Abstract

We theoretically investigate the fluctuations in charge, spin, and orbital degrees of freedom in mixed valence spinels. We focus on two compounds, AlV_2O_4 and LiV_2O_4, which show contrasting behavior: AlV_2O_4 exhibits a peculiar structural phase transition with a self-organization of seven V clusters (heptamers) at 700 K, while LiV_2O_4 does not show any transition down to the lowest temperature except for crossover to an unconventional heavy fermion state at 20-30 K. We adopt the combined method between the first-principles calculation and the perturbation in terms of electron correlations. Specifically, we derive the one-body parameters in the multi-band Hubbard model by the maximally-localized Wannier functions that reproduce the band structure obtained by the local density approximation. We then calculate the generalized susceptibility, which includes all the information of fluctuations in charge, spin, and orbital sectors, by incorporating the electron correlations at the level of the random phase approximation. We systematically investigate the effects of the trigonal crystal-field splitting, spin-orbit interaction, electron-electron interactions, and temperature, for the two compounds, AlV_2O_4 and LiV_2O_4. For AlV_2O_4, we find that the dominant fluctuations appear in the vicinity of the Γ point in the Brillouin zone. Although there are many eigenmodes entangled each other, we unveil that peculiar charge fluctuations are sensitively enhanced by the inter-site interaction. The enhanced fluctuations are of σ-bonding type with strong orbital dependence, which originate from the dominant $dd\sigma$ transfer for nearest-neighbor sites. The importance of similar σ-bonding states in the hepmater formation was suggested in the previous experimental and theoretical studies. Hence, our results provide a key for understanding of the self-organization in AlV_2O_4. In contrast, for LiV_2O_4, we find that the sixteen eigenmodes are well separated from other modes even in the non-interacting case. We show that the on-site interaction enhances peculiar optical-type spin fluctuations at an incommensurate wave number, in which the net spin fluctuation vanishes in the four-site tetrahedron. In addition, another fluctuations in the a_{1g} electron density are sensitive to the inter-site repulsion. We clarify that these fluctuations are enhanced at very low temperature, in the order of 10 K, which is suggestive of the peculiar behavior in LiV_2O_4. Through the present studies, we unveiled the contrasting behavior in charge-spin-orbital fluctuations in the two compounds. The success will stimulate further systematic studies by the present method including other mixed valence spinels.