

Slow magnetic relaxation in cerium chloride hexahydrate and its intercalation into synthetic saponite

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The crystal structure of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ features dimeric complex cations, $[\text{Ce}_2(\text{H}_2\text{O})_{14}\text{Cl}_2]^{4+}$, accompanied by chloride anions, a motif that enables magnetic coupling within $\{\text{Ce}_2\}$ dimers as confirmed by investigation of static susceptibility, magnetization, and low-temperature specific heat. A decrease in effective magnetic moment upon cooling can be ascribed to two lowest excited doublets induced by single-ion anisotropy with energies 82.6 K and 203 K, respectively. The analysis of alternating susceptibilities suggests a narrow distribution of relaxation times. A crossover from a temperature-independent relaxation time governed by cross-relaxation to a thermally activated process of the Orbach type with an energy gap $\Delta/k_{\text{B}} = 51.5$ K was found in the dynamic response of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. The magnitude of the gap agrees reasonably with the energy of the first excited doublet and the energy of the local vibrational mode with the value of 72 K, the latter being revealed by simulation of molecular dynamics.

Upon intercalation into synthetic saponite, the parent hydrate structure $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ is significantly changed, and the Ce(III) centres are expected to become more spatially separated within the interlayer space. On this basis, we tentatively assume that the dominant interlayer species may resemble highly hydrated Ce^{3+} aquacomplexes, such as $[\text{Ce}(\text{H}_2\text{O})_9]^{3+}$ (or closely related hydration states), in line with literature precedent [1]. This increased isolation provides a plausible structure–magnetism link: it would disfavour cross-relaxation typical of closely spaced Ce^{3+} centres and instead promote thermally activated relaxation, which we tentatively associate with a phonon-bottleneck scenario enabled by weak coupling between the hydrated Ce^{3+} ions and the host lattice.

References:

[1] P. Lindqvist-Reis and F. Réal, *Inorg. Chem.* 57 (2018) 10111

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