Comment on "Spectroscopic Evidence for Localized and Extended *f*-Symmetry States in CeO_2"

In a recent Letter, Wuilloud, Delley, Schneider, and Baer (WDSB)[1] presented combined x-ray photoelectron spectroscopy and bremsstrahlung isochromat spectroscopy (BIS) studies of CeO_2 focusing on the possibility of valence mixing in this insulating compound, which has been a controversial issue for recent years.[2–4] They concluded that in CeO_2 *f*-symmetry states exist as extended states as calculated by band theory[5] and that valence mixing as proposed by the cluster model of Fujimori with configuration mixing[4] is definitely excluded. They argued that, whereas the valence band contains an admixture of *f* symmetry ($n_f^h \neq 0$), the occupancy of localized 4*f* states n_f^l is zero.

In this Comment, I would like to point out that their results are consistent with the valence mixing of Ref. 4 rather than excluding it. I note that the cluster model[4] and the band model[5] have given quite similar physical pictures in spite of the very different approaches as far as the ground state is concerned. While the band model considers the Ce 4*f*–O 2*p* hybridization in a one-electron picture, the cluster model considers it in a configuration-mixing framework.[6] In both cases, 4*f* electrons are delocalized in the sense that they lose localized magnetic moments and participate in chemical bonding. In fact, their "extended *f*-symmetry states" can be regarded as linear combinations of O 2*p* and Ce 4*f* atomic orbitals as can be seen from the shape of the wave function in Ref. 5. Therefore, the conclusion of WDSB that $n_f^h \neq 0$ and $n_f^l = 0$ is fully consistent with the cluster-model results: The result of Ref. 4 that CeO_2 is mixed valent with $n_f \sim 0.6$ corresponds well to $n_f^h \sim 0.5$ used by WDSB in their model calculations.[1]

Then, which is a more relevant definition for the 4*f* occupancy, $n_f = n_f^l + n_f^h$ or n_f^l? Core-level[7] and valence-band[8] photoemission measures n_f rather than n_f^l. So-called tetravalent compounds such as $CeRh_3$ and $CeRu_2$, for which $n_f^l \sim 0$, have been assigned the 4*f* number of ~ 0.8.[7] The 4*f* occupancy measured by Compton scattering[9] also corresponds to n_f, as this experiment measures spatial electron distribution and does not distinguish localized, magnetic 4*f* electrons, and 4*f* electrons hybridized with conduction electrons. Generally it is not possible to separate unambiguously n_f into n_f^l and n_f^h in metallic Ce systems both experimentally and theoretically. Therefore we believe that n_f is a parameter more relevant to recent arguments on the 4*f* occupancy than n_f^l, and in this sense CeO_2 should be regarded as mixed valent, although the chemical term "valence" might be confusing.

Finally, the BIS spectrum of CeO_2 has shown an intense $4f^1$ peak and no clear $4f^2$ peak, which WDSB considered to be a strong indication of unoccupied localized 4*f* states. WDSB used a large 4*f*-valence (conduction) band hybridization parameter in their Gunnarsson-Schönhammer (GS)[10] model calculations ($N_f\Delta = 5.6$ eV as compared to V or $N_f\Delta = 0.5$–2.5 eV used in the cluster calculations[4] and previous GS model calculations[7,10]). As a result of the large hybridization the intense BIS peak is an admixture of $4f^1$ and $4f^2$ configurations with comparable weight rather than pure $4f^1$, and cannot be assigned to localized $4f^1$ states. Alternatively, the intense "$4f^1$" peak might be explained by a formation of 4*f* band in the BIS final state,[11] which cannot be described by single-Ce-ion theories such as the GS and cluster models. In any case, unoccupied 4*f* states are fairly extended rather than localized.

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