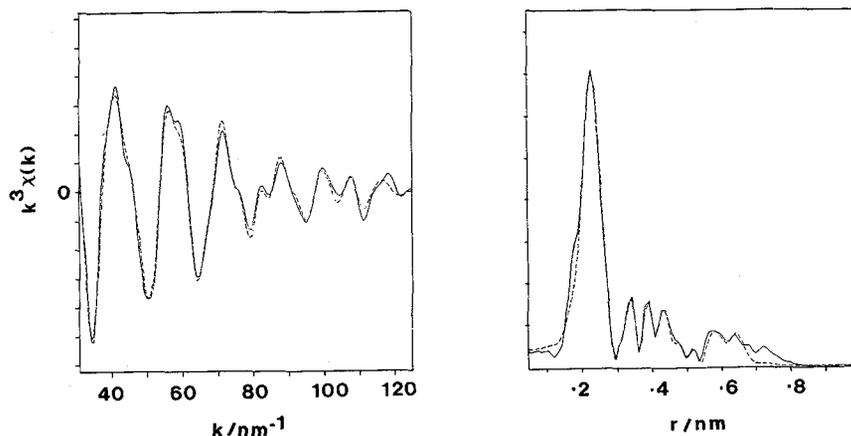
## MULTIPLE SCATTERING IN THE EXAFS OF CALCIUM PHOSPHATES

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**Résumé** Pour analyser les spectres EXAFS de l'hydroxyapatite, du brushite et du monetite qui ont été enregistrés au dessus de la limite d'absorption K de calcium, il faut utiliser la diffusion multiple par les atomes de phosphore à une distance de 0,37 nm du calcium. Si on n'utilise pas la diffusion multiple, quelques-uns des paramètres variables prennent des valeurs qui ne sont pas physiquement raisonnable. Nous n'avons jamais été obligés de varier les valeurs des rayons des atomes par plus de 0,01 nm de leur valeur dans les structures reconnues des cristaux.

**Abstract** Analysis of the EXAFS spectra of hydroxyapatite, brushite and monetite, recorded above the calcium K edge, requires the inclusion of multiple scattering by phosphorus atoms at 0.37 nm, from calcium. If multiple scattering is not included, some variable parameters acquire physically unreasonable values. Atomic radii never had to be varied by more than 0.01 nm from their values in the accepted crystal structures.

EXAFS spectra of hydroxyapatite  $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$ , brushite  $[\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}]$  and monetite  $[\text{CaHPO}_4]$  have been recorded above the calcium K edge at the SERC Daresbury Laboratory Synchrotron Radiation Source when operating at 2 GeV and 200 mA. A monochromatic beam was obtained using a silicon (111) double crystal monochromator set at 50% harmonic rejection. Spectra were recorded out to photoelectron wave number  $k=120 \text{ nm}^{-1}$  as shown for brushite in Fig. 1.



**Fig. 1** Experimental (solid line) and theoretical (broken line) EXAFS of brushite recorded above the calcium K edge with the moduli of their Fourier transforms. Spectra are presented as  $k^3\chi(k)$  plotted against  $k$ .

The spectra were modelled theoretically by the curved wave theory [1] as described elsewhere [2]. Initial values for the atomic radii (*ie.* distances from calcium) were calculated from the crystal structures of hydroxyapatite, brushite and monetite [3,4,5]. These radii and Debye-Waller factors were refined to obtain the best fit between theory and experiment.

A comparison of the experimental and theoretical EXAFS of brushite, together with the modulus of the Fourier transform, is shown in Fig. 1. The refined atomic radii did not differ by more than 0.01 nm from the values calculated from the accepted crystal structure of brushite [4]. Similar agreement was found between the atomic radii as determined by EXAFS and by crystallography for hydroxyapatite [2] and monetite (unpublished).

However, in the EXAFS of these three calcium phosphates the single scattering contribution of phosphorus atoms at 0.37 nm had an unrealistically high Debye-Waller factor if single scattering alone was considered. This effect was observed both when fitting experimental EXAFS spectra and after these spectra had been Fourier filtered as described below.

Fig. 2(a) shows a region of the Fourier transform of the EXAFS spectrum of brushite corresponding to atoms whose radii are in the range 0.3-0.5 nm. The contribution of these atoms to the EXAFS was obtained by inverse transformation back into  $k$  space. Atomic radii and Debye-Waller factors were refined to obtain the best agreement between the theoretical and this filtered spectrum. As a result of this refinement, the Debye-Waller factor of phosphorus at 0.37 nm had an unreasonably high value of  $>6 \times 10^{-4} \text{ nm}^2$ . Figs. 2(b) and 2(c) show comparable calculations for hydroxyapatite and monetite where again, unreasonably high values of the Debye-Waller factors were obtained for phosphorus.

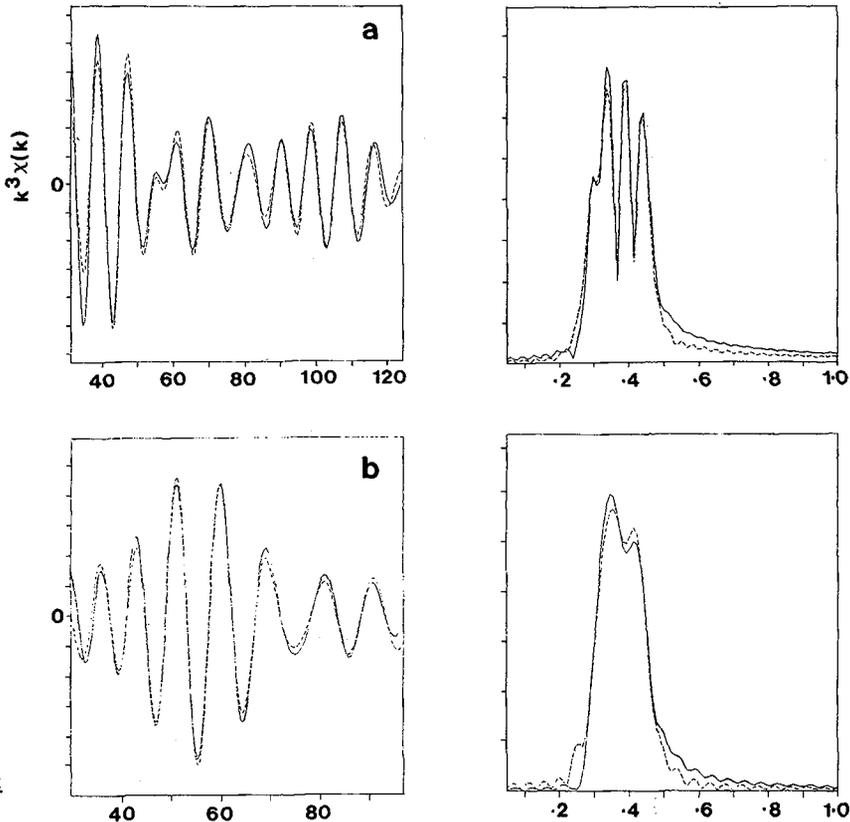
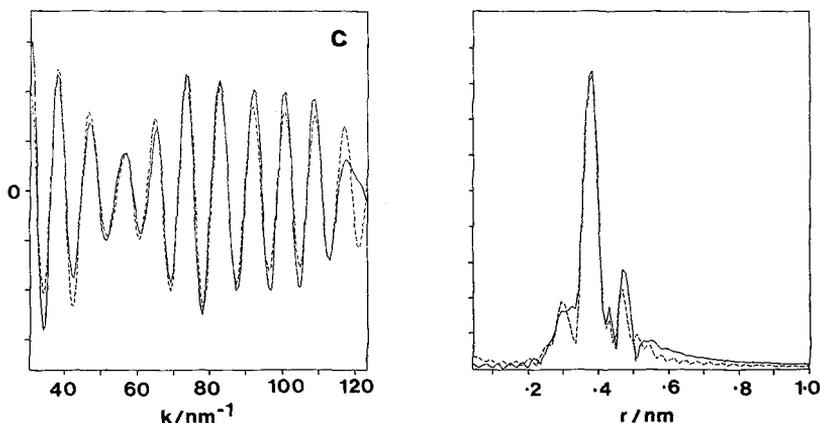
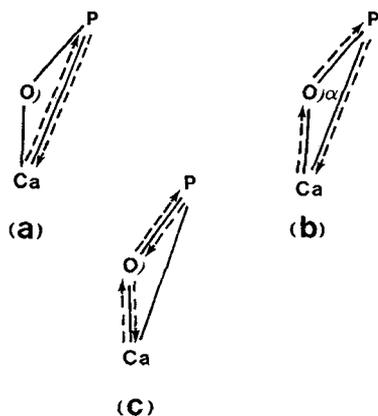


Fig. 2

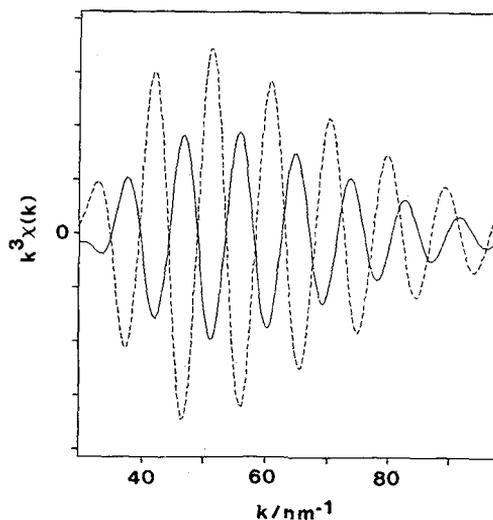


**Fig. 2** EXAFS spectra shown as solid lines are the Fourier filtered contributions to the EXAFS arising from atoms located between 0.3 and 0.5 nm from calcium. These are shown for (a) brushite (b) hydroxyapatite and (c) monetite. The broken lines represent the best single scattering models for each compound based on crystallographic data. In each case the Debye-Waller factor for phosphorus atoms at 0.37 nm is  $>6 \times 10^{-4} \text{ nm}^2$ .

An examination of the geometry of the arrangement of phosphate groups around calcium in each compound shows that the phosphorus atoms at 0.37 nm lie partially in the shadow of oxygen atoms situated at 0.24 nm from calcium (Fig.3). Calculations based on the co-ordinates of these oxygen and phosphorus atoms in the three crystal structures show that the forward scattering angle,  $\alpha$ , shown in Fig. 3, is approximately  $140^\circ$  in each of the calcium phosphates.



**Fig. 3** Schematic representation of scattering pathways for an array of Ca, O, P atoms found in calcium phosphates. The forward scattering angle,  $\alpha$ , is  $140^\circ$ . The pathways shown are (a) single scattering from phosphorus, (b) double scattering, which is the most dominant MS term in this instance and (c) triple scattering.



**Fig. 4** Comparison of single scattering contribution to EXAFS of P atoms at 0.37 nm (solid line) and MS contribution (broken line) in hydroxyapatite.

Multiple scattering (MS) contributions from arrays of Ca, O, P atoms were calculated as described elsewhere [6]. In each case the MS contribution was found to destructively interfere with the single scattering contribution from phosphorus as shown in Fig. 4 for hydroxyapatite. When this MS contribution was included in the analysis of the spectra, and the refinement repeated, the Debye-Waller factor for the phosphorus atoms acquired a physically reasonable value ( $\sim 2 \times 10^{-4} \text{ nm}^2$ ). Hence, MS needs to be taken into account when analysing the EXAFS of these calcium phosphates.

#### Acknowledgements

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