Mixed-valence state in the dilute-impurity regime of La-substituted SmB_6

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Rare-earth compounds are an intriguing class of materials which can host a variety of different phenomena, such as heavy fermion behaviour, superconductivity, Kondo physics and mixed-valence behaviour. In particular, mixed valence (MV) refers to the presence in the system of a given rare-earth element holding more than one electronic occupation for the *f*-shell. Although MV is observed in a wide range of rare-earth systems, a full microscopic understanding of its nature and limits remains elusive.

Here we present an experimental study of La-substituted SmB_6 aiming to track the crossover of the MV character going from a periodic *f*-electron lattice to a dilute *f*-impurity system. While SmB_6 is a prototypical mixed-valent system characterized by the nearly equal presence of Sm^{2+} ($4f^6\ 5d^0$) and Sm^{3+} ($4f^5\ 5d^1$) configurations for the Sm ions, its counterpart LaB_6 has a metallic ground state and lacks 4*f* electrons. By employing trivalent La ions as substituent in the $Sm_xLa_{1-x}B_6$ hexaboride series, we combine angle-resolved photoemission spectroscopy (ARPES) and x-ray absorption spectroscopy (XAS) to investigate the evolution of the mean Sm valence, v_{Sm}. Upon decreasing x, we observe a linear decrease of v_{Sm} to an almost complete suppression of valence fluctuations in the intermediate substitution regime with v_{Sm}~2 at x=0.2. Interestingly, a re-emergent MV character develops upon further lowering x, with v_{Sm} approaching the value of v_{imp}~2.35 in the dilute-impurity limit. Such behaviour departs from a monotonic evolution of v_{Sm} across the whole series, as well as from the expectation of its convergence to an integer value for $x\to 0$. Our experimental results, complemented by a phenomenological model, provide evidence of the realization of a dilute-impurity MV state in the $Sm_xLa_{1-x}B_6$ series, and they may stimulate further theoretical and experimental considerations on the concept of MV and its influence on the macroscopic electronic and transport properties of rare-earth compounds in the dilute-to-intermediate impurity regime[1].

[1]M. Zonno, et al., Nature Communications **15**, 7621 (2024).