An investigation of the electronic and magnetic structure of LiV_2O_4

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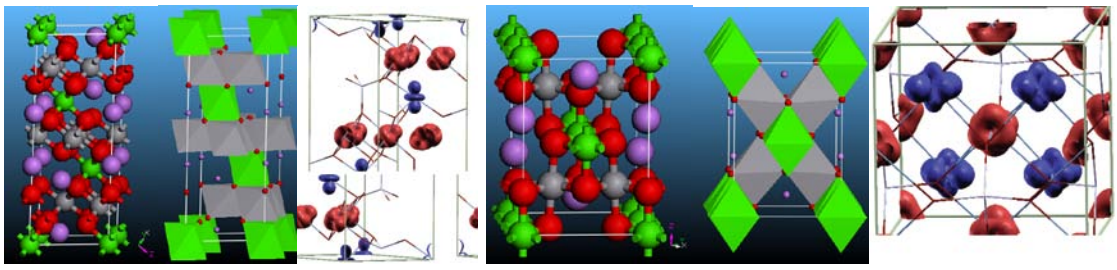
Abstract – First principles based on density functional theory (DFT) calculations within generalized gradient approximations (GGA) and GGA+U approach using the full-potential, augmented plane wave + local orbitals (APW+lo) method, as implemented in the WIEN2k code, have been used to investigate the structural, electronic and magnetic properties of spinel-structure LiV_2O_4 (Figure 1), in particular regarding heavy fermion (HF) behavior. The calculations were performed for ferromagnetic, anti-ferromagnetic, and ferrimagnetic configurations using two kinds of magnetic structure (tetragonal and rhombohedral). Our GGA+U method reveals that the ground state of LiV_2O_4 is the tetragonal anti-ferromagnetic configurations with metallic character, and ferromagnetic order with half-metallic character at slightly higher energy, which is consistent with experimental results. The geometric frustration and hybridization between 3*d* (V) and 2*p* (O) could induce the spin fluctuation and hence instability of specific heat, susceptibility as well as HF behavior.

The phenomenology of HF behavior in systems usually contains *f*-electron materials such as nearly localized lanthanide and actinide intermetallic atoms [1]. HF behavior is not expected for *d*-electron compounds because of the much smaller spatial extent of *d* orbitals than that of *f* orbitals. However, transition metal oxide compound LiV_2O_4 has been found to hold many hallmarks of the heaviest mass *f*-electron HF.

Experimentally, a high Sommerfeld coefficient of heat capacity (γ=0.42J/mol K^2) at 1 K and neither static magnetic order nor superconductivity above 0.02 K [2] ; a T^2 temperature dependence $\rho = \rho_0 + AT^2$ with an enormous A [3]; the negative Weiss temperature (θ =-63 K), large *g*-factor (*g*=2.23) [4], and other exotic nature effects in this system, makes it attractive to investigate the complex physical nature, especially the origin of HF behavior. Theoretically, the local-density approximation (LDA), as well as other methods: a full-potential of the linear augmented-plane-wave method (FP-LAPW), the augmented spherical wave method (ASW), the effective Anderson impurity model, adding the random phase approximation (RPA) scheme, dynamical mean field theory (DMFT) yield controversial conclusions.

We have used FP-LAPW+lo within GGA as well as U (Hubbard item considering Coulomb repulsion) to make a detailed analysis of the densitiy of states (DOS) for this system in the ferromagnetic (FM) (cubic), antiferromagnetic (AFM, 2:2) and ferrimagnetic (FIM, 1:3) states. Our new results suggest that it is necessary to include the Hubbard item U to obtain the magnetic ground state in agreement with the experimental results.



(a) V_1:V_2=1:3 (b) V_1:V_2=2:2

Figure 1. The structure (Green, grey, purple and red ball express V_1, V_2, Li and O, respectively) and spin-density (blue and red part express V_1, and V_2, respectively) of LiV_2O_4 (a) FIM (b) AFM.

[1]. G. R. Stewart, *Heavy-fermion systems,* Rev. Mod. Phys, 56, 755 (1984).
[2] S. Kondo, D. C. Johnston, C. A. Swenson, F. Borsa, A. V. Mahajan, L. L. Miller, T. Gu, A. I. Goldman, M. B. Maple, D. A. Gajewski, E. J. Freeman, N. R. Dilley, R. P. Dickey, J. Merrin, K. Kojima, G. M. Luke, U. J. Uemura, O. Chmaissen, and J. D. Jorgensen, Phys. Rev. Lett. 78, 3729 (1997).
[3] C. Urano, M. Nohara, S. Kondo, F. Sakai, H. Takagi, T. shiraki, and T. Okubo, Phys. Rev, Lett. 85, 1052 (2000).
[4] M. Reehuis, A Krimmel, N. Büttgen, A. Loidl, and A. Prokofiev, Eur. Phys. J. B 35, 311 (2003).