ON THE COMPETITION BETWEEN FERROMAGNETIC AND ANTIFERROMAGNETIC STATES IN Sr$_2$MnMoO$_6$

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It is argued that the magnetic behavior of Sr$_2$MnMoO$_6$ is determined by the existence of two total energy minima corresponding to the metallic ferromagnetic and insulating antiferromagnetic states, which may be nearly degenerate depending on the magnitude of the breathing distortion.

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1. Introduction

Recently, the ordered double perovskites Sr$_2$MM$'$O$_6$ ($M$ being the magnetic 3$d$ element, and $M'$ being the 4$d$ or 5$d$ element) have attracted a great deal of attention. The interest to these systems was spurred on by large intergrain-tunneling magnetoresistance observed at room temperature in Sr$_2$FeMoO$_6$ and Sr$_2$FeReO$_6$ [1], which opens wide perspectives for technological applications. On the contrary, Sr$_2$MnMoO$_6$ remains paramagnetic down to the very low temperature [2]. The magnetic susceptibility of Sr$_2$MnMoO$_6$ obeys the Curie-Weiss law with fairly large effective moment. However, there is something that prevents formation of the long-range magnetic order in this material (a similar situation occurs in double-layer manganites La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ around $x=0.7$ [3]). In this work we argue that such a behavior may be due to the competition between ferromagnetic (FM) and type-II antiferromagnetic (AFM) phases.

2. Total energy and local stability of the collinear state

The main idea of this work is to complement the standard total energy calculations with the analysis of inter-atomic magnetic interactions in the collinear magnetic state characterized by the directions $\{e_i^0\}$ of the spin magnetic moments. The latter can be described in terms of a perturbation theory expansion for small rotations $\{\delta \varphi_i\}$ near $\{e_i^0\}$. The "perturbed" direction of the magnetic moment at the site $i$ is given by $e_i = e_i^0 + [\delta \varphi_i \times e_i^0] - 1/2 (\delta \varphi_i)^2 e_i^0$, and the total energy change $\Delta E = E(\{e_i\}) - E(\{e_i^0\})$ in the second order of $\{\delta \varphi_i\}$ can be exactly mapped onto the Heisenberg model as [4]:

$$\Delta E = -\frac{1}{2} \sum_{i,m} J_{im} \left[ e_i \cdot e_{i+m} - e_i^0 \cdot e_{i+m}^0 \right].$$

Eq. (1) originates from the Taylor series expansion for $E(\{e_i\})$ near $\{e_i^0\}$, and $\{J_{im}\}$ are related with the second derivatives of $E(\{e_i\})$ with respect to $\{\delta \varphi_i\}$. $\{J_{im}\}$ can

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be expressed through the matrix elements of the one-electron Green function and the magnetic part of the Kohn-Sham potential at the site $\mathbf{m}$, $\Delta_{\text{ex}}^{m} = \frac{1}{2} (v_{\mathbf{m}}^{+} - v_{\mathbf{m}}^{-})$, as [6]:

$$J_{m} = \frac{1}{2\pi} \text{Im} \int_{-\infty}^{\infty} d\varepsilon \text{Tr}_{L} \left\{ \Delta_{\text{ex}}^{0} G_{0m}^{+} (\varepsilon) \Delta_{\text{ex}}^{m} \tilde{G}_{m0}^{+} (\varepsilon) \right\},$$

with $\text{Tr}_{L}$ denoting the trace over the orbital indices.

All calculations have been performed in the local-spin-density approximation, using the ASA-LMTO method [5].

### 3. Electronic structure and magnetic interactions

The calculated densities of states for the FM and AFM phases are shown in Fig.4, as a function of the breathing distortion $\delta = d_{\text{Mn-O}} / d_{\text{Mn-Mo}}$ (the ratio of Mn-O and Mn-Mo bondlengths).

When $\delta \leq 0.52$, the FM state is metallic. The Fermi level crosses Mn($e_{g}$) band in the majority ($\uparrow$)-spin channel and the Mo($t_{2g}$) band in the minority ($\downarrow$)-spin channel. Therefore, one can expect two main contributions, which tends to stabilize the FM ordering: the canonical double exchange (DE) operating in the $\uparrow$-spin Mn($e_{g}$) band, similar to the colossal magnetoresistive manganites [6]; and a generalized DE mechanism associated with partial filling of the $\downarrow$-spin Mo($t_{2g}$) band and originating from the strong Mn-Mo hybridization [7, 8]. The breathing distortion $\delta > 0.5$ tends to fully populate the Mn($e_{g}$) band and depopulate the Mo($t_{2g}$) band. Therefore, when $\delta$ increases, the DE interactions of the both types will decreases.

The AFM phase is metallic in the undistorted cubic structure ($\delta = 0.5$). However, even small oxygen displacement towards the Mo sites opens the band gap. The situation corresponds to the formal configurations $3d_{z^2}^{5} 3d_{x^2-y^2}^{6}$ (Mn$^{2+}$) and $4d^{0}$ (Mo$^{6+}$) of the transition-metal sites. The half-filled Mn($3d$) states give rise to the AFM superexchange (SE) interactions, similar to the rock-salt monoxide MnO, which are roughly proportional to $-t_{\text{eff}}^{2} / \Delta_{\text{ex}}^{\text{Mn}}$. The effective hoppings $t_{\text{eff}}$ between nearest-neighbor ($nn$) Mn($3d$) orbitals are smaller in Sr$_{2}$MnMoO$_{6}$ (in comparison with MnO), as they are mediated by much longer Mn-O-Mo-O-Mn paths. However, $\Delta_{\text{ex}}^{\text{Mn}}$ is expected to be also smaller in Sr$_{2}$MnMoO$_{6}$, which is more itinerant material than MnO. Thus, smaller $t_{\text{eff}}$ in Sr$_{2}$MnMoO$_{6}$ is compensated by smaller $\Delta_{\text{ex}}^{\text{Mn}}$, and the resulting SE interactions are expected to be comparable with those in MnO.

The qualitative discussions are supported by direct calculations of inter-atomic magnetic interactions (Fig.2). In the FM state, the $180^\circ$ exchange $J_{2}^{\text{Mn-Mn}}$ between next-nearest-neighbors in the Mn sublattice is the strongest interaction. The $nn$ ($90^\circ$) interaction $J_{1}^{\text{Mn-Mn}}$ is significantly weaker and becomes antiferromagnetic around $\delta = 0.51$. However, the FM interaction $J_{2}^{\text{Mn-Mn}}$ largely prevails and the FM phase remains stable at least up to $\delta = 0.52$. The $nn$ interactions $J_{1}^{\text{Mn-Mo}}$ between Mn and Mo sublattices is small and does not play any role in the problem.

The breathing distortion in the AFM state stabilizes the AFM coupling (both between first and second nearest neighbors in the Mn-sublattice). $J_{1}$ and $J_{2}$ are of the order of 5-8 meV, and comparable with similar interactions in MnO [9].

Thus, within the interval $0.5 < \delta \leq 0.52$ both FM and type-II AFM phases are locally stable. Next, we argue that these two local minima of the total energy may exist in the very narrow energy range, so that two magnetic solutions are nearly degenerate. This is qualitatively supported by results of direct total energy calculations shown in Fig.3. The
situation when the FM and AFM solutions become nearly degenerate can occur roughly around $\delta=0.51$.

4. Conclusions

We have argued that $\text{Sr}_2\text{MnMoO}_6$ may have (at least) two total energy minima corresponding to the metallic FM and insulating type-II AFM states, which coexist in the very narrow energy range. We expect the competition between these states to prevent the formation of the long-range magnetic order which features the experimental behavior of $\text{Sr}_2\text{MnMoO}_6$ down to the very low temperature. The quantitative description of such a situation, using results of first-principles electronic structure calculations, could be one of the possible extensions of the present work.

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[8] Since there is no direct hoppings between the $e_g$ and $t_{2g}$ orbitals in the cubic lattice, these two contributions can be considered separately.
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Figure 1: Local densities of states for the ferromagnetic (left) and type-II antiferromagnetic (right) phases of Sr$_2$MnMoO$_6$ as a function of breathing distortion.

Figure 2: Inter-atomic magnetic interactions calculated in the ferromagnetic (left) and antiferromagnetic (right) states of Sr$_2$MnMoO$_6$ as a function of breathing distortion. $J_{1}^{↑↑}$ and $J_{1}^{↑↓}$ are the nearest-neighbor interactions between Mn sites with the same and opposite directions of spins in the type-II antiferromagnetic structure.

Figure 3: Total energy difference between ferromagnetic and antiferromagnetic configurations as a function of breathing distortion.