DFT characterisation of structural and EPR properties of Rh defects in alkali halide lattices

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Rh^{2+} defects in alkali and silver halide lattices have been extensively studied in the past by means of EPR and ENDOR because of their role in the photographic process. Indeed, Rh^{3+} is known to act as a deep electron trap in silver halides and even in small dopant concentrations it is able to control the contrast and sensitivity of photographic films. In NaCl, which was studied as a model system for AgCl, three Rh^{2+}.*n*Vac (Vac =Na^{+} vacancy) monomer centers (S= 1/2) and a *2*Rh^{2+}.*2*Vac dimer center (S=1) were identified, for which spin Hamiltonian parameters (g tensor, ^{35}Cl superhyperfine (SHF) and quadrupole (Q) tensors and zero field splitting tensor) were determined very accurately.[1,2] In the present contribution we calculate these parameters using density functional (DFT) methods, in order to validate both the proposed structural defect models and the computational approaches for calculating their parameters.
The geometry of the *n*Rh.*m*Vac complexes is optimized in a periodic computational model using the CP2K code. Out of these optimized structures, a cluster is cut on which EPR property calculations are performed using the ORCA program package.[3]
In agreement with experiment and previous calculations for the Rh^{2+}.0Vac center,[4] Rh^{2+} ions are found to undergo a Jahn-Teller elongation as a result of which all centers exhibit a nearly axial g tensor with $g_{\perp} > g_{//} \approx g_e$ and a strong SHF interaction with the nearest Cl^{-} ions along the elongation axis. In particular, for the dimer center (S=1), a very small rhombicity of the g tensor and very slight tilting of the ^{35}Cl SHF and Q tensors are found back, in accordance with experiment. Current research efforts are directed towards calculating also the zero field splitting parameters of this dimer complex.

References

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