The breathing mode revisited: Ce^{3+} energy levels in calcium scandium germanium garnet calculated from scratch

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In this work, we have applied known ab initio calculations techniques such as cell-based DFT and multiconfigurational embedded cluster calculations, to describe a broad excitation band in the Ce-doped garnet $Ca_3Sc_2Ge_3O_{12}$. The RASSCF/CASPT2 calculations agree with the group theory assessment of Ce^{3+} 5d level splitting, and illustrate strong non-degeneracy in the ^2F_J Stark levels. The 3 lowest spin-free levels for the $^2F_{5/2}$ manifold, closely followed by 3 out of 4 levels of $^2F_{7/2}$ manifold: these lie no higher than 500 cm^{-1} from the ground state. The highest $^2F_{7/2}$ level is about 4000 cm^{-1} from the ground state. These 7 levels exhibit slightly different responses to the cluster deformations, resulting in variable energy differences between them.

From comparison between the modeled and the experimental band shapes, conclusions regarding underlying atomic motion can be made, regarding the roles of both CeO_8 cluster motion, and distortions in the geometries of the nearby GeO_4 units. In this context, we propose to extend the concept of breathing mode from coordination surround scaling to more complex yet very similar (and more chemical) deformations.

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