Multiplet calculations of V^{2+} ($3d^2$) states in orbital-ordered spinel-type oxides

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Couplings between orbital and spin degrees of freedom in transition metal (TM) oxides exhibit a wide variety of interesting physical phenomena in strongly correlated electron systems. The orbital degeneracy of t_{2g} or e_g orbitals, split by the crystal field in TM oxides, gives rise to the orbital ordering in perovskite-type oxides accompanied by Jahn-Teller distortion. Spinel-type FeV_2O_4 is a candidate to study orbital ordering since orbital magnetic moments of Fe^{2+} (d^6) are strongly affected by the Jahn-Teller distortion in the Fe sites, which brings the ferro orbital ordering in V sites through the spin-orbit interaction [1]. In the case of MnV_2O_4, real wave functions in the V sites which are described as d_{yz} and d_{zx} are ordered alternatively, resulting in an antiferro orbital ordering with quenching orbital moments [2]. An unresolved issue is the relationship between the orbital magnetic moments in vanadium sites and orbital ordering. Therefore, the investigation of orbital moments in V sites enables to discuss the types of orbital ordering. In this study, the investigation of configuration-interaction (CI) cluster model calculations for V^{2+} states to reproduce x-ray magnetic circular dichroism (XMCD) results is discussed.

Cluster-model calculations including the CI for TM^{2+} and V^{3+} sites in MnV_2O_4 as tetrahedral (T_d) TMO_4 and octahedral (O_h) VO_6 clusters were employed, modeled as a fragment of the spinel-type structures. The Hamiltonian included the electronic structure parameters of full on-site TM $3d$–$3d$ and $2p$–$3d$ (core–valence) Coulomb interactions (U) and the T_d or O_h crystal fields ($10Dq$) in the TMs, along with the hybridization between the TM $3d$ and O $2p$ wave functions. The charge-transfer energy was defined as $\Delta = E(d^{n+1}\underline{L}) - E(d^n)$, where $\underline{L}$ denotes a hole in a ligand p orbital.

Tetragonal local lattice distortion around the V sites must also be considered. The t_{2g} states are split into two levels by the tetragonal distortion and the lowest xy states are occupied by one of the electrons. The other electron occupies the yz or zx states. We determined the tetragonal distortion value for the V $3d$ states (D_{tet}) to be 0.02 eV in order to reproduce the complicated XMCD spectral line shapes qualitatively. The best fitted parameter sets reveal the spin magnetic moment of 1.2±0.2 μ_B, which is not sensitive to the electronic structure parameters. At least, the peak positions in each multiplet structure are reproduced by the calculations. Spin-orbit interaction coefficients (λ) also become the parameters, where the non-zero value of 0.5λ is adopted for the fitting. Therefore, the orbital mixing of V yz and zx orbitals in both FeV_2O_4 and MnV_2O_4 induces the small but finite orbital magnetic moments in V sites for orbital ordering.

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[1] J. Okabayashi et al, J. Phys. Soc. Jpn. **84**, 104703 (2015). [2] J. Okabayashi et al., Jpn. J. Appl. Phys. **57**, 0902BD (2018).