Orbital-selective behavior in $Y_5Mo_2O_{12}$ and $(Cd,Zn)V_2O_4$

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Abstract

We present two examples of the real materials, which show orbital-selective behavior. In both compounds a part of the electrons is localized on the molecular orbitals, which lead to a significant reduction of the magnetic moment on the transition metal ion.

Keywords: Orbital degrees of freedom, dimers

1. Introduction

It was recently shown that there may exist so called orbital-selective state in the dimerized systems with orbital degrees of freedom [1]. This is the state in which different orbitals behave in different manners. All electrons (orbitals) in the orbital-selective state are split on two qualitatively different groups. One part of the electrons occupy molecular orbitals and form spin singlets being magnetically inactive, while other electrons are effectively decoupled from them and have local magnetic moments (which can be ordered, i.e. lead to formation of ferro- or antiferromagnetic states, or disordered, i.e. paramagnetic). As a result one of the main features of the orbital-selective state is substantially reduced magnetic moment. Because of the formation of molecular orbitals this moment turns out to be much smaller, than expected basing on the purely ionic model consideration.

In the present paper we show that the orbital-selective state is realized in two real materials: $Y_5Mo_2O_{12}$ and ZnV_2O_4 (and also in CdV_2O_4, which is

iso-electronic and iso-structural to ZnV_2O_4).

2. Calculation details

We used the density functional theory within the generalized gradient approximation (GGA) [2] to study electronic properties of $Y_5Mo_2O_{12}$. We used full-potential WIEN2k code [3]. The radii of atomic spheres were set as following $R_Y = 2.19$ a.u., $R_{Mo} = 1.88$ a.u., and $R_O = 1.70$ a.u. The Brillouin-zone (BZ) integration in the course of the self-consistency was performed over a mesh of 200 **k**-points. The parameter of the plane wave expansion was chosen to be $R_{MT}K_{max} = 7$, where R_{MT} is the smallest atomic sphere radii and K_{max} - plane wave cut-off.

3. $Y_5Mo_2O_{12}$

The crystal structure of $Y_5Mo_2O_{12}$ is formed by the edge sharing MoO_6 chains, which are dimerized. These chains are separated by the Y ions, see Fig. 1. The electronic configuration of Mo having formal valence 4.5+ is $4d^{1.5}$. Hence one may expect that the local magnetic moment would be $\mu_{loc} = 1.5\mu_B/$Mo, while effective magnetic moment in the Curie-Weiss theory will be $\mu_{eff} = 2.29\mu_B/$Mo or $\mu_{eff} = 1.15\mu_B/$dimer. Experimentally, however, effective moment equals $\mu_{eff} = 1.7\mu_B/$Mo [4]. We attribute this feature to the fact that this compound is actually in the orbital-selective state.

The total density of states obtained in the nonmagnetic GGA calculation is shown in Fig. 2. In the edge-shared geometry there are two types of the t_{2g} orbitals: σ-bonded xy orbitals (which look directly to each other) and π-bonded yz and zx orbitals on different Mo centers (it is assumed that the local z axis is perpendicular to the plane defined by the Mo-Mo bond and common edge for two MoO_6 octahedra). Direct overlap between the xy orbitals on two Mo sites leads to huge bonding-antibonding splitting $\sim$2.7 eV. Therefore one may gain energy occupying bonding orbital with two electrons (total number of electron is 3 per dimer). Remaining electron will provide net magnetic moment of the

dimer, giving $S = 1/2$ per dimer. This yields $\mu_{eff} = 1.74 \mu_B/$Mo, which agrees

with experimental data [4]. Resulting state is orbital-selective and is realized due to rather uncommon set of the parameters: one of the hopping parameter $t_{xy/xy} \sim 1.35$ eV is much larger both than intra-atomic Hund's rule exchange (which is estimated for early $4d$ transition metals to be ~ 0.7 eV [5, 6]) and hopping integrals between other orbitals $(t_{xz/xz}, t_{yz/yz}) \ll t_{xy,xy}$.

4. CdV$_2$O$_4$ and ZnV$_2$O$_4$

The electronic and magnetic properties of the V spinels are thoroughly investigated last years. [7, 8] E.g. it was found that CdV$_2$O$_4$ is multiferroic below $T_N =33$ K [7]. The mechanism of the multiferroicity is the magnetostriction: unconventional $\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow$ magnetic order results in the dimerization of the V ions having the same spin projection (i.e. $\uparrow\uparrow$). This in turn leads to the shift of the oxygen ions away from the high symmetry positions and onset of the spontaneous electric polarization [7]. The missing element in this microscopic model is why the spins of V ions forming dimers show ferromagnetic order. We know from the basics of the quantum mechanics that the spin singlet (i.e. antiferro
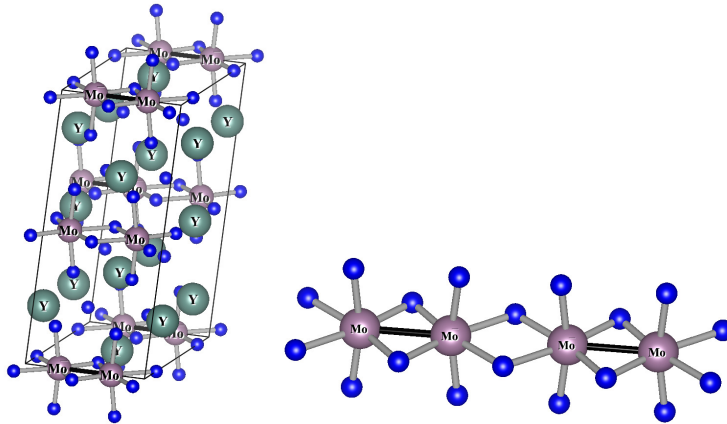

Figure 1: Left: the unit cell of Y$_5$Mo$_2$O$_{12}$; Mo ions are shown in violet, O $-$ in blue, and Y $-$ in grayish green. Right: main structural element of Y$_5$Mo$_2$O$_{12}$ $-$ dimerized Mo chain.
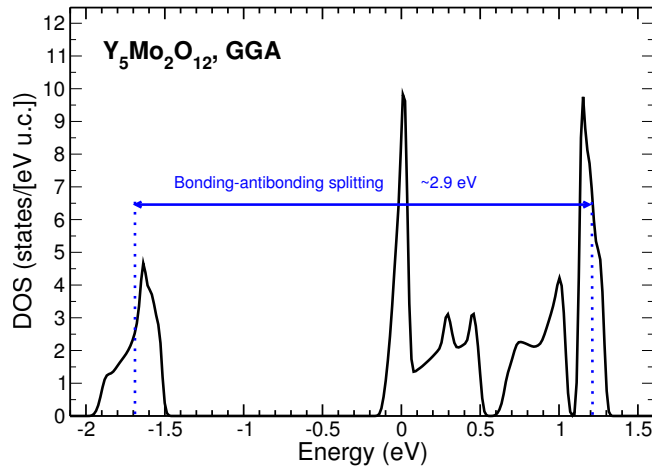
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Figure 2: Total density of states of the $Y_5Mo_2O_{12}$, obtained in the nonmagnetic GGA calculation.

ordering of the spins, as e.g. in the hydrogen molecule) is more typical for dimers.

We argue that it can be related with the orbital-selective physics. The situation here is rather similar to $Y_5Mo_2O_{12}$, since neighboring VO_6 octahedra also share their edges. There is again strong overlap between the xy orbitals. Since V^{3+} has $3d^2$ electronic configuration, there are four d electrons per dimer. Two electrons may occupy molecular orbital of the xy symmetry, while other two stay on the yz and zx local orbitals and provide $S = 1$ per V dimer, or $S = 1/2$ per V. Corresponding exchange constant (added in the revised version of the manuscript) in this short V-V pair in CdV_2O_4 is ferromagnetic and equals $J = 56$ K as calculated in the LSDA+U method for $U - J_H$=0.7 eV using the Green's function formalism [9, 10].

The distortions of the crystal structure and type of the magnetic structure in ZnV_2O_4 are the same as in CdV_2O_4 [8], but there is an additional information about magnetic properties of ZnV_2O_4. The local magnetic moment on V was found to be 0.66 μ_B in ZnV_2O_4 [11]. This qualitatively agrees with the model treatment presented above. In the ionic model this corresponds to the local spin moment $\mu = gS = 1\mu_B$, but this value is further reduced due to hybridization
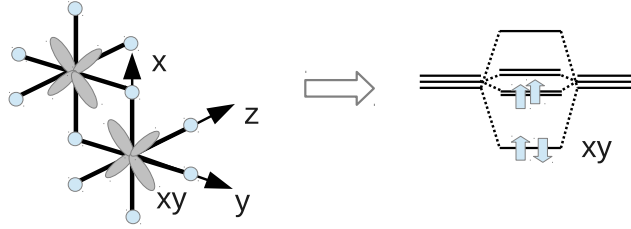
Figure 3: Left: the pair of the xy orbitals in V dimer, which have the largest hopping parameters in the system. Right: sketch illustrating energy levels splitting in $(Cd,Zn)V_2O_4$.

effects, which are always exist in real materials.

5. Conclusions

In the present paper we show two examples of the orbital-selective behavior, which results in the suppression of the magnetic moment in $(Cd,Zn)V_2O_4$ and $Y_5Mo_2O_{12}$.

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