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Calculation of magnetic exchange couplings in the $S = 3/2$ honeycomb system $(Bi_3Mn_4O_{12})NO_3$ from first principles

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Absence of magnetic ordering in $Bi_3Mn_4O_{12}(NO_3)$ (BMNO) which has a magnetic subsystem that consists of honeycomb bilayers of Mn^{4+} ions with spin $S = 3/2$ has raised the expectation that its ground state is strongly frustrated due to longer range antiferromagnetic interactions. We calculate the magnetic exchange coupling constants of the BMNO complex within a density functional approach and find that the dominating interactions between Mn spins are the antiferromagnetic nearest-neighbor J_1 and the effective interlayer interaction J_c. The largest interaction is J_c, which substantially exceeds J_1. Longer range interactions are antiferromagnetic but not strongly frustrating.

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In frustrated magnets spins interact through competing exchange interactions that cannot be simultaneously satisfied, giving rise to a large degeneracy of the system's ground state. The resulting fluctuations of the spins are at the root of remarkable collective phenomena such as emergent gauge fields and fractional particle excitations.[1] In this context the particular magnetic properties of $Bi_3Mn_4O_{12}(NO_3)$ (BMNO) have recently received considerable attention.[2–7] BMNO is a layered manganese oxide with its main magnetic building block a honeycomb lattice of Mn^{4+} ions, each carrying a spin $S = 3/2$. These manganese honeycomb lattices form bilayers (see Fig. 1) with interactions between the spins that are antiferromagnetic. In magnetic susceptibility and specific heat studies the absence of long-range ordering down to 0.4 K was reported,[2] which was confirmed in a high-field electron spin resonance study.[3] It was subsequently observed by inelastic neutron scattering[5] that long-range spin order can be induced by an external magnetic field.

The lack of spontaneous magnetic ordering within the Mn honeycomb lattices down to very low temperature was proposed to be due to frustration of magnetic interactions, in particular a competition between first and second neighbor antiferromagnetic Mn-Mn exchange interactions.[2] Currently BMNO is therefore viewed as a model system with strongly fluctuating $S = 3/2$ spins on honeycomb lattice, with a magnetic frustration that is due to the presence of longer range antiferromagnetic exchange interactions.[2–8]

The usefulness of this paradigm critically depends on the exact values of the exchange magnetic interactions in this material. The exchange coupling constants have been extracted from inelastic neutron scattering experiments,[5] where however the values of the couplings are not fully constrained. Theoretically, coupling constants have been estimated from unrestricted Hartree-Fock calculations and a perturbation method,[8] which puts forward that a *ferromagnetic* third nearest-neighbor interaction is responsible for the absence of long-range magnetic order in BMNO. We performed *ab initio* calculations of the magnetic exchange coupling constants of BMNO based on density functional theory and find that the nearest-neighbor J_1 and the effective interlayer interaction J_c are the most important interactions. In-plane longer range interactions, including the third neighbor one, are antiferromagnetic and much smaller. Taking all these into account we find the system is significantly away from full frustration within the honeycomb planes. In contrast to what has been asserted so far for BMNO, we find that the dominant interaction is the coupling between the honeycomb bilayers J_c with a value that can be as large as twice J_1. The existence of interlayer interaction was recognized in a recent study by Ganesh *et al.* in Ref. [7], but our finding that it actually dominates the exchange requires an alternate perspective on the factual origin of the observed magnetic frustration in BMNO.

We extract the exchange coupling constants in BMNO within GGA + U for different values of the Coulomb repulsion U on the Mn site. So far BMNO has not been studied with first-principles calculations and we use frozen collinear spin configurations to calculate very accurately the energies for different spin configurations. For the calculations we used an all-electron full potential local-orbital scheme implemented in FPLO code[9,10] with basis sets: Bi ($5s$, $5p$, $5d$, $6s$, $6d$, $6p$, $7s$, $7p$), Mn ($3s$, $3p$, $3d$, $4s$, $4p$, $4d$, $5s$), N ($1s$, $2s$, $2p$, $3s$, $3p$, $3d$), and O ($1s$, $2s$, $2p$, $3s$, $3p$, $3d$) states. The exchange-correlation energy functional was evaluated within the generalized gradient approximation (GGA) using the Perdew, Burke, and Ernzerhof parametrization.[11] The number of irreducible k points used in the calculations were 48 from a sampling of $4\times4\times3$ mesh.

We use experimental crystal structure of $Bi_3Mn_4O_{12}(NO_3)$, which is trigonal with space group $P3$ and consists of two MnO_6 layers separated by Bi and NO_3 layers (see Fig. 1).[2] The edge-shared MnO_6 octahedra lie in the ab plane and form a honeycomb lattice as shown in Fig. 1(b). The four inequivalent Mn atoms form two hexagonal planes separated by Bi atoms. These hexagonal planes are in distorted environments of MnO_6 octahedra resulting in small differences between the planes. We simplify the situation by treating the two layers as if they were the same, thus having the same in-plane magnetic interactions. The main purpose of presenting this streamlined picture is to understand and illustrate nature and main trends of magnetic interactions. But the small crystallographic differences will cause changes in the details of magnetic interactions that are presented here. Five different magnetic spin configurations (as shown in Fig. 2) are considered in order to calculate the magnetic interactions within the honeycomb lattice and between the bilayers with the GGA + U method for $U = 4.0$, 6.0, and 8.0 eV at the transition metal Mn site,

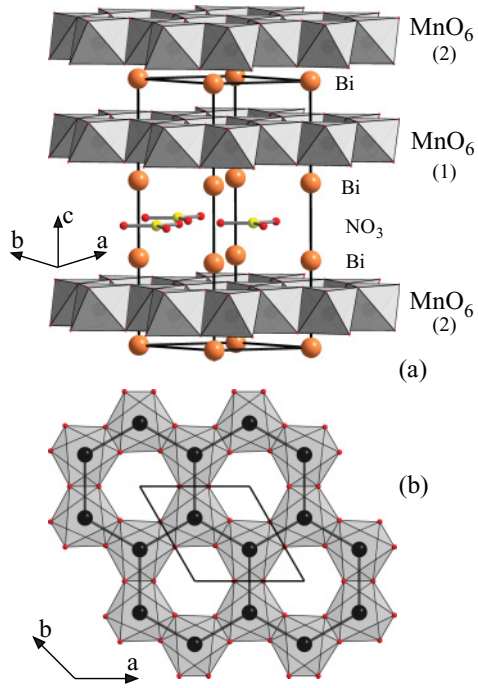

FIG. 1. (Color online) Crystal structure of BMNO. (a) Distorted MnO_6 octahedra are edge sharing with oxygen at the vertices, forming hexagonal bilayers. For clarity the bottom hexagonal layer is repeated along the c direction, which emphasizes the bilayer structure. (b) Top view of the network of edge-sharing octahedra in BMNO. The honeycomb lattice is indicated by the dark black lines that connect Mn atoms (black dots). The oxygen atoms shared by the MnO_6 units form layers. The orange (medium gray) spheres are Bi atoms, the yellow (light gray) spheres nitrogen atoms, and red (dark gray) spheres are oxygen atoms.

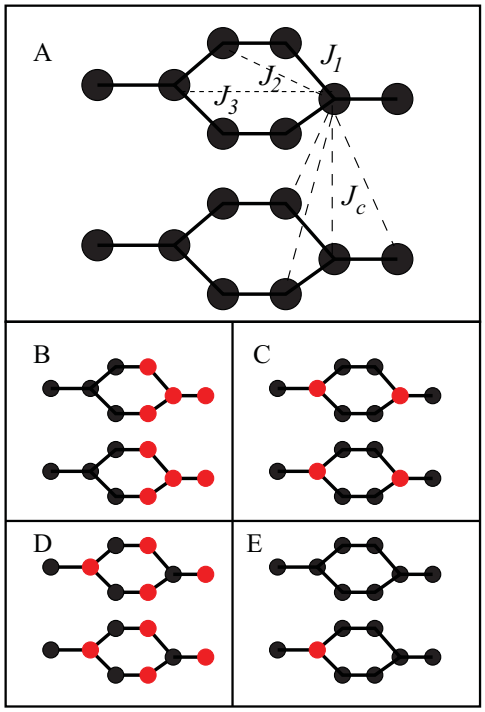

FIG. 2. (Color online) Schematic representation of five ordered spin states A, B, C, D, and E in a $2\times2\times1$ supercell of BMNO used for the determination of exchange constants. Only Mn atoms with the spin exchange paths are shown. Red filled (dark gray) circles are used to highlight spins that are flipped with respect to the reference configuration. Three in-plane magnetic interactions given as J_1, J_2, and J_3, whereas J_c represents the interbilayer interaction.

which is within the range that of U values extracted from spectroscopic measurements (4–5 eV)[12,13] and used in other *ab initio* calculations (4–10 eV).[14–17] The Hund's rule coupling J_H is 1 eV.

Total energies for different Mn spin configurations in a supercell with 92 atoms were obtained in the GGA+U formalism employing the atomic limit functional. The calculated relative energies for the spin configurations A, B, C, D, and E with the different U values are listed in Table I, where the energy of the most stable configuration "D" energy was used as the zero of energy. With the energies of five ordered spin states, all four exchange constants (J_1, J_2, and J_3, between first, second, and third nearest neighbors, respectively and J_c the interbilayer coupling) can be determined. The interlayer coupling is an effective parameter that represents the magnetic interactions between a spin in one honeycomb layer with all the magnetic moments in the other layer.

TABLE I. Relative energies in eV of different spin-states structures (as shown in Fig. 2) of BMNO obtained from GGA + U (U = 4.0, 6.0, and 8.0 eV) calculations.

	$U = 4.0$ eV	$U = 6.0$ eV	$U = 8.0$ eV
A	0.3745	0.2213	0.1118
B	0.1180	0.0684	0.0335
C	0.1687	0.1013	0.0518
D	0	0	0
E	0.2983	0.1752	0.0852

To evaluate the magnetic interactions we map the DFT energy differences of five magnetic spin configurations onto a classical spin-3/2 Heisenberg model. The magnetic exchange coupling constants are calculated from the following equations:

$$E_A - E_B = 9(6J_1 + 12J_2 + 12J_3), \quad (1)$$

$$E_A - E_C = 9(6J_1 + 12J_2), \quad (2)$$

$$E_A - E_D = 9(12J_1 + 12J_3), \quad (3)$$

$$E_A - E_E = \frac{9}{2}(3J_1 + 6J_2 + 3J_3 + J_c). \quad (4)$$

In Table II J_1, J_2, J_3, and J_c are listed as calculated from the relative energies of these spin configurations for different values of U. All interactions come out to be antiferromagnetic and we observe that the dependence on U is rather moderate as far as the relative values of the exchange constants is concerned: U roughly tends to scale the different exchange interactions in the same manner. The in-plane J_1 is almost an order of magnitude larger than J_2. It is also considerably larger than J_3, so that these interactions are only weakly frustrating. The magnitude of the couplings J_2 and J_3 are similar. As the bond length corresponding to J_1 (2.8697 Å) is much shorter than that for J_2 or J_3 (4.9692 Å or 5.7383 Å), it is not surprising that J_1 is the strongest interaction within the

TABLE II. Exchange constants in BMNO in meV calculated by FPLO GGA + U with the atomic limit functional on the basis of Eqs. (1)–(4). Slater parameters are chosen as $F_0 = U$, $F_2 = 8.6$ eV, and $F_4 = 5.4$ eV, i.e., $J = (F2 + F4)/14 = 1$ eV. Values in Kelvin (K) in parentheses. The direct evaluation of J_c is based on the energy difference between ferro and antiferro coupled honeycomb planes.

Exchange	$U = 4.0$ eV	$U = 6.0$ eV	$U = 8.0$ eV
J_1	3.00 (34.8)	1.7 (19.7)	0.9 (10.4)
J_2	0.4 (4.6)	0.2 (2.3)	0.1 (1.2)
J_3	0.47 (5.4)	0.3 (2.7)	0.2 (2.3)
J_c	4.10 (47.6)	2.7 (31.3)	2.1 (24.4)
J_2/J_1	0.13333	0.1176	0.1111
J_3/J_1	0.15667	0.17647	0.2222
J_c (direct)	2.97 (34.5)	1.88 (21.8)	1.08 (12.5)

honeycomb plane. However, the largest exchange interaction is the effective interlayer J_c, which is also antiferromagnetic and has about two times the value of J_1 for larger values of U.

Let us compare these results with the exchange constants found by inelastic neutron scattering. Matsuda *et al.* have investigated magnetic ordered and disordered ground state using inelastic neutron scattering experiments.[5] From the data they extract a constraint that relates the spin-spin interactions based on the observed magnetic excitations $3J_1 + 6J_2 + J_c \sim 6$ meV. By subsequently using in addition an approximated value of $J_c/J_1 = 1/2$ from their experiments and the critical value of $J_2/J_1 = 0.15$ from literature,[18] which ensure very strong frustration and are consistent with the observed absence of long-range magnetic ordering, Matsuda *et al.* obtain $J_1 = 2J_c = 1.4$ meV and $J_2 = 0.20$ meV. Compared to the experimental analysis, we consider in our theoretical calculations a fourth interaction (J_3) corresponding to the third nearest-neighbors interaction within the honeycomb lattice. In this case the experimental constraint of Matsuda *et al.* is $C = 3J_1 + 6J_2 + J_c + 3J_3 \sim 6$ meV, where we find from our calculations $C = 5.9$ meV, for $U = 8.0$ eV. The calculated constraint and therefore also the calculated exchange interaction are in full agreement with the dispersion of magnon excitations that were measured by inelastic neutron scattering. We obtain a ratio of J_1/J_2 that is similar to the one that was used by Matsuda *et al.*[5] However, our effective interlayer coupling J_c is larger than the in-plane coupling constants, contrary what was calculated from inelastic neutron scattering experiments.[5] To cross check this result we also calculated the energies of fully spin polarized honeycomb planes that are coupled either ferro- or antiferromagnetically. This allows for the direct evaluation of the effective intraplane exchange but has the disadvantage that because a state with ferromagnetic planes is the one furthest away from the in-plane antiferromagnetic ground state, significant renomalizations of the interplane magnetic bonds can occur. As shown in Table II we find in this case a ratio of J_c/J_1 closer to one, the exact value of which depends on U. This is a substantial renormalization, but does not change the conclusion that the interlayer coupling is the leading exchange interaction. This relatively large J_c is related to the fact that the in-plane Mn-O-Mn angles are close to 90°, implying a strong competition between antiferromagnetic and ferromagnetic superexchange, of which it is *a priori* not clear which will win. The interplane exchange paths, via the covalent bismuth states, do not suffer as much from such a geometric frustration of interactions.

Thus from the theoretical evaluation of magnetic exchange coupling constants for BMNO, we find all of them (first neighbors, second, and as well as third neighbors within the honeycomb plane and between the planes) to be antiferromagnetic. The calculated values fulfill the constraint that is put on the weighted sum of exchange interactions by inelastic neutron scattering data.[5] In this constellation only the second nearest-neighbor interaction J_2 would be frustrating a full-blown antiferromagnetic ordering. As J_2 is comparable to J_3, both of which are much smaller than J_1, which is again exceeded by J_c, we find from the calculations that the effect of this frustration is not strong. We conclude that the observed absence of magnetic ordering down to temperatures lower than the temperature scale set by the calculated exchange interactions requires an explanation that goes beyond in-plane magnetic frustration. Possibly oxygen vacancies are of importance which will not only lead to disorder of magnetic bonds but might also lead to doping of the manganese layers, in which case the presence of Mn^{3+} would lead to a competition between ferromagnetic double exchange and antiferromagnetic superexchange, which is known to strongly affect the magnetic properties and ordering in weakly doped Mn^{4+} perovskite manganites.[19] At any rate, a description of the magnetic properties of BMNO will have to considered the dominating coupling constant, interbilayer exchange, explicitly.

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