Cluster magnetism of Ba$_4$NbMn$_3$O$_{12}$: localized electrons or molecular orbitals?

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Recently synthesized Ba$_4$NbMn$_3$O$_{12}$ belong to cluster magnets - systems with tightly bound groups of magnetic ions, in this case Mn$_3$ trimers. Often such magnetic clusters can be described by molecular orbitals (MO), however strong electron correlations may invalidate this description. To understand the electronic and magnetic state of Ba$_4$NbMn$_3$O$_{12}$ we carried out ab initio calculations and show that this system is better described not in MO picture, but as a system with electrons localized on the Mn ions, with strong intra-cluster and weaker inter-cluster exchange. The calculated spin of the Mn$_3$ trimer is $S = 2$, in agreement with the experiment. The predicted magnetic structure of Ba$_4$NbMn$_3$O$_{12}$ is that of ferromagnetic layers of Mn$_3$ trimers, stacked antiferromagnetically.

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[1]. There exist however many materials in which such ions form relatively tightly bound clusters - dimers, trimers, or bigger objects. Electron hopping within such clusters $t$ can be sufficiently large - comparable or even larger than the respective intra-atomic interactions: Hubbard repulsion $U$ and Hund’s coupling $J_H$. In such cases the electronic state of such clusters may be described by molecular orbitals (MO), and electrons would occupy such MO levels. Depending on the electron filling, such clusters can still have localized magnetic moments, and the solid composed of such clusters may develop magnetic ordering. But in this case the “carriers” of magnetism would be not isolated TM ions, but rather such clusters. We can speak in this case of “molecules in solids”, cluster magnetism, or cluster Mott insulators[2]. These systems have everything the usual Mott insulators have (electrons localized on such clusters may be localised due to the “on-cluster” electron repulsion, substituting the Hubbard $U$ in the usual Hubbard model; they can hop from cluster to cluster and become itinerant, etc.). But, besides all the features the usual correlated electron system have, there are extra intrachannel degrees of freedom which can lead for example to charge ordering (e.g. electrons occupying always the “top” site of a triangle), they can also have extra orbital ordering (due to possible degeneracy of some molecular orbitals), and other specific features. The study of such “cluster” systems present definite interest and is starting to attract more and more attention.

A few examples of such systems are for instance: materials like Ba$_3$Mn$_2$O$_9$[3, 4], with metals M (Ru or Ir) forming dimers of face-sharing MO$_6$ octahedra. There may be also edge-sharing dimers, e.g., in Li$_2$RuO$_3$[5, 6] or Y$_5$Mo$_2$O$_{12}$[7]. Some of the “best” spin liquid materials - molecular crystals[8] also have spins 1/2 localized on dimers. Many materials having Peierls or spin-Peierls transition may be treated as systems of this type.

Such clusters may be trimers: linear trimers e.g. in Ba$_4$Ru$_3$O$_{10}$[9] or Ba$_5$AlIr$_2$O$_{11}$[10], or “flat” triangular clusters, e.g. Mo$_3$ clusters in Zn$_2$Mo$_3$O$_8$ or Fe$_2$Mo$_2$O$_{11}$[11] (which may be doped, e.g., LiZn$_2$Mo$_2$O$_8$[12]); or V$_3$ clusters formed in LiVO$_2$ below structural transition at ~540 K[13].

Clusters of four TM ions are met e.g. in CaV$_4$O$_9$ (planar plaquettes[14]) or in lacunar spinels (tetrahedral clusters in GaV$_4$O$_8$; GaTa$_4$O$_8$) which attracted a lot of attention because of their multiferroic properties (GaV$_4$S$_8$[15]) or superconductivity (GaTa$_4$S$_8$[16]). Also the famous COSO (Cu$_2$OSO$_4$) - the first insulating material possessing skyrmions - also contains clusters of four Cu ions, and each such cluster is a carrier of a spin 1[17].

Even bigger clusters were proposed in the literature, e.g., heptamers (clusters of 7 V ions) in AlV$_2$O$_4$[18] (although more recent data show that here we are dealing rather with trimers (triangles) and tetramers (tetrahedra) of V[19], see also Ref. [19]). Even much larger objects can be considered in this picture - for example

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In dealing with specific material containing such structural clusters, the first question arising is whether we should consider such materials as composed of TM ions as the main units, or the better description is that of MOs on a cluster. The situation may be different from system to system, not only depending on the specific geometry of the material, but also it can differ for different TM metals. Thus, for example, 4d and 5d, thus they may behave as more localized, and one might expect better conditions for the formation of MO states in 4d and 5d systems than in 3d ones (although of course such MO states are not excluded also in some 3d systems). In this respect it is interesting to compare materials with the same crystal structure, but with different TM ions, 3d vs. 4d or 5d. An interesting example of such systems are materials with the general formula Ba₄M′M₃O₁₂, with different metals M′ occupying single octahedra, and, more important, with the possibility to put either 3d ions, e.g. Mn, or 4d (Ru) and 5d elements (Ir) at M sites forming face-sharing trimers, see Fig. 1. Recently two such materials were synthesized by the group of R. Cava [22, 23]. There exist also similar systems with Ir trimers, e.g. BaIrO₃ [21], Ba₃Ir₃O₁₂ [24, 25], BaCuIr₃O₁₂ [26]. And whereas for Ru and Ir trimers most probably the MO picture is a good starting point [9], for 3d system Ba₃NbMn₃O₁₂ the situation is not so obvious.

The structure of Ba₄NbMn₃O₁₂ is shown in Fig. 1. The main interesting for us building block is a linear trimer of three face-sharing MnO₆ octahedra. There are two crystallographically different Mn ions: those siting in the middle of the trimer (Mnₘ) and outer Mn ions (Mnₒ). The average valence of Mn here is Mn³⁺, i.e. it nominally contains two Mn⁺⁺⁺ (d⁰) and one Mn⁺⁺ (d¹). In principle they could form charge-ordered (CO) state, but structural data [23] 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 $\mu_{\text{eff}} = 4.89\mu_B$ corresponds to spin $S_{\text{tot}} = 2$ per Mnₘ trimer [23].

There are different possibilities to get such $S = 2$ state of a trimer. The first one (1), discussed in [23], is that in which two Mn⁺⁺ ions with the configuration $t₂g$, e.g., at the edges of a trimer, have spins $S₂ = +3/2$, and Mn⁺⁺ in the center is in the low-spin configuration $t₂g$ with spin $S₁ = -1$, so that the total spin of a trimer is $S_{\text{tot}} = 2$. But the low-spin state for Mn⁺⁺ ions is very uncommon.

Another possibility (2) is the state with localized electrons and with the $t₂g$ occupation for all three sites, the remaining electron occupying the $e_g$ orbitals is delocalized over the whole trimer. In this case $t₂g$ shells of Mn ions may have spins +3/2, -3/2, +3/2, and due to intra-atomic exchange coupling the $e_g$ electron should have spin corresponding to the total spin of $t₂g$ electrons, i.e. it will have spin up, $S = +1/2$. As a result we would again have $S_{\text{tot}} = 2$, but without assuming the low-spin state of Mn⁺⁺.

And finally, (3) in principle all electrons, both $t₂g$ and $e_g$ ones, may form MO states. Direct overlap of the $t₂g$ orbitals in a common face geometry may be significant, cf. for example [27, 28]. It is easy to show [9] that in this case both the $t₂g$ and $e_g$ states form bonding, nonbonding, and antibonding orbitals and the level di-

![Fig. 1. Crystal structure of Ba₄NbMn₃O₁₂. The Mn ions (violet balls) are in the oxygen (small red balls) octahedra. Three nearest MnO₆ octahedra form a trimer sharing their faces. The Mn ions, which are in the middle of the trimer, are labeled as Mnₘ throughout the text, while Mnₒ are outer Mn ions in the trimer. Ba (large green balls) ions sit in the voids and Nb ions are not shown.](image-url)
a strong antiferromagnetic exchange coupling between
TM ions. Here we assume that bonding \( e_g \) orbitals are
higher than nonbonding \( t_{2g} \) due to substantial \( t_{2g} - e_g \)
splitting. (b) The spin-density corresponding to the
band centred, at \( \sim -7.5 \text{ eV} \) in Fig. 2.

![Diagram](image)

Fig. 2. (a) Possible level diagram of a trimer formed by
TM ions. Here we assume that bonding \( e_g \) orbitals are
higher in energy. Thus, we see that there is
no low-spin state of Mn
3+
ions. One may expect FM double exchange-like, contribu-
tion, 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 ex-
change.

We proceed with the analysis of the lowest in en-
ergy \( \uparrow\downarrow\uparrow \) configuration. Both types of the Mn ions
have nearly the same number of \( d \)-electrons \( \delta n = n_{Mn_m} - n_{Mn_o} = 0.05 \). Thus, there is no charge-ordering
in Ba4NbMn3O12. The total magnetic moment is 3.9 \( \mu_B \)
per formula unit (f.u.), which is very close to what one
might expect for \( S_{tot} = 2 \) per trimer and to experi-
mental results. Further analysis of the occupation matri-
ces shows that all \( t_{2g} \) states are half-filled and provide
\( m_{Mn_m}^{t_{2g}} = -2.5 \mu_B \) and \( m_{Mn_o}^{t_{2g}} = 2.6 \mu_B \) to total mag-
netic moments on these ions, which were found to be
\( m_{Mn_m} = -2.9 \mu_B \) and \( m_{Mn_o} = 3.3 \mu_B \). The difference
between \( t_{2g} \)-only and total magnetic moments is due to
spin polarization of the \( e_g \) shell. The spin density cor-
responding to 1 \( \mu_B \) is spread over \( e_g \) orbitals (Mn
3+
has \( m_{Mn}^{e_g} = -0.4 \mu_B \), each Mn: \( m_{Mn}^{e_g} = 0.7 \mu_B \)). This
shows that there is no low-spin state of Mn
3+
ion (which
would correspond to the \( t_{2g} \) state, without any \( e_g \) con-
tribution), i.e. the scenario (1) is apparently not realised
here.

We get further insight as to the details of electronic
structure (which affects magnetic properties) from the
density of states and spin density plots shown in Figs. 3
and 2(b). The spin density in Fig. 2(b) corresponds to
the lowest in energy \( d \) band at \( -7.5 \text{ eV} \). We see that
this spin density is mostly due to the \( t_{2g} \) orbitals (in fact

a_{ij}$), and it is centered on one Mn ion and therefore scenario (2) with the site-localized $t_{2g}$ electrons looks plausible. The $e_g$ electrons in this picture are spread over the trimer.

Thus according to our calculations Ba$_4$NbMn$_3$O$_{12}$ is apparently much closer to the localized limit, in contrast to many 4$d$ and 5$d$ systems. Indeed, scenario (3) 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. First of all, in this picture one would expect the formation of well-separated bonding and antibonding bands. However, the obtained electronic structure, see Fig. 3 does not show such bands - clearly seen for example in similar calculations of Ba$_4$Rb$_3$O$_{10}$[7]. The second, more important and easier to follow argument is that 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, see Fig. 2a). However, we have seen that in fact different Mn ions have different spin orientations in the GGA+U calculation.

Finally, in order to test possibility of cluster magnetism in Ba$_4$NbMn$_3$O$_{12}$ we simulated its magnetic susceptibility, $\chi(T)$ using classical Heisenberg model $H = \sum_{i>j} J_{ij} \vec{S}_i \cdot \vec{S}_j$. The spin model consists of $S = 2$ trimers forming triangular planes with in-plane exchange $J_{ab}$, coupled by the diagonal interlayer interaction $J_c$ as shown in the inset of Fig. 4. We used classical Monte-Carlo (MC) method employing local and cluster updates with the box size $10 \times 10 \times 10$ as realized in the ALPS library[23] with interface generated by the JaSS code[?]. Number of sweeps in the MC run was chosen to be 10 000 000. Because of too large unit cell we have not calculated intercluster exchanges directly, but fitted them to $\chi(T)$. For comparison experimental results taken from Ref. [23] are shown.

The matter should rather be described by the picture of electrons localized on TM sites (here Mn), which, being strongly antiferromagnetically coupled, form $S = 2$ Mn$_3$ trimers. Apparently the inter-site 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 or pure MO state of Fig. 2(a), are the limiting cases. The real situation is always somewhere in between (which actually helps to form total moment $S_{tot} = 2$. 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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1. D. I. Khomskii, Transition Metal Compounds (Cambridge University Press, 2014).
2. S. V. Streltsov and D. I. Khomskii, Physics-Uspekhi 60, 1121 (2017).
3. D. Ziat, A. A. Aczel, R. Sinclair, Q. Chen, H. D. Zhou, T. J. Williams, M. B. Stone, A. Verrier, and J. A. Qillaum, Phys. Rev. B 95, 184424 (2017).
4. A. Nag, S. Middey, S. Bhowal, S. K. Panda, R. Mathieu, J. C. Orain, F. Bert, P. Mendels, P. G. Freeman, M. Mansson, et al., Phys. Rev. Lett. 116, 097205 (2016)
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5. Y. Miura, Y. Yasui, M. Sato, N. Igawa, and K. Kaku-rai, Journal of the Physical Society of Japan 76, 033705 (2007).

6. J. Park, T.-y. Tan, D. T. Adroja, A. Daoud-Aladine, S. Choi, D.-y. Cho, S.-h. Lee, J. Kim, H. Sim, T. Morioka, et al., Scientific reports 6, 25238 (2016).

7. C. C. Torardi, C. Fecketter, W. H. McCarroll, and F. J. DiSalvo, Journal of Solid State Chemistry 60, 332 (1985).

8. Y. Zhou, K. Kanoda, and T.-k. Ng, Rev. Mod. Phys. 89, 025003 (2017).

9. S. V. Streltsov and D. I. Khomskii, Phys. Rev. B 86, 064429 (2012).

10. J. Terzic, J. C. Wang, F. Ye, W. H. Song, S. J. Yuan, S. Aswartham, L. E. DeLong, S. V. Streltsov, D. I. Khomskii, and G. Cao, Phys. Rev. B 91, 235147 (2015).

11. T. Kurumaji, Y. Takahashi, J. Fujioka, R. Masuda, H. Shishikura, S. Ishiwata, and Y. Tokura, Phys. Rev. Lett. 110, 077206 (2017).

12. J. P. Sheckelton, J. R. Neilsion, D. G. Soltan, and T. M. McQueen, Nature Materials 11, 493 (2012).

13. N. Katayama, M. Uchida, D. Hashizume, S. Niitaka, J. Matsuno, D. Matsumura, Y. Nishihata, J. Mizuki, N. Takeshita, A. Gauzzi, et al., Phys. Rev. Lett. 103, 146405 (2009).

14. O. A. Starykh, M. E. Zhitomirsky, D. I. Khomskii, R. P. Singh, and K. Ueda, Phys. Rev. Lett. 77, 2558 (1996).

15. I. Kezsmarki, S. Bordacs, P. Milde, E. Neuber, L. M. Eng, J. S. White, H. M. Ronnow, C. D. Dewhurst, M. Mochizuki, K. Yanai, H. Nakamura, D. Ehlers, V. Tsurkan, and A. Loidl, Nature Materials 14, 1116 (2015).

16. M. M. Abd-Elmeguid, B. Ni, D. I. Khomskii, R. P. Singh, and K. Ueda, Phys. Rev. Lett. 77, 2558 (1996).

17. O. Janson, I. Rousochatzakis, A. A. Leonov, U. K. Roler, J. Van den Brink, and H. Rosner, Nature Communications 5, 5376 (2014).

18. K. Matsuno, T. Katsufuji, S. Mori, M. Nohara, A. Machida, Y. Moritomo, K. Kato, E. Nishihara, M. Nakamura, D. Ehlers, V. Tsurkan, and A. Loidl, Nature Materials 14, 1116 (2015).

19. M. V. Talanov, V. B. Shirokov, L. A. Avakyan, V. M. Talanov, and K. S. Borlakov, Acta Crystallogr. B 74, 1 (2018).

20. A. J. Browne, S. A. J. Kimber, and J. P. Attfield, Phys. Rev. Mat. 1, 052003 (2017).

21. H. W. Kroto, J. R. Heath, S. C. O’Brien, R. F. Curl and R. E. Smalley, Nature 318, 162 (1985).

22. L. T. Nguyen, T. Halloran, W. Xie, T. Kong, C. L. Broholm, and R. J. Cava, Physical Review Materials 2, 054414 (2018).

23. L. Nguyen, T. Kong, and R. Cava, arXiv:1810.00763