Electronic, Magnetic Structure and Orbital Ordering in CdV₂O₄ from First Principles

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Abstract – First principles calculations using the APW+lo method, as implemented in the WIEN2k code, have been used to investigate the structural, electronic and magnetic properties of CdV₂O₄ within generalized gradient approximations (GGA), GGA+U and GGA+U+SO approach, especially as regards orbital ordering. The calculations were performed for paramagnetic, ferromagnetic and antiferromagnetic configurations using cubic and two kinds of magnetic structure (AFM-I and AFM-II, Fig. 1), respectively. The GGA results falsely gave ferromagnetic half-metallic ground state. Exciting, our GGA+U method rectify this error and revealed that the ground state is AFM-I configurations, which is Mott insulator with a staggered \(d_{xy} \uparrow d_{xz} \downarrow \) (V₂) and \(d_{xy} \downarrow d_{yz} \uparrow \) (V₁) orbital ordering. However, especially interesting, our GGA+U+SO method obtained AFM-II ground state with a staggered \(V₁ \left( d_{xz} \downarrow d_{yz} \uparrow \right) \) and \(V₂ \left( d_{xz} \downarrow d_{yz} \uparrow \right) \) orbital ordering. Analysis shows that electron correlation, spin-orbital coupling and co-operative Jahn-Teller distortions play a significant role in determining the orbital ordering.

Spin, charge, orbital and lattice degrees of freedom play important roles in electronic, magnetic and transport properties of transition metal-oxide. The origin of these complex natures is presently a debate subject, especially on geometrically frustrated lattice systems [1]. Vanadium spinel-type AV₂O₄ [2-4] belongs to frustrated antiferromagnets and show many interesting phenomena such as Heavy-Fermi behavior; two successive phase transitions, complicated charge and orbital ordering, which extensively enrich the physical properties of vanadium-oxide.

CdV₂O₄ is Mott insulator where magnetic ions V⁵⁺ are characterized by orbital degenerate due to partly occupancy of \(t_{2g} \) orbital \( (n_{t_{2g}} = 2) \). These partially filled \(t_{2g}\) orbitals leave the orbital degrees of freedom open and have the possibility of orbital order. Otherwise, to the best of our knowledge, the experimental investigation was limited to a pseudotetramer proposition [5] and sporadic doped systems, no theoretical study have been performed on it so far, therefore first-principles calculations are urgent to understand structure and magnetic properties.

We have used FP-LAPW+lo within GGA, GGA+U and GGA+U+SO to make a detailed analysis of the density of states (DOS) for this system in the paramagnetic (PM, cubic), ferromagnetic (FM, cubic), antiferromagnetic (AFM-I and AFM-II Fig. 1) states. The GGA results falsely gave ferromagnetic half-metallic ground state. Exciting, our GGA+U method rectify this error and revealed that the ground state is AFM-I configurations, which is Mott insulator with a staggered \(d_{xy} \uparrow d_{xz} \downarrow \) (V₂) and \(d_{xy} \downarrow d_{yz} \uparrow \) (V₁) orbital ordering. However, especially interesting, our GGA+U+SO method obtained AFM-II ground state with a staggered \(V₁ \left( d_{xz} \downarrow d_{yz} \uparrow \right) \) and \(V₂ \left( d_{xz} \downarrow d_{yz} \uparrow \right) \) orbital ordering (Fig. 2), which need experimental results to confirm.

![AFM-I](image1.png) ![AFM-II](image2.png) ![AFM-I (GGA+U)](image3.png) ![AFM-II (GGA+U+SO)](image4.png)

**Fig.1.** Two kinds of different magnetic structure of CdV₂O₄.

**Fig.2.** Spin density plot [isosurface at 0.1 e/Å³ produced using XcrySden] red and blue denote spin-up and spin-down respectively.