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Ordering of Fe and Zn ions and magnetic properties of $FeZnMo_3O_8$

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One of the main problems in mixed $(Fe_{1-x}Zn_x)_2Mo_3O_8$ materials is the distribution of constituent ions among inequivalent sites, octahedral and tetrahedral ones [1, 2]. Also the magnitude and the sign of exchange interactions in these materials is not clear a priori. As one sees from the crystal structure, shown in Fig. 1, there are several inequivalent exchange

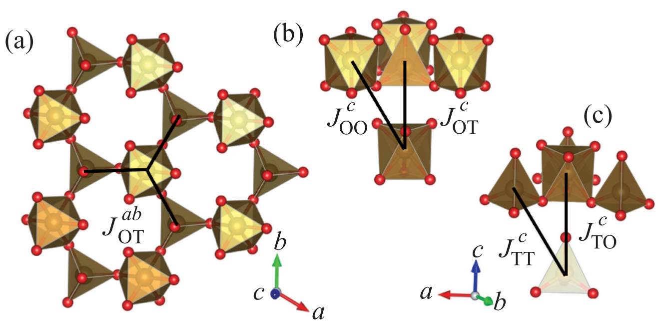

Fig. 1. (Color online) Different possible exchange coupling parameters in $M_2Mo_3O_8$ type of structures

passes even for nearest neighbour interaction: in-plane J^{ab}_{OT} and interlayer J^c_{OO}, J^c_{TT}, and J^c_{OT} exchanges. Moreover, the "vertical" exchanges between octahedral and tetrahedral Fe ions might be also different – J^c_{OT} and J^c_{TO}, because of the orientation of MO_4 tetrahedra (which all point in the same direction, this is in fact what makes these systems polar). Since $Fe_2Mo_3O_8$ is known to be a multiferroic, i.e., a material in which electronic, magnetic, and structural properties are strongly coupled, one might expect that exchange interaction may affect crystal structure of doped $(Fe_{1-x}Zn_x)_2Mo_3O_8$ as well.

The bulk experimental data show that the substitution of Fe by Zn in $Fe_2Mo_3O_8$ changes magnetic ordering from antiferromagnetic (AFM) to ferromagnetic (FM), in particular for half-doping $x = 1$, in $FeZnMo_3O_8$[1, 3]. Our preliminary spectroscopic data [4] point toward preferential location of Zn in tetrahedral sites; this also agrees with the old estimates [5]. If true, this would make the magnetic subsystem in $FeZnMo_3O_8$ relatively simple: only octahedral sites would be occupied by magnetic ions Fe^{2+}, so that only one type of exchange, the diagonal interlayer Fe-Fe exchange J^c_{OO} remains, and if this would be ferromagnetic, it could explain the observed magnetic behavior. However, from the existing experimental data one cannot yet make definite conclusions in this respect, although they indeed point in this direction.

We used pseudopotential VASP code to calculate electronic, magnetic, and structural properties of $FeZnMo_3O_8$ [6]. Exchange parameters for Heisenberg model were calculated using JaSS code [7].

We start our investigation by studying effect of exchange interaction on distribution of Fe and Zn ions among octahedral and tetrahedral positions. In particular we calculated exchange parameters in $FeZnMo_3O_8$ for various occupations of four available positions in the unit cell by two Fe ions keeping the crystal structure untouched. Finding total energy difference between FM and AFM configurations we obtain that $J^{ab}_{OT} = 0.96$ meV, $J^c_{OT} = -0.61$ meV, $J^c_{TT} = 0.03$ meV, and $J^c_{OO} = 0.01$ meV, if Heisenberg model is written in the form $H = \sum_{i \neq j} J_{ij} \mathbf{S}_i \mathbf{S}_j$. Thus, one may see from these results that exchange interaction would stabilize configuration with Fe ions occupying equally tetrahedral and octahedral positions, but concentrated in the same plane (to maximize gain in magnetic energy due to J^{ab}_{OT}).

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Next we relaxed the crystal structure of $FeZnMo_3O_8$ for different Fe and Mo distributions in two possible magnetic orders (FM and AFM). Results are summarized in Table 1. First, one may see that the state with all Fe ions occupying octahedral positions has the lowest total energy. Moreover, the energy of any 50 : 50 configuration (50 % Fe is octahedral and 50 % Zn is in tetrahedral positions) is equal to about half of the energy difference between configurations, where all Fe ions are in octahedral positions. This means that this is not magnetic energy, but lattice distortions (i.e., elastic energy), which decides which positions are occupied by Fe ions. Quite naturally, the energy scales of magnetic and elastic interactions differ by about three orders of magnitude.

Table 1. Energies (per formula unit) of different distributions of Fe and Zn ions among octahedral (O1 and O2) and tetrahedral (T1 and T2) positions, as obtained after optimization of the ionic positions in the GGA + U (Generalized gradient approximation taking into account Coulomb correlations) calculations

O1	O2	T1	T2	Magnetic order	Energy, eV
Fe	Fe	Zn	Zn	FM	0
Fe	Fe	Zn	Zn	AFM	0.0002
Zn	Zn	Fe	Fe	FM	1.2702
Zn	Zn	Fe	Fe	AFM	1.2698
Fe	Zn	Fe	Zn	FM	0.6405
Fe	Zn	Fe	Zn	AFM	0.6403
Fe	Zn	Zn	Fe	FM	0.6440
Fe	Zn	Zn	Fe	AFM	0.6301

Preferable occupations of octahedral positions by Fe and not by Zn ions is due to its larger ionic radius ($R^{\rm octa}_{\rm Fe^{2+}} = 0.78$ Å, $R^{\rm octa}_{\rm Zn^{2+}} = 0.74$ Å and $R^{\rm tetra}_{\rm Fe^{2+}} = 0.63$ Å, $R^{\rm tetra}_{\rm Zn^{2+}} = 0.60$ Å [8]), so that it is natural for larger ions to go in a larger polyhedron. Indeed, if we put smaller Zn to an octahedron it gets more distorted. For example, the bond angle variance defined as $\langle \sigma^2 \rangle = \sum_{i=1}^{m} (\phi_i - \phi_0)^2/(m-1)$ (here m is the number of bond angles and ϕ_0 is the bond angle for regular octahedron) increases from 69.1°, when Fe is in octahedral positions, to 74.4°, when Zn sits in octahedra.

To summarise, we studied theoretically the very interesting system of the novel class $M_2Mo_3O_8$ (M = Mn, Fe, Co, Ni, Zn) with polar crystal structure, which shows diverse magnetic properties and very interesting magnetoelectric effects. Specifically we concentrated on the mixed materials of this class $(Fe_{1-x}Zn_x)_2Mo_3O_8$, for which most experimental studies are done at present [3, 9, 10]. The most important question here is the distribution of Fe and Zn at different positions (octahedral, tetrahedral) existing in these systems. This is very important for all the properties of corresponding systems. We demonstrated that there is very strong preference of Zn to occupy the tetrahedral sites, so that for 50 % substitution, in the title compound $FeZnMo_3O_8$, all tetrahedral sites are occupied by nonmagnetic Zn, and magnetic Fe ions are all in octahedral positions. This, together with the ferromagnetic octahedral-octahedral exchange, which we calculated theoretically, naturally explains ferromagnetic ordering observed in $FeZnMo_3O_8$ experimentally. These results will be also very useful for interpreting spectroscopic data on $FeZnMo_3O_8$ [4]. Apparently the tendency of relative distribution of different ions in this class of materials, determined, as we demonstrated above, mainly by the size of respective ions, might also work in other systems of this interesting class.

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