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# Cluster magnetism of $Ba_4NbMn_3O_{12}$: localized electrons or molecular orbitals?

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Typical strong magnets are transition metal (TM) or rare earth (RE) compounds, and the "carriers" of magnetic moments are TM or RE ions with strongly correlated electrons. There exist however many materials in which such ions form relatively tightly bound clusters – dimers, trimers, or bigger objects. The study of such "cluster" systems present definite interest and is starting to attract more and more attention. In this paper we present results of investigation of $Ba_4NbMn_3O_{12}$, which crystal structure is shown in Fig. 1. The main interesting for us building block is a linear trimer of three face-sharing $MnO_6$ octahedra. There are two crystallographically different Mn ions: those siting in the middle of the trimer ($Mn_m$) and outer Mn ions ($Mn_o$). The average valence of Mn here is $Mn^{3\frac{2}{3}+}$, i.e., it nominally contains two $Mn^{4+}$ ($d^3$) and one $Mn^{3+}$ ($d^4$). In principle they could form charge-ordered (CO) state, but structural data [1] do not show any indication for that – at least not strong CO. The system is magnetic, with the Curie–Weiss susceptibility, and the most interesting result is that the effective moment $\mu_{\rm eff} = 4.89\,\mu_{\rm B}$ corresponds to spin $S_{\rm tot} = 2$ per $Mn_3$ trimer [1].

We carried our *ab initio* calculations using pseudopotential VASP code [2] to study magnetic properties of $Ba_4NbMn_3O_{12}$. Perdew–Burke–Enzerhof variant of the generalized gradient approximation (GGA) [3] was chosen. The crystal structure was taken from [1]. Integration over the Brillouin zone was performed of the mesh of $7 \times 7 \times 7$ **k**-points. To take into account electronic correlations we used GGA + U method as formulated in [4] with $U = 4.5$ eV and $J_H = 0.9$ eV [5] (we also checked that variation of $U$ on $\pm 1$ does not change the results).

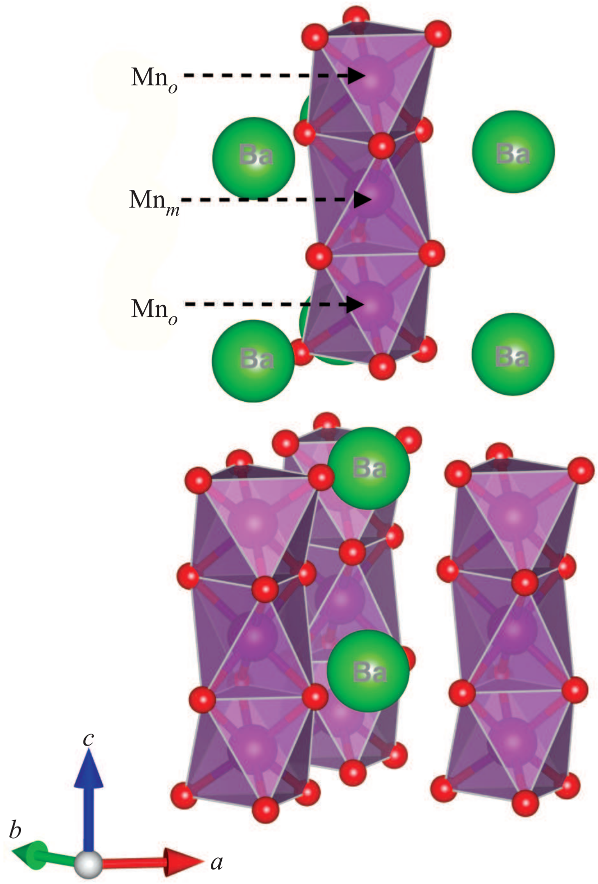


Fig. 1. (Color online) Crystal structure of $Ba_4NbMn_3O_{12}$. The Mn ions (violet balls) are in the oxygen (small red balls) octahedra. Three nearest $MnO_6$ octahedra form a trimer sharing their faces. The Mn ions, which are in the middle of the trimer, are labeled as $Mn_m$ throughout the text, while $Mn_o$ are outer Mn ions in the trimer. Ba (large green balls) ions sit in the voids and Nb ions are not shown

The lowest in energy magnetic configuration is the one with spins on middle and outer Mn ions ordered antiferromagnetically (i.e., ↑↓↑). The FM (↑↑↑) is 116 meV/f.u higher in energy. Thus, we see that there is a strong antiferromagnetic exchange coupling between

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nearest Mn ions. This coupling is due to both direct and oxygen assisted $t_{2g}$–$t_{2g}$ hoppings. We found that the $e_g$ states are partially filled in $Ba_4NbMn_3O_{12}$ and one may expect FM double exchange-like, contribution, but our calculations show that the total exchange interaction is AFM and thus direct and superexchange due to half-filled $t_{2g}$ orbitals overwhelms the double exchange.

We proceed with the analysis of the lowest in energy ↑↓↑ configuration. Both types of the Mn ions have nearly the same number of $d$-electrons $\delta n = n_{\mathrm{Mn}_m} - n_{\mathrm{Mn}_o} = 0.05$. Thus, there is no charge-ordering in $Ba_4NbMn_3O_{12}$. The total magnetic moment is $3.9\,\mu_{\mathrm{B}}$ per formula unit (f.u.), which is very close to what one might expect for $S_{\mathrm{tot}} = 2$ per trimer and to experimental results. Further analysis of the occupation matrices shows that all $t_{2g}$ states are half-filled and provide $m^{t_{2g}}_{\mathrm{Mn}_m} = -2.5\,\mu_B$ and $m^{t_{2g}}_{\mathrm{Mn}_o} = 2.6\,\mu_B$ to total magnetic moments on these ions, which were found to be $m_{\mathrm{Mn}_m} = -2.9\,\mu_B$ and $m_{\mathrm{Mn}_o} = 3.3\,\mu_{\mathrm{B}}$. The difference between $t_{2g}$–only and total magnetic moments is due to spin polarization of the $e_g$ shell. The spin density corresponding to $1\,\mu_{\mathrm{B}}$ is spread over $e_g$ orbitals ($\mathrm{Mn}_m$ has $m^{e_g}_{\mathrm{Mn}_m} = -0.4\,\mu_{\mathrm{B}}$, each $\mathrm{Mn}_o$: $m^{e_g}_{\mathrm{Mn}_o} = 0.7\,\mu_{\mathrm{B}}$). This shows that there is no low-spin state of $Mn^{3+}$ (which would correspond to the $t^4_{2g}$ state, without any $e_g$ contribution).

According to our calculations $Ba_4NbMn_3O_{12}$ is apparently much closer to the localized limit, in contrast to many $4d$ and $5d$ systems. Indeed, scenario with pure MO state of a trimer, for both $t_{2g}$ and $e_g$ electrons does not seem to correspond to what we have in the GGA+U calculations. In the MO picture the spin polarization of all $t_{2g}$ electrons would be positive on *any* Mn sites (bonding orbitals are completely filled and do not contribute to the total magnetization on any site, whereas spin moment is provided by nonbonding orbitals only). However, we have seen that in fact different Mn ions have different spin orientations in the GGA + U calculation.

Summarizing, we showed $Ba_4NbMn_3O_{12}$ can be considered as a cluster magnet. However, in contrast to many similar systems with the $4d$ and $5d$ electrons, for which the MO description applies [6, 7], it is not the case for the considered $3d$ material $Ba_4NbMn_3O_{12}$. This material should rather be described by the picture of electrons localised on TM sites (here Mn), which being strongly antiferromagnetically coupled form $S = 2$ $Mn_3$ trimers. Apparently the inter-cite hopping here is not large enough to overcome the strong on-site Hubbard and Hund interactions. Of course these two pictures, of completely localized electrons and pure MO state are the limiting cases. The real situation is always somewhere in between (which actually helps to form total moment $S_{\mathrm{tot}} = 2$). We also predict that the ordered magnetic structure of this system would be that of ferromagnetic layers of $Mn_3$ trimers stacked antiferromagnetically.

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