

Electron paramagnetic resonance spectroscopic study of synthetic fluorapatite: Part II. Gd³⁺ at the Ca1 site, with a neighboring Ca2 vacancy

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ABSTRACT

A W-band (94 GHz) electron paramagnetic resonance (EPR) study of synthetic fluorapatite with 57 ± 4 ppm Gd has been made on single crystals at ~ 287 K. The spectra disclosed the presence of a previously unreported type of Gd³⁺ center denoted by “b” herein ($S = 7/2$), in addition to the Gd³⁺ center “a” assigned to the Ca2 site using the results of a previous X-band (9.5 GHz) EPR study (Chen et al. 2002). In particular, the single-crystal W-band EPR spectra from three orthogonal-rotation planes allowed determination of an appropriate spin-Hamiltonian for center “b,” including the spin terms of type BS (matrix **g**) and S² (matrix **D**) and the parameters associated with the high-spin terms of type S⁴ and S⁶ as well as BS³ and BS⁵. Agreement between the observed and simulated single-crystal spectra confirmed the validity of the spin-Hamiltonian analysis.

The principal values of the matrices **g** and **D** [e.g., $D/g_e\beta_e = 1069.2(1)$ G and $E/g_e\beta_e = 52.4(3)$ G] suggest a considerably distorted rhombic local environment for the Gd³⁺ ions in center “b.” The principal directions of **D** suggest that “b” corresponds to Gd³⁺ at the Ca1 site. This site assignment is supported by a pseudo-symmetry analysis of the term S⁴, i.e., approximate matching of the directions of the calculated pseudo-symmetry axes to the bond directions and face normals of the coordination polyhedron of the ideal Ca1 site. The data suggest that the incorporation of Gd³⁺ into the Ca1 site is achieved by a coupled substitution ($2\text{Gd}^{3+} + \square \leftrightarrow 3\text{Ca}^{2+}$) involving a Ca²⁺ vacancy \square and that the vacancy is located at a next-nearest-neighbor Ca2 site, resulting in a Gd³⁺- \square -Gd³⁺ arrangement, with the cations well separated.