

Cation distribution in calcium-strontium-hydroxyapatites

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Table 1. Eigenvalues and eigenvectors of 3H_4 term in the crystal field of C_{2v} symmetry calculated with values listed in Fig. 2. $|\bar{J}_z\rangle$ represents $|-J_z\rangle$

Eigen value (cm ⁻¹)	Eigen vector
4784	$0.0171(4\rangle+ \bar{4}\rangle)-0.4091(2\rangle+ \bar{2}\rangle)+0.8153 0\rangle$
4780	$-0.1454(3\rangle- \bar{3}\rangle)+0.6920(1\rangle- \bar{1}\rangle)$
1578	$-0.1267(4\rangle- \bar{4}\rangle)+0.6957(2\rangle- \bar{2}\rangle)$
1560	$-0.4466(3\rangle+ \bar{3}\rangle)+0.5482(1\rangle+ \bar{1}\rangle)$
-1135	$-0.1804(4\rangle+ \bar{4}\rangle)+0.5551(2\rangle+ \bar{2}\rangle)+0.5646 0\rangle$
-1307	$0.6920(3\rangle- \bar{3}\rangle)+0.1454(1\rangle- \bar{1}\rangle)$
-2162	$0.5482(3\rangle+ \bar{3}\rangle)+0.4466(1\rangle+ \bar{1}\rangle)$
-4040	$0.6957(4\rangle- \bar{4}\rangle)+0.1267(2\rangle- \bar{2}\rangle)$
-4056	$0.6835(4\rangle+ \bar{4}\rangle)+0.1567(2\rangle+ \bar{2}\rangle)+0.1287 0\rangle$

The calculation of the magnetic susceptibility from the energy splitting behavior thus obtained has been done with use of the Van Vleck formula to the first excited state, including an additional open variable Q introduced by Amberger *et al.*[10]. As shown in Fig. 1, a good agreement with the experimental result up to 170°K is obtained, when R_4 and Q are taken to be 2.35 Å and 0.829, respectively, ($2\theta_4 = 67.2^\circ$). The eigenvalues and the eigenvectors are listed in Table 1. The value of Q is intermediate between that of uranocene ($Q = 0.94$)[11] and that of $(\eta^5\text{-C}_5\text{H}_5)_4\text{U(IV)}$ ($Q = 0.707$)[10]. The distance R_4 and the angle θ_4 seems to be reasonable values considering that the U-N distance of $\text{U(NCS)}_8 \cdot 4(\text{C}_2\text{H}_5)_4\text{N}$ is 2.38 Å[12] and the angle of $\text{O}^{\text{THF}}\text{-U-O}^{\text{THF}}$ is 67.2° [5]. The small deviation from the experimental value above about 170°K may be explained by taking into account higher excited states.

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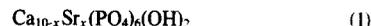
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Cation distribution in calcium-strontium-hydroxyapatites

(First received 16 June 1978; in revised form 14 September 1978)

Contradictory data about the effect of Sr^{2+} ions in drinking water on dental caries[1, 2] necessitate a reinvestigation of Ca^{2+} and Sr^{2+} containing phosphates. Especially those with the apatite structure might be of interest as calcium hydroxyapatite (CaOHA) has been reported to form a continuous series of solid solutions with strontiumhydroxyapatites (SrOHA)[3, 4], whereas strontium analogues of octocalciumphosphate $\text{Ca}_8(\text{PO}_4)_4(\text{HPO}_4)_2 \cdot 5\text{H}_2\text{O}$ and brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ do not exist[5, 6]. Moreover, SrOHA can incorporate large amounts of carbonate like the biological apatites[6] which are derived from CaOHA as the prototype[7].

In this study pure CaOHA and SrOHA were prepared by titrating a boiling slurry of either calcium- or strontiumhydroxyde with phosphoric acid[8]. Solid solutions of the formula



at $x = 1, 2, 4, 5, 6, 8$ and 9 were prepared by solid state reaction of the respective ternary apatites at 1200°C in a stream of CO_2 -free water vapour of 1 atm. After two days the temperature of heating was decreased to 900°C for one consecutive day. Then the samples were slowly cooled, crushed and powdered. The

pure end-members CaOHA and SrOHA were also subjected to this heat treatment prior to X-ray diffraction.

Both the Philips Guinier XDC-700 and the Nonius Guinier-de Wolff camera were used, either with $\text{CrK}\alpha_1$ or $\text{CuK}\alpha_1$. The cell parameters were determined by measuring the position of at least 28 reflections for each sample. The accuracy of the cell parameters a and c of the hexagonal cell which were calculated by using a least squares procedure is estimated to be better than ± 0.003 and ± 0.002 respectively. The results with both cameras were the same and are represented in Fig. 1. They confirm the linear variation with composition found earlier [3, 4].

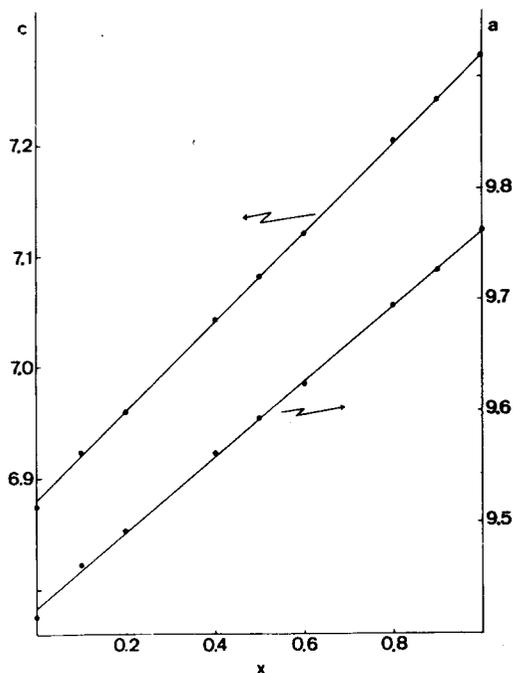
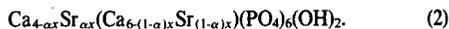


Fig. 1. Lattice parameters of CaOHA and SrOHA and of their solid solutions found in this study.

In the apatite structure two sublattices occur for the cations. Position I is fourfold (Wyckoff notation f) and position II is six-fold (denoted by h). The structure formula of solid solutions of CaOHA and SrOHA can thus be written as



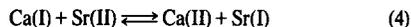
As the cation distributions were not known, we derived them from a comparison of the experimental values of the intensity ratios 210/002, 300/002, 222/002, 002/202, 321/202, 321/410 and 213/312 with their theoretical values depending on α . In the calculation of the theoretical values Lorentz-polarisation and multiplicity factor were taken into account, absorption correction and temperature factor were neglected. Both peak heights and peak areas were taken as a measure for the intensities of reflections.

In this way two sets of seven α values were obtained for each composition x . The average per set was independent of the fact whether peak heights or peak areas were taken. A distribution coefficient K was defined as

$$K = \frac{[6 - (1-\alpha)x][\alpha x]}{[4 - \alpha x][(1-\alpha)x]} \quad (3)$$

and its value and standard deviation were calculated from the two sets of α values at a given x . A constant value for K was found throughout the range $1 \leq x \leq 9$ within the limits of experimental error. Its overall weighted mean was 0.841 ± 0.065 .

This means (a) that apparently an equilibrium is reached according to



at the temperature of preparation and (b) that the solid solutions are close to ideal in the thermodynamical sense [9]. The latter conclusion enables the quantitative estimation of the effect of Sr^{2+} ion incorporation on the solubility product of CaOHA from knowledge about the solubility products of both CaOHA and SrOHA [7].

N.B. The individual values of α and K derived from the intensity ratios are available on request.

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Synthesis and characterization of complexes of palladium(II) and platinum(II) with a tetraaza macrocycle

(First received 13 March; in revised form 20 July 1978; received for publication 20 September 1978)

Transition metal complexes with synthetic tetraaza macrocyclic ligands have been extensively investigated in recent years. Most

of these studies have involved first row transition metals with emphasis on examining the role of the macrocyclic ligand on the