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Is the discussion about the electronic structure of CeO2 just missunderstanding?

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Ceria (CeO2) has been a benchmark system in experimental and theoretical X-ray spectroscopy for three decades. It is also of immense practical importance as a redox partner in many chemical applications including medicine because of its ability to do Ce3+ ↔ Ce4+ + e-. We have used the "advanced"spectroscopies HERFD, RXES and (indirect) RIXS to study the electronic structure of bulk and nanoparticles of CeO2. The presentation will discuss the techniques and demonstrate the information on the electronic structure that can be obtained.
The interpretation of X-ray spectra in ceria requires some theoretical finesse. Most theorists who took up this task use a single impurity Anderson model (SIAM) and agree that ceria is a homogeneous mixed valence compound, i.e. the charge that should be identified with the Ce ion is not 4+ as formally expected but somewhere between 3+ and 4+.[2] This has been proposed already in 1983.[1] At the same time, the macroscopic properties in general and chemical activity in particular are commonly addressed using density functional theory (DFT). These studies find sites of Ce4+ in bulk and Ce3+ and Ce4+ in ceria surfaces and nanoparticles. [3] At first sight, this is in disagreement with SIAM that rejects the idea of Ce4+ already in bulk ceria. Then again, it may only be a different way of describing electronic structure and the disagreement is limited to nomenclature. Such reflections are of broad relevance because SIAM and DFT represent two fundamentally different theoretical approaches to X-ray spectroscopy. The dilemma gains in practical importance when one attempts to describe the changes in electronic structure during chemical reactions, e.g. in ceria nanoparticles.

[1] A. Kotani, and H. Ogasawara, J. Electron Spectrosc. Relat. Phenom. 60, 257 (1992); A. Fujimori, Phys. Rev. B 28, 2281 (1983); D. D. Koelling et al. Solid State Commun. 47 227 (1983)
[2] K. Kvashnina et al. J. Anal. At. Spectrom. 26, 1265 (2011); A. Kotani et al. J. Electron Spectrosc. Relat. Phenom. 184, 210–215 (2011)
[3] Esch et al., Science 309, 752 (2005)

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