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Electronic structure of RVO_3 (R = La and Y): Effect of electron (U) and exchange (J) correlations

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A B S T R A C T

We have studied the influence of electron correlation energy (U) and exchange correlation energy (J) on the electronic structure of RVO_3 (R = La and Y) compounds using all-electron full-potential linearized augmented plane wave method within density functional theory. Our calculated electronic band structure shows metallic character with generalized gradient approximation (GGA) formalism though $LaVO_3$ and YVO_3 are both known to be insulators with a band gap of 1.1 eV and 1.2 eV, respectively. Our GGA+U approach has succeeded in describing the correct ground state yielding insulating band structures for both $LaVO_3$ and YVO_3. However, this insulating ground state is obtained by adjusting the parameter, U to reproduce the correct experimental band gap. To determine the optimal U value for the onsite coulomb potential, we have performed a series of GGA+U calculations by varying the U_{eff} (difference between U and J) parameter keeping J fixed. We have also varied the exchange parameter J, (though not as strong as that of U) keeping U_{eff} fixed to see its influence on the band gaps of $LaVO_3$ and YVO_3 and it has been shown that both the U and J have great impact on the electronic structure of these two compounds.

1. Introduction

Strongly correlated transition metal oxides (TMO) exhibit many interesting properties such as metal-insulator transition, colossal magneto-resistance, high-T_c superconductivity *etc.* due to the strong interactions of d electrons of the transition metal. The origin of such properties can be understood by investigating thoroughly the electronic structure of these systems. Study of electronic structure of strongly correlated TMO is one of the most interesting and active areas of research in condensed matter physics for the last few decades. It is well known that the standard band theory based on independent electron approximation [1] fails to predict the correct insulating state of many strongly correlated transition metal compounds [2]. Strong electron-electron interactions of d electrons of the transition metal ions are mainly responsible for their insulating character. This class of insulators which emerges due to strong on-site electron correlation, U is known as Mott insulators [3] and this was beautifully explained by Mott in 1937. [4] One of such transition metal compounds, RVO_3 (R = La and Y) belongs to this class of Mott insulators. Both the compounds exhibit structural phase transitions as a function of temperature. The crystal structure of $LaVO_3$ is orthorhombic at room temperature with lattice parameters a = 5.555, b = 5.553, c = 7.848, Åand space group (S.G) *Pbnm*. (In some literature [5] it has been mentioned that the S.G is *Pnma*. Both *Pbnm* and *Pnma* can be transformed to each other by switching b and c lattice parameters.) The orthorhombic structure is derived from 2 × 2 × 2 standard perovskite structure with lattice constant$a$ ~ 3.9 Å by the deformation of VO_6 octahedra due to the displacement of V and O atoms from its mean positions as shown in Fig. 1. Another system of similar structure is YVO_3, which has even more rich phase diagram and magnetic structures as compared to $LaVO_3$ [6]. Both $LaVO_3$ and YVO_3 are found to be insulators with band gap of 1.1 eV and 1.2 eV, respectively [7,8]. Both the systems have different magnetic ordering at different temperatures. At room temperature, $LaVO_3$ and YVO_3 are orthorhombic paramagnetic Mott insulators, whereas at low temperature both the compounds show anti-ferromagnetic (AFM) ordering [9].

Previous studies shows that the local density approximation (LDA) fails to predict the correct insulating ground state of these RVO_3 (R = La and Y) systems and generalized gradient approximation (GGA) highly underestimates the band gap. [10] Electron correlation energy (U) of vanadium d electrons plays a great role in deciding the ground state properties and hence it is necessary to take the U in a proper way such that LDA+U or GGA+U method can correctly describe the ground state of this strongly correlated Mott-Hubbard system. Several electronic structure calculations [9,11,12] have been performed for $LaVO_3$ and YVO_3 by using LDA+U method with different U to match the

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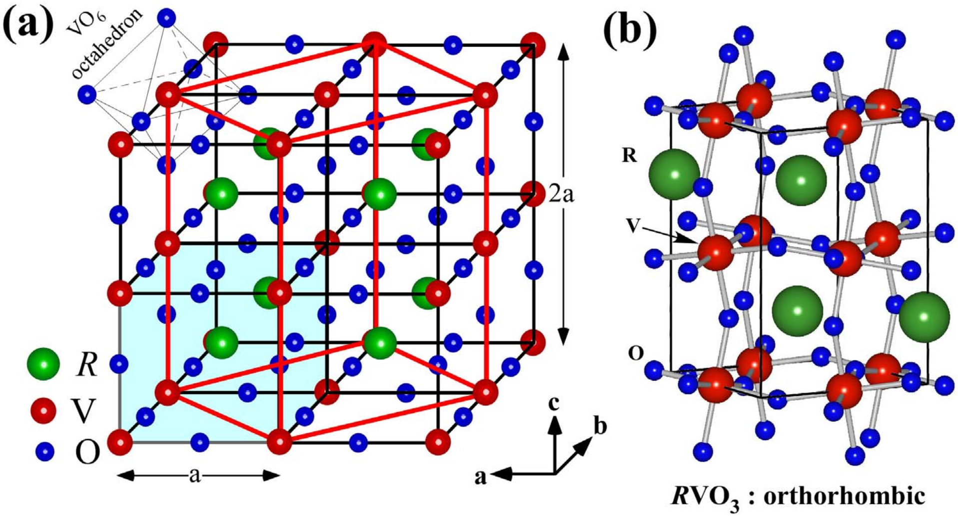

Fig. 1. (Color online) (a) Schematic representation of a 2 × 2 × 2 standard perovskite (RVO_3) structure. Each vanadium atom is surrounded by an oxygen octahedron. (For simplicity only one oxygen octahedron is shown). Orthorhombic RVO_3 structure is derived from the above 2 × 2 × 2 standard perovskite structure as shown by thick red line. (b) Orthorhombic crystal structure of RVO_3, where R = La, Y.

correct experimental band-gap. In all calculations the U is introduced by hand to the GGA+U calculation and no proper systematic estimation of U has been done. Fang et al. [13] has taken U_{eff} = 3.0 eV to match properly the experimental band-gap. U_{eff} has been defined as the difference between electron correlation energy (U) and exchange correlation energy (J). Raychaudhury et al. [9] has chosen U = 5 eV and J = 0.68 eV to reproduce the correct band-gaps for these two oxides. Therefore in order to obtain the optimal values of U and J for these Mott compounds we have performed a series of GGA+U calculations by systematically varying the electron correlation parameter, U by fixing the exchange parameter J = 1 eV initially. Then we have fine-tuned the exchange correlation parameter, J to study the variation of band-gap and finally obtain the optimal U and J value. All the calculations have been performed by full-potential linearized-augmen-

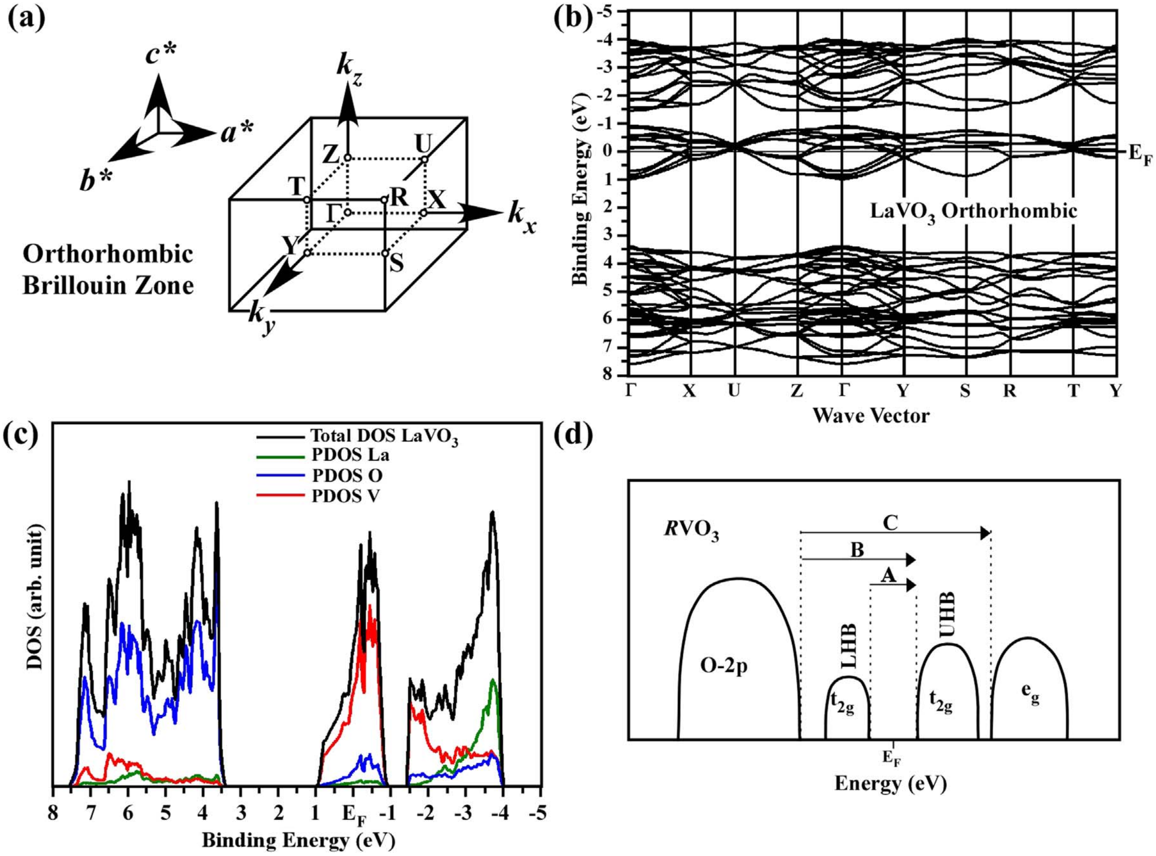

Fig. 2. (a) Brillouin zone showing the high-symmetry directions of orthorhombic RVO_3 crystal structure. (b) Band structure of $LaVO_3$ (orthorhombic phase) along major high symmetry directions in the Brillouin zone calculated by the first principle all-electron FP-LAPW method with GGA formalism. (c) Density of states of $LaVO_3$ and its decomposition into partial density of states of La, V and O. (d) Schematic model of the electronic structure of RVO_3 showing transitions A, B, C corresponding to different gap energies as found in optical transitions.