Investigations on the Spin Hamiltonian Parameters and the Local Structures for Various Rh^{2+} Centers in NaCl

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The spin Hamiltonian parameters (the g factors, the hyperfine structure constants, and the superhyperfine parameters) and the local structures for various Rh^{2+} centers OI, OII, and RTAX in NaCl are theoretically investigated from the perturbation formulas of these parameters for a $4d^7$ ion in tetragonally and orthorhombically elongated octahedra. The related molecular orbital coefficients and the ligand unpaired spin densities are determined quantitatively from the cluster approach in a uniform way. The centers OI, OII (orthorhombic) or RTAX (tetragonal) are attributed to the substitutional Rh^{2+} on Na^+ site, associated with two, one or none next nearest neighbour cation vacancies V_{Na} along [100] (or [010]) axis, respectively. The ligand octahedra in the orthorhombic centers OI and OII are found to suffer the relative elongations $\Delta Z \approx 0.071$ and 0.068 Å along the [001] axis due to the Jahn-Teller effect, and the intervening ligand(s) in the V_{Na} and the Rh^{2+} may undergo the inward displacements $\Delta X \approx 0.001$ and 0.011 Å towards Rh^{2+}, respectively. As for the tetragonal center RTAX, the uncompensated $[RhCl_6]^{4-}$ cluster is found to experience the relative elongation $\Delta Z \approx 0.067$ Å along the [001] axis of the Jahn-Teller nature. The calculated spin Hamiltonian parameters based on the above local structures show good agreement with the observed values for all the centers.

Key words: Crystal-Fields and Spin Hamiltonians; Electron Paramagnetic Resonance (EPR); Rh^{2+}; NaCl.