Pis'ma v ZhETF, vol. 110, iss. 9, pp. 595 – 596

Mechanism of ferromagnetic ordering of the Mn chains in $CaMnGe_2O_6$ clinopyroxene

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Submitted 30 September 2019
Resubmitted 30 September 2019
Accepted 3 October 2019

DOI: 10.1134/S0370274X19210045

Pyroxenes are a large group of rock-forming minerals widespread in the Earth's crust and its upper mantle [1]. Some of such pyroxenes show orbitally assisted Peierls effect and opening of the spin gap [2, 3], others demonstrate cooperative Jahn–Teller distortions [4] or rare combination of ferromagnetism and insulating behaviour [5], and there are even multiferroics among pyroxenes [6].

Discovery of magneto-electric effect in pyroxenes with general formula $ATM(Si,Ge)_2O_6$ (where TM is a transition metal ion and A can be alkali or alkaline earth metals) resulted in intensive studies of their magnetic structure and its coupling with electronic properties and lattice distortions. Depending on particular choice of TM or A ions there were observed very different types of magnetic structures in pyroxenes including collinear antiferromagnets, commensurate and incommensurate spin spirals and even ferromagnets [5]. Such a variety of magnetic orderings is due to low dimensionality of the crystal structure and frustration effects intrinsic for the pyroxene lattice.

In pyroxenes transition metal ions are in the ligand octahedra, which form one dimensional (zigzag) chains sharing their edges. The strongest exchange coupling is typically within these chains. The chains are connected by $(Si/Ge)O_4$ tetrahedra and this provides various interchain couplings, which could make a whole spin system frustrated.

In the present paper we perform density functional theory (DFT) calculations to study electronic and magnetic properties of $CaMnGe_2O_6$, which magnetic structure was recently refined [7]. It was found that it can be described as antiferromagnetic chains running along c direction, ordered, however, ferromagnetically. It was known from long ago that any ferromagnetic coupling is rather untypical for insulating strongly correlated materials, since it is due to overlap between half-filled and empty orbitals, which scales as $1/U^2$ with Hubbard U, while conventional exchange interaction between half-filled orbitals behave as $1/U$ [8, 9]. Thus, it is important to find out the mechanism resulting in ferromagnetic ordering in $CaMnGe_2O_6$.

In order to find origin of ferromagnetic ordering of Mn chains we calculated exchange parameters J_{ij} of the Heisenberg model, which was written in the following form:

$$H = \sum_{ij} J_{ij} \mathbf{S}_i \mathbf{S}_j, \qquad (1)$$

where i and j numerate lattice sites. The total energy method as realized in the JaSS code [10] was applied to calculate intrachain, J, and interchain exchange parameters J_1 (via two GeO_4 tetrahedra) and J_2 (via one GeO_4 tetrahedron). The total energy of four different magnetic configurations presented in Fig. 1 were calculated within GGA + U approximation with on-site Hubbard interaction $U = 4.5\,\text{eV}$ and Hund's coupling parameter $J_H = 0.9\,\text{eV}$ [2, 11] using the Vienna ab initio simulation package (VASP) [12].

According to our calculations AFM1 configuration has the lowest total energy and hence it corresponds to the ground state in agreement with experiment [7]. In this configuration neighboring spins in the chain are ordered antiferromagnetically while in neighboring chains – ferromagnetically. Calculated magnetic moment on Mn^{2+} ions (electronic configuration $3d^5$, $S = 5/2$) for the ground state magnetic order was found to be $4.6\,\mu_B$ that is in line with experimentally obtained $4.71\,\mu_B$ [7].

It is interesting, that in spite of ferromagnetic order of neighboring chains all isotropic exchange parameters turned out to be antiferromagnetic. The dominating exchange parameter is intrachain exchange $J = 3.6\,\text{K}$, it is 3 times larger than $J_1 = 1.2\,\text{K}$ and 10 times larger than $J_2 = 0.3\,\text{K}$. In general, both J and J_1 determine mag-

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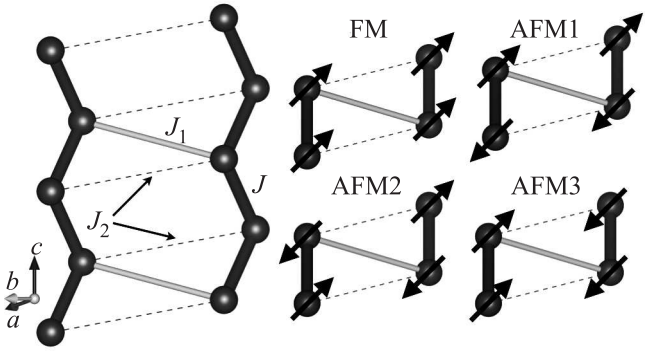

Fig. 1. Four spin configurations used in the total energy calculations. The thick black solid line corresponds to the exchange along the chain J, the others describe interchain interactions – thin grey solid line shows J_1 path (via two GeO_4 tetrahedra), dashed line – J_2 (via one GeO_4 tetrahedron)

netic structure of the investigated pyroxene and suppress weak AFM J_2 exchange making spins in neighboring chains to order ferromagnetically (see Fig. 1). This is exactly what we see in AFM1 configuration and this is consistent with the experimental magnetic structure given in [7]. It allows us to answer the question raised in the beginning: these are two strong antiferromagnetic exchange interactions, which drive ferromagnetic arrangement of Mn chains in $CaMnGe_2O_6$. Obtained values of isotropic exchange parameters also show that $CaMnGe_2O_6$ can be considered as a quasi-one-dimensional magnet.

For calculated exchange parameters we estimated Curie–Weiss temperature using the mean-field theory $\theta_{\text{calc}} = 62.8\,\text{K}$ while experimental value is $\theta_{\text{exp}} = 35.1\,\text{K}$ [7]. Taking into account that the mean field approach often overestimates θ by 2–3 times, one sees that calculated θ agrees with experimental estimation. In order to verify calculated exchange parameters further we obtained magnetic susceptibility within classical Monte Carlo simulations of (1) using SPINMC algorithm of the ALPS package [13]. The magnetic susceptibility was simulated for the 3D spin model including three exchange paths J, J_1, and J_2 and for the isolated spin chain with the main exchange J. The comparison of magnetic susceptibilities with experiment shows that the isolated chain model does not match experimental data for $CaMnGe_2O_6$ neither in absolute values nor in slope while 3D spin model corresponds to experimental $\chi(T)$ quite well.

To summarize, electronic structure and magnetic properties of $CaMnGe_2O_6$ were studied using the GGA + U calculations. The calculated values of exchange interaction parameters allow to explain the experimentally observed magnetic structure with antiferromagnetic interaction within the zigzag Mn chains and ferromagnetic ordering of these chains. The Monte Carlo simulation of magnetic susceptibility within 3D spin model with calculated exchange parameters agrees with experimental data much better than the one for isolated spin chains stressing importance of interchain coupling. The obtained values of exchange interactions also indicate that in $CaMnGe_2O_6$ magnetic frustration is weak. Such a weak frustration could explain the commensurate collinear antiferromagnetic structures common for Ca^{2+}-bearing pyroxenes.

This work was supported by the Russian Science Foundation through RSF 17-12-01207 research grant.

Full text of the paper is published in JETP Letters journal. DOI: 10.1134/S0021364019210033

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