

# The nature of the ferromagnetic ground state in the $\text{Mn}_4$ molecular magnet.

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Using *ab initio* band structure and model calculations we studied magnetic properties of one of the  $\text{Mn}_4$  molecular magnets ( $\text{Mn}_4(\text{hmp})_6$ ), where two types of the Mn ions exist:  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$ . The direct calculation of the exchange constants in the GGA+U approximation shows that in contrast to a common belief the strongest exchange coupling is not between two  $\text{Mn}^{3+}$  ions ( $J_{bb}$ ), but along two out of four exchange paths connecting  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  ions ( $J_{wb}$ ). Within the perturbation theory we performed the microscopic analysis of different contributions to the exchange constants, which allows us to establish the mechanism for the largest ferromagnetic exchange. In the presence of the charge order the lowest in energy virtual excitations, contributing to the superexchange, will be not those across the Hubbard gap  $\sim U$ , but will be those between the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions, which cost much smaller energy  $V (\ll U)$ . Together with strong Hund's rule coupling and specific orbital order this leads to large ferromagnetic exchange interaction for two out of four  $\text{Mn}^{2+}$ - $\text{Mn}^{3+}$  pairs.

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## I. INTRODUCTION

The magnetic materials are so ubiquitous and essential for a plenty of devices used in the every day life that their properties are just taken for granted. The refrigerator magnets, medical implants, loudspeakers, magnetic resonance imaging scanners, magneto-optical disks, electrical motors and generators, etc. - all these devices use permanent or nonpermanent magnets. Yet such an ancient and customary phenomenon as magnetism offers plenty of amazing new aspects. One of them is the molecule based magnetism discovered about two decades ago. [1]

It was revealed that single-molecule magnets (SMMs) and single-chain magnets having large spin and strong easy-axis anisotropy can self-assemble into 2D and 3D networks. This gives a great hope that one bit of information could be stored on a single molecule. [2] The new multidisciplinary field developed at the interface of chemistry and solid state physics was triggered by the finding that SMMs, exhibit both classical and exotic quantum magnetic properties. [3] Challenged by the promising molecular spintronics and quantum computing applications sophisticated SMMs based not only on 3d transition metals but also on the 4d and even on the lanthanide and actinide elements were developed. [4–7] The theoretical studies have mostly concentrated on the description of the resonant tunneling experiments, [8, 9] *ab initio* simulations, [10–12] and investigation of the role of the correlation effects. [13]

The single-molecule magnets consist of a core and bridging polynuclear complexes. The physical insight

into the magnetic interactions within the core is essential for both fundamental and technological development. At present the values of the exchange constants in SMMs are typically estimated by the fitting of the experimental magnetic susceptibility to a some solution of the Heisenberg model. There are number of deficiencies in such a strategy mainly related with the large number of fitting parameters and sometimes with an arbitrariness in the choice of the model Hamiltonian, which in general must include not only different direct and superexchange interactions, but also magneto-crystalline anisotropy, Dzyaloshinskii-Moriya terms etc.

In the present paper we calculate the exchange constants in one of the  $\text{Mn}_4$  molecular magnets ( $[\text{Mn}_4(\text{hmp})_6(\text{NO}_3)_2\text{FeNO}(\text{CN})_5]\cdot 4\text{CH}_3\text{CN}$ ) with two types of Mn ions ( $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$ ) having “butterfly” geometry. Experimentally it is established that the ground state of this molecule is ferromagnetic. It is commonly assumed that there are two exchange interactions in the  $\text{Mn}_4$  molecule magnets:  $J_{bb}$  (body-body) between two  $\text{Mn}^{3+}$  ions and  $J_{wb}$  (wing-body) between  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  ions (see Fig. 1, where  $J_1$  and  $J_2$  are two different  $J_{wb}$ ), both of which are ferromagnetic with the first being much larger than the second. [14] The direct calculations presented in this paper reveal that this accepted picture is in fact incorrect: the dominant ferromagnetic exchange is not  $J_{bb}$ , but  $J_{wb}$ , with two inequivalent  $J_{wb}$  being very different. The magnetic susceptibility obtained by the exact diagonalization method with the use of the calculated exchange integrals agrees with experimental data.

The detailed microscopic analysis shows that there are many exchange processes in the  $\text{Mn}_4(\text{hmp})_6$  molecular magnet, which partially compensate each other, but its magnetic properties are mainly defined by two features of this system. First of all, the Jahn-Teller distortions

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leads to a specific orbital order, which in turn makes two exchange paths between  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  ions inequivalent. Second, the charge order strongly modifies the exchange processes between Mn ions of different valences and favors ferromagnetic exchange coupling. The results obtained allows not only to describe magnetic properties of the  $\text{Mn}_4(\text{hmp})_6$  molecular magnet, but can be applied to other systems, including transition metal oxides, with a charge ordered ground state. In conclusion, we suggest some recipes to increase the value of the ferromagnetic exchange in the  $\text{Mn}_4$  molecule magnets on the basis of the microscopic model developed in the present study. We believe that the strategy presented here will be useful for other SMMS.

## II. CRYSTAL STRUCTURE AND CALCULATION DETAILS

The crystal structure for system  $[\text{Mn}_4(\text{hmp})_6(\text{NO}_3)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ , abbreviated as  $\text{Mn}_4(\text{hmp})_6$  in what follows, was taken from Ref. 15. The main building block of  $\text{Mn}_4(\text{hmp})_6$  is the core consisting of four Mn ions (two  $\text{Mn}^{2+}$  and two  $\text{Mn}^{3+}$ ) and surrounding ligands shown in Fig. 1. Since  $\text{Mn}^{3+}$  are Jahn-Teller active ions, the ligand octahedra surrounding them are strongly distorted. It was shown

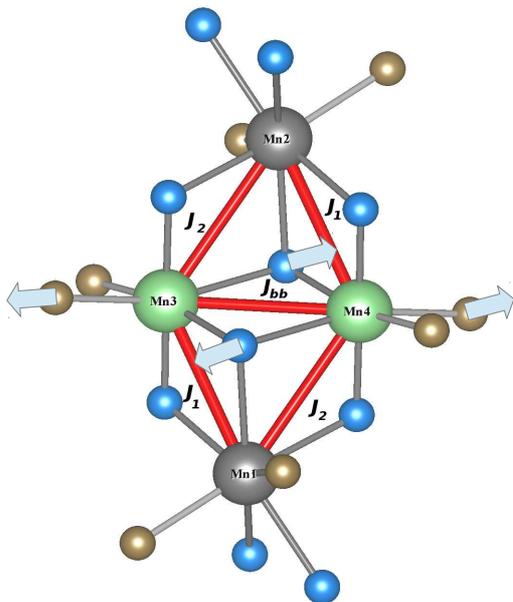


FIG. 1: (color online). A fragment of the  $\text{Mn}_4$  crystal structure is shown. The  $\text{Mn}^{2+}$  ions (Mn1 and Mn2) are shown as grey,  $\text{Mn}^{3+}$  (Mn3 and Mn4) as green, O as blue, and N as brown balls. Arrows show the direction of the Jahn-Teller elongation of the  $\text{Mn}^{3+}\text{O}_6$  octahedra. The path for the “body-body” exchange coupling is labeled as  $J_{bb}$ , while two different the “wing-body” exchange integrals are denoted via  $J_1$  and  $J_2$ .

in Ref. 16 that in the case of identical ligands the elastic interaction favors a parallel order of the elongated Mn-O bonds in the Jahn-Teller octahedra having a common edge. Surprisingly this is also the case in  $\text{Mn}_4(\text{hmp})_6$ .

Note right away that for the  $J_2$  bonds (Mn1-Mn4 and Mn2-Mn3) the long  $\text{Mn}^{3+}$ -O bonds, shown in Fig. 1 by broad arrows, lie in the plane of corresponding Mn1-O-Mn4-O and Mn2-O-Mn3-O plaquettes, whereas for the bonds  $J_1$  (Mn1-Mn3 and Mn2-Mn4) these long bonds are perpendicular to such plaquettes. As we show below, this will finally give very different exchange constants  $J_1$  and  $J_2$ .

The band structure calculations were performed within the Density Functional Theory (DFT). This type of the calculations was proven to provide adequate description of many organic compounds including mixed-valence systems, [11, 17, 18] while some restrictions related with the computation of the low spin states has to be mentioned. [19] The projector augmented wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP) was used. [20] The exchange-correlation potential was chosen to be in Perdew-Burke-Ernzerhof (PBE) form. [21] Non-spherical contributions from the gradient corrections inside the PAW spheres were included in the calculation scheme. In order to take into account strong electronic correlations on the Mn sites the GGA+U approximation (the generalized gradient approximation taking into account on-site  $U$  Hubbard correction) was applied [22] with the on-site Coulomb repulsion parameter  $U=4.5$  eV and the intra-atomic Hund’s rule exchange  $J_H=0.9$  eV. [23] The spin-orbit coupling was not taken into account in the present calculations, so that the effects related to this interaction (such as, e.g., the single-ion anisotropy) were not considered.

The mesh of 8  $\mathbf{k}$ -points was used in the course of the self consistency. The integration of the bands was performed by the tetrahedron method with the Blöchl corrections. [24]

The magnetic susceptibility was calculated using the exact diagonalization technique of the Heisenberg model

$$\hat{H} = 2J_{bb}\hat{S}_3\hat{S}_4 + 2J_1(\hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_4) + 2J_2(\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3) \quad (1)$$

implemented in the ALPS package. [25] The exchange constants  $J_{bb}$ ,  $J_1$ , and  $J_2$  were calculated from the total energies of four different magnetic configurations as discussed in Sec. III. The numeration of the spins and Mn ions in Eq. (1) and Fig. 1 is the same.

## III. RESULTS OF THE CALCULATIONS AND COMPARISON WITH EXPERIMENT

The total and partial density of states (DOS) obtained in the GGA+U calculation for the fully ferromagnetic order (Fig. 2a) are presented in Fig. 3. One may see that

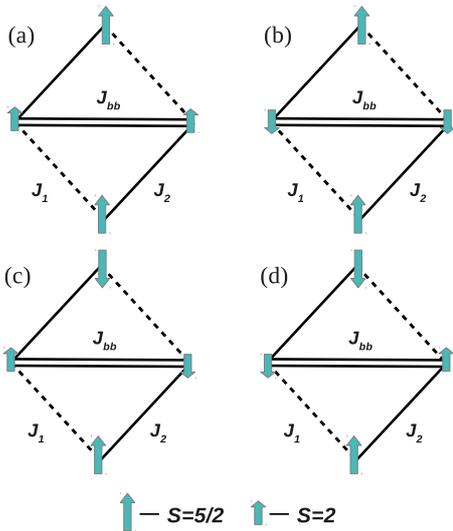


FIG. 2: (color online). Magnetic configurations used for the exchange coupling calculations.

the top of the valence band is formed mostly by the O 2p states with admixture of the N 2p, Mn<sup>3+</sup> and Mn<sup>2+</sup> 3d states. The lower Hubbard bands corresponding to the 3d states of the Mn<sup>3+</sup> and Mn<sup>2+</sup> ions are in the range from -5 eV to  $\sim$ -2 eV. The magnetic moments on the Mn<sup>2+</sup> and Mn<sup>3+</sup> were found to be 4.6  $\mu_B$  and 3.7  $\mu_B$ , respectively. The deviations from the ionic values (5  $\mu_B$  and 4  $\mu_B$ ) are related with the hybridization and covalency effects, which result in a transfer of a part of the spin density to the ligands. Similar effects were found in many other systems based on the transition metal ions. [26, 27] The lowest total energy corresponds to the magnetic configuration, when all Mn ions are ordered ferromagnetically.

As was already mentioned, typically only two exchange constants  $J_{bb}$  and  $J_{wb}$  are considered in the analysis of the magnetic properties of the Mn<sub>4</sub> molecular magnets. [15, 28]. In Mn<sub>4</sub>(hmp)<sub>6</sub>  $J_{wb}$  is the exchange constant between Mn<sup>2+</sup> and Mn<sup>3+</sup>, and  $J_{bb}$  between two Mn<sup>3+</sup>. However, a close inspection of the available crystal structure [15] shows that there are two different distances between the Mn<sup>2+</sup> and Mn<sup>3+</sup> ions:  $d_1(\text{Mn}^{2+} - \text{Mn}^{3+}) = 3.28 \text{ \AA}$ , and  $d_2(\text{Mn}^{2+} - \text{Mn}^{3+}) = 3.34 \text{ \AA}$ , which may result in two different exchange couplings  $J_{wb}$ . In order to check this hypothesis we calculated total energies of four magnetic structures presented in Fig. 2, which allows to extract three different exchange constants:  $J_{bb}^{\text{Calc}} = -0.3 \text{ K}$ ,  $J_1^{\text{Calc}} = -6.3 \text{ K}$ , and  $J_2^{\text{Calc}} = -0.5 \text{ K}$ , all of them are ferromagnetic. Here  $J_1$  and  $J_2$  are two inequivalent  $J_{wb}$  exchange couplings, which are shown in Fig. 1 and 2. This result is quite in contrast to the common opinion that  $J_{bb}$  must be much larger than any of  $J_{wb}$ .

The conventional assumption ( $|J_{bb}| > |J_{wb}|$ ) was justified by two arguments. First of all the Mn-Mn distance along the diagonal (3.20  $\text{\AA}$  in the present system) is much

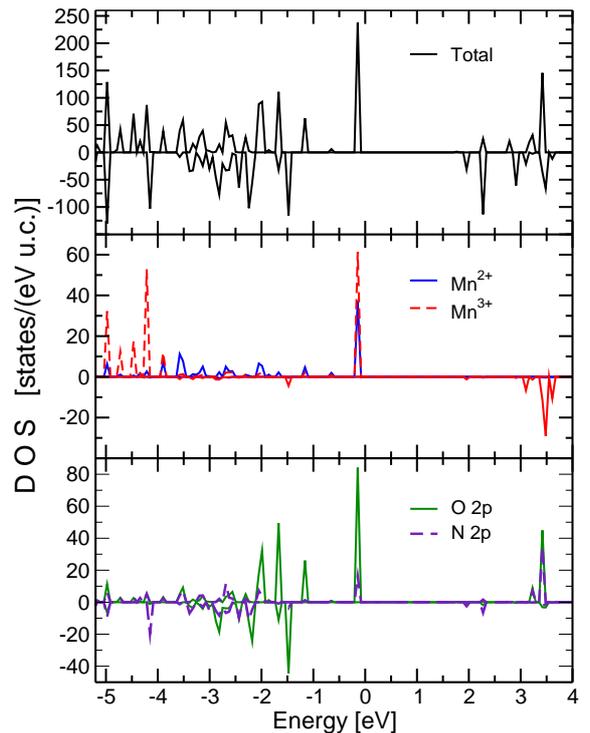


FIG. 3: (color online). The total and partial density of states (DOS) of the Mn<sub>4</sub> obtained in the ferromagnetic GGA+U calculation. The positive (negative) values correspond to the spin up (down) states. The Fermi energy is in zero.

smaller than along the edges of the Mn<sub>4</sub> rhombus. Since the exchange constant in the simplest case [29]

$$J \sim \frac{t_{dd}^2}{U} \quad (2)$$

and the hopping integral for the  $d$  orbitals ( $t_{dd}$ ) is supposed to be inversely proportional to the distance between ions  $t_{dd} \sim 1/r^5$ , [30] this viewpoint seems to be justified. However the expression for the superexchange interaction in a particular situation can be quite different from Eq. (2). The detailed analysis performed in Sec. IV shows that for the given system  $J_1$  is indeed expected to be ferromagnetic and its absolute value is much larger than  $|J_2|$  and possibly larger than  $|J_{bb}|$ .

Second, the values of the exchange constants are typically extracted from the fitting of the experimental magnetic susceptibility  $\chi(T)$  by the theoretical curve obtained from the solution of the Heisenberg model. [15, 31] There are three ( $g$ ,  $J_{bb}$ , and  $J_{wb}$ ) or even four ( $g$ ,  $J_{bb}$ ,  $J_1$ ,  $J_2$ ) fitting parameters, which results in an arbitrariness of this procedure. Instead of the fitting we first performed a direct calculation of the temperature dependence of  $\chi T$  (as described in Sec. II) with the exchange constants

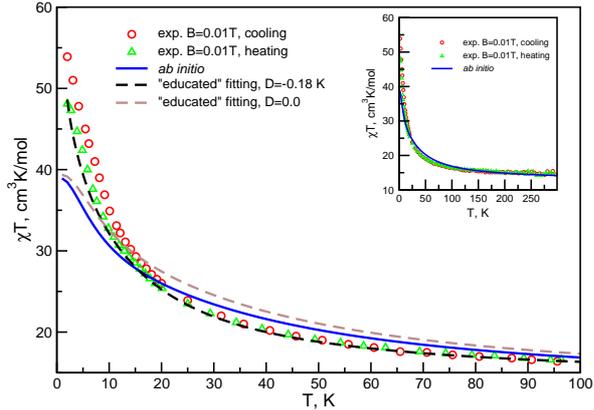


FIG. 4: (color online). Temperature dependence of the experimental and calculated  $\chi T$ . All theoretical curves were obtained by exact diagonalization of the isotropic exchange interaction described by Hamiltonian (1) with the exchange constants, obtained in the GGA+U approximation, or using fitting taking into account or neglecting by the single ion anisotropy ( $D$ ).  $\chi$  is the molar susceptibility.

obtained in the band structure calculations. The single variable parameter ( $g$ -factor) was chosen to fit the high-temperature tail of  $\chi T$  and it was found to be equal 1.86.

One may see from Fig. 4 that there is a reasonable agreement between calculated and experimental curves for  $B=0.01$  T. One may improve this agreement in the range from 20 to 100 K performing the fit to experimental data using calculated in the GGA+U exchange constants as a starting point. This yields  $J_{bb}^{fit} = -0.01$  K,  $J_1^{fit} = -6.5$  K,  $J_2^{fit} = -0.2$  K, and  $g = 1.87$  K. Further improvement can be achieved by adding the single ion anisotropy (via  $DS_z^2$  terms for the Jahn-Teller  $Mn^{3+}$  ions) into the fitting scheme. This gives  $J_{bb}^{fit,D} = -0.3$  K,  $J_1^{fit,D} = -3.6$  K,  $J_2^{fit,D} = -0.4$  K,  $D^{fit,D} = -0.18$  K, and  $g = 1.94$  K. Thus while  $J$  obtained in this “educated” fitting differ from those calculated in the GGA+U, the main result is the same –  $J_1$  is the largest exchange constant. The difference between theoretical and experimental data for  $T < 10$  K is related with experimental features of the measurements and  $Mn_4(hmp)_6$  samples, as discussed in Sec. III A.

#### A. Low temperature behavior of $\chi(T)T$ - experimental difficulties

Fig. 5 discloses the details of measurements for the dried (aged) polycrystalline sample  $[Mn_4(hmp)_6(NO_3)_2FeNO(CN)_5]4CH_3CN$  in Ref. 15. Due to low spin state,  $S = 0$ , the  $Fe^{2+}$  ion does not contribute to the total paramagnetic response. Temper-

ature dependencies for the product  $\chi T$  are obtained at magnetic fields  $B=0.01$  and 0.20 T. The measurements are performed at cooling from 300 K down to 2.0 K and at heating to ambient conditions. The temperature axis in Fig. 5 is in logarithmic scale for better view of low temperature behavior. While treatment the mass of solvent acetonitrile molecules was subtracted from the total molecular weight, so that it was taken as 1208.448 g/mol. Solvent losses is a characteristic feature of  $Mn_4(hmp)_6$  structures. Fresh crystals lose solvent with time making the molar weight out of control, so that the error may reach 12%. Therefore, in the present paper the data for dry (aged) crystals left in the open dry air for several months were used.

One may see in Fig. 5 that the position of the low temperature maximum of  $\chi T$  depends on the applied magnetic field,  $B$ : it shifts to higher temperatures with increase of  $B$ . Such a behavior is common for most of high spin molecules and molecular magnets. [3] The origin of the maximum and its position in particular is not related with the microscopic characteristics of the exchange-coupled core. There are few possible explanations of the low temperature behavior of the experimental  $\chi T$  curve.

First of all, in paramagnetic systems the Curie law is only observed at temperatures  $k_B T \gg g\mu_B S H$ . For  $T \lesssim T_p = g\mu_B S H$  thermal excitations are ineffective in providing dynamic Boltzmann equilibrium on higher Zeeman levels and the lowest level becomes “overpopulated”. In theory, it means that one cannot expand the Brillouin function in the Taylor series at  $x \ll 1$  (where  $x = g\mu_B S H / k_B T$ ) and get the Curie law. In practice, the data points will not lay on the equilibrium  $\chi(T)T$  curve. For  $B=0.2$  T, where the maximum in  $\chi(T)T$  is first clearly observable,  $T_p = 2.4$  K and hence for the temperatures of order of  $T_p$  or lower the deviations from the Curie law has to be observed. This is exactly what is seen in Fig. 5. It’s worthwhile mentioning that the stronger magnetic fields shift this region of the “inapplicability” of the Curie law to higher temperatures. [32]

Second, there is no phase transition from correlated state (with spins  $S_{Mn^{3+}} = 2$  and  $S_{Mn^{2+}} = 5/2$ ) to high spin state  $S=9$  for the individual  $Mn_4(hmp)_6$  complex as well as for other heterospin SMMs. Experimentally, there is no Curie temperature that can be measured. There is a temperature domain, in which a crossover from correlated paramagnetic to a high spin superparamagnetic state occurs in an individual tiny single crystal. In this domain both our Heisenberg model and dynamic  $S = 9$  approach are not applicable. However, there is a blocking temperature  $T_b \sim 1 \div 2$  K, below which every complex in a tiny crystal becomes an anisotropic quantum magnet. In the measurement starting from that low temperature,  $T_b$ , the magnetic response becomes quantitatively irreversible and dependent on magnetic history due to magnetic anisotropy of individual complex. In particular, this leads to a divergence of field cooled (FC) and zero field cooled (ZFC)  $\chi T$  curves, as it happens in spin

glasses. The FC type curves prevail in published data. A typical sample mass of order of 10 mg requires fields 1000 G and higher to get satisfactory paramagnetic response at 300 K. For more than 40 various  $\text{Mn}_4(\text{hmp})_6$  systems listed in Ref. 14, 28, 33 the experimental  $\chi(T)T$  data were obtained at  $B > 0.1$  T, so that a sharp peak was present on every curve. In the experimental protocols  $\chi(T)$  measurements are performed at heating from helium to ambient temperatures. They usually follow after magnetization field measurements,  $M(B)$ , where the excursions to high fields  $B=5$  to 7 T take place. The dependence of that type inherits magnetic history of the sample and imports excessive (or deficient) magnetization from low to higher temperature region. This makes a broader temperature domain inappropriate for numerical analysis.

Third, the magnetic fields as low as  $\sim 0.1$  T are capable to produce a texture in thin polycrystalline magnets. For textured samples, the product  $\chi(T)T$  reaches maximum at higher temperatures. Ignoring the anisotropy the maximal  $\chi(T)T$  values in high spin state are limited by 45 to 50 emu K/mol for  $g = 2.0$  to 2.1 respectively. Note also that g-factor for  $S = 9$  state differs from its average value at high temperatures. As an example, a broad maximum of 42 emu K/mol at  $T \approx 10$  K was observed in polycrystals of  $[\text{Mn}_2\text{Mn}_2(\text{teaH})_2(\text{teaH}_2)_2(\text{O}_2\text{CPh})_4] \cdot 0.7\text{MeCN} \cdot 0.3\text{EtOH}$  nearly isostructural to the similar system not revealing it. [34] That might be an indication of a texture rather than drastic enhancement of exchange coupling.

For analysis we select  $\chi(T)T$  data points measured at  $B=0.01$  T in order to avoid the effect of the “overpopulation” of the lowest Zeeman level and reduce  $T_p$  as described above. Two sets of data “at cooling” and “at heating”, presented in Fig. 4, allow to estimate the difference between these regimes. Down to 20 K both data coincide with the accuracy of 3.5%. At 2.0 K the data diverge reaching 48.1 emu K/mol “at cooling” and 53.9 emu K/mol “at heating”. The values 14.3 emu K/mol at 300 K are in agreement with other results reported on  $\text{Mn}_4(\text{hmp})_6$  structures and with the theoretical value 13.90 emu K/mol for  $g=1.94$ . The value of the effective activation barrier  $\Delta_{eff} = |D_{eff}|S^2 = 17.9$  K extracted from the ac data in Ref. 4 ( $\Delta_{eff}$ ,  $\tau_0=4.89 \cdot 10^{-9}$ s - parameters of Arrhenius law) fits in the range of published data usually found around 15-23 K (see Ref. 5-7 in Ako et al. [34]). This gives an estimate for the effective ZFS constant  $D_{eff} = -0.2$  K in  $S=9$  state. In the temperature domain  $1.8 \div 3.5$  K ( $T > T_b$ ), the interplay of thermal and quantum relaxation processes of the magnetization occurs. The thermal barrier is therefore “short-cut” by the quantum tunneling of the magnetization and the obtained  $D_{eff}$  value gives lowest estimate for the theoretical parameter. Upper estimate for  $D_{S=9}$  may reach -0.4 K.

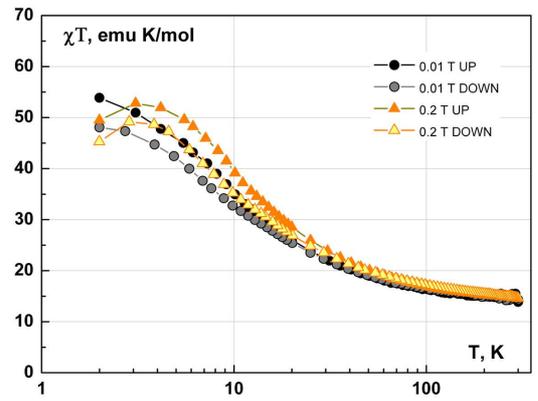


FIG. 5: (color online). The experimental  $\chi T$  vs.  $T$  data obtained for polycrystalline sample in different magnetic fields  $B = 0.01$  and 0.20 T for the cooling (DOWN) and heating (UP) regimes. The solid lines are guided by eye.

#### IV. MICROSCOPIC MECHANISM OF THE FM EXCHANGE COUPLING

In order to understand why  $J_1$  is much larger than  $J_2$  and  $J_{bb}$  one needs to find all the contributions to these exchange integrals. It is especially nontrivial to explain the difference between  $J_1$  and  $J_2$  because both constants describe coupling between  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  ions in a similar geometry.

We will consider the superexchange coming from the virtual hopping of  $d$ -electrons via  $p$ -states of ligands, and use the 4th order of the perturbation theory. The perturbation resulting to different energies of  $\uparrow\uparrow$  and  $\uparrow\downarrow$  states is given by the hopping integral  $t$ . 4th order of the perturbation theory means that we are considering only those paths which consists of 4 hoppings and the initial and final states are the same. The energy difference between initial and excited states (which appear while electrons hop) define the denominators in Eqs. (3-7). The numerators in Eqs. (3-7) are given by the corresponding hopping integrals  $t_{pd}$  between the ligand  $p$  and Mn  $d$  orbitals with different coefficients, which take into account the symmetry of the hoppings, number of the hoppings of a given type etc. The detailed description of this method can be found elsewhere. [29, 35–37]

One needs to introduce the following parameters to find explicit expressions for the exchange parameters:  $U$  - is the on-site Coulomb repulsion parameter, and  $\Delta_{CT}$  - is the charge transfer energy (energy of the excitation from the ligand  $2p$  orbitals to the  $3d$  shell of a transition metal ion). In general  $\Delta_{CT}$  depends both on the valence state of the transition metal ion and type of the ligand [38, 39]. For instance, according to the result of T. Mizokawa the charge transfer energy for  $\text{Mn}^{2+}$  is  $\Delta_{2+} \sim 7$  eV, which is much larger than in the case of the  $\text{Mn}^{3+}$  ions, for which  $\Delta_{3+} \sim 4$  eV. [39]

According to the terminology of Ref. 29 there are two important types of the exchange processes related with

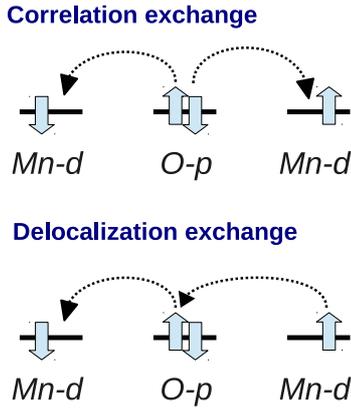


FIG. 6: (color online). Two types of the contributions to the superexchange according to the notations of Ref. 29.

delocalization and correlation effects. They are sketched in Fig. 6. The delocalization contribution to the exchange interaction involves the transfer of the ligand  $p$  electron to one of the Mn ions, while  $d$  electron from another Mn occupies the vacant place in the ligand  $p$  shell (after that both electrons must return to their initial places). The correlation effects are related with the transfer of two  $p$  electrons to two  $d$  sites on the right and on the left and then back.

For the simplicity in the analysis we will neglect the crystal-field splitting between  $t_{2g}$  and  $e_g$  orbitals (which in general is not small,  $\sim 2$  eV, in the case of the transition metal ions) and the splitting of the  $\text{Mn}^{3+}$   $e_g$  levels due to the Jahn-Teller effect. These terms will effectively increase the denominators in Eqs. (4-7).

#### A. Delocalization contribution to $J_1$ and $J_2$

There are two special features of the studied  $\text{Mn}_4$  molecular magnet which must be taken into account to find the expression for the delocalization contribution to the  $J_1$  and  $J_2$  exchange constants.

First of all the electron transfer from  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$  (back and forth) is quite different from the transfer from  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  (back and forth). Neglecting the intra-atomic Hund's rule coupling ( $J_H$ ) in the first case the energies of the excited states (with respect to the energy of the unperturbed state) are  $\Delta_{2+}$ ,  $2U$  and again  $\Delta_{2+}$ . So that this electron transfer is highly unfavorable, because it costs  $2U$ , where  $U \sim 4.5-8$  eV. [23, 40] In contrast the second type of the electron transfer (from  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  back and forth) cost neither  $2U$  nor even  $U$ , one only needs to spend the energy  $V$ .  $V$  is the energy of transfer (excitation) of an electron from  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$ , determined by the local coordination of these ions and by the intersite Coulomb interaction. Note that this energy  $V$  is much smaller than the on-site Coulomb (Hubbard) repul-

sion  $U$ , therefore the process of the virtual transfer of an electron from  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$ , leading to superexchange between these ions, costs much less energy than that between the similar Mn ions,  $\text{Mn}^{2+}-\text{Mn}^{2+}$  and  $\text{Mn}^{3+}-\text{Mn}^{3+}$ , and also less than the transfer in the pair  $\text{Mn}^{2+}-\text{Mn}^{3+}$  in opposite direction, which would correspond to the "reaction"  $(\text{Mn}^{2+}, \text{Mn}^{3+}) \rightarrow (\text{Mn}^{1+}, \text{Mn}^{4+})$ . Correspondingly, this process of virtual hopping from  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  would give largest exchange, which agrees with our numerical results.

The inter-site Coulomb interaction for Mn was estimated to be  $\sim 0.5$  eV using constrained random-phase approximation. [41] The constrained LDA calculation for charge ordered  $\text{Fe}_3\text{O}_4$  (where the number of the  $d$  electrons is just slightly larger than in our situation) gives  $V = 0.18$  eV. [42] One may expect that  $V \ll 2U$  in our case of  $\text{Mn}_4(\text{hmp})_6$  as well. In effect the second type of the electron transfer (i.e. from  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$ ) will dominate and one may neglect the first type of the transfer (from  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$ ). This is shown in Figs. 7-10 by arrows.

Moreover, the electron transfer from  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  back and forth costs also less charge transfer energy, since one needs to spend  $\Delta_{3+}$ , and as it was mentioned above  $\Delta_{3+} < \Delta_{2+}$ . Thus, we see that the charge order strongly modifies the electron transfer processes (and exchange processes as it will be shown below) and should be explicitly taken into account.

Secondly, since the  $3d$  shell in the case of the  $\text{Mn}^{2+}$  is half-filled and in  $\text{Mn}^{3+}$  is close to half-filling, i.e. to the situation where the energy gain due to the intra-atomic exchange coupling is maximal, one needs to properly count the number of the Hund's rule constants  $J_H$  for each electron transfer process. As we will see below this will additionally stabilize ferromagnetic contributions to the exchange coupling between  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$ .

We start with the calculation of the contributions coming from exchange coupling between  $t_{2g}$  orbitals on  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  ions. This term is nearly the same for  $J_1$  and  $J_2$ , since all considered orbitals are half-filled on all sites, while the angle dependence of the hoppings can be neglected in the first approximation:

$$J_{1,2}^{t_{2g}/t_{2g}} = \frac{2t_{pd\pi}^4}{\Delta_{3+}^2(V + 4J_H)} \equiv J_0. \quad (3)$$

This contribution is antiferromagnetic and  $J_0 > 0$ . The factor 2 appears because there are two pairs of the  $t_{2g}$  orbitals, which take part in this superexchange process (one of the pairs for  $J_1$  is shown in Fig. 7, while the another one will act via the second common oxygen).

The  $e_g/e_g$  contribution in the shared edge geometry is expected to be small, since the electrons are supposed to hop via almost orthogonal ligand  $2p$  orbitals, [23] and will not be considered here. In contrast the cross terms from the  $t_{2g}$  and  $e_g$  orbitals are of the great importance. They will be different for  $J_1$  and  $J_2$  because the single half-filled  $e_g$  orbital of  $\text{Mn}^{3+}$  is directed differently in the pairs providing  $J_1$  and  $J_2$  exchange couplings.

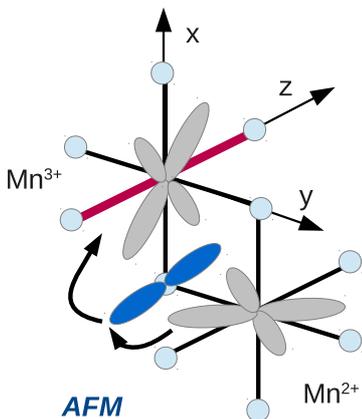


FIG. 7: (color online). The pair of the  $t_{2g}$  orbitals participating in the superexchange interaction between  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  in the case of the  $J_1$ . There will be the second pair for same ions, when the orbitals are interchanged and hopping occurs via the another common ligand. The ligands are shown as light blue circles, Mn  $3d$  orbital in grey, empty  $x^2 - y^2$  orbital in white, while ligand  $2p$  orbitals in blue. Here and in Fig. 8-10 arrows show the how the electrons move from one Mn to another.

There are two types of the  $t_{2g}/e_g$  contributions. One is the hopping from the half-filled  $e_g$  orbital of  $\text{Mn}^{2+}$  to the half-filled  $t_{2g}$  states of  $\text{Mn}^{3+}$  ( $t_{2g} \rightarrow e_g$ ) and back, see Fig.8(a). These terms are antiferromagnetic and the same for both  $J_1$  and  $J_2$ . However there is also the “opposite” process, hopping of  $e_g \rightarrow t_{2g}$ , from  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and back. Due to Jahn-Teller character of the  $\text{Mn}^{3+}$  ion, with its particular orbital occupation (one  $e_g$  electron of  $\text{Mn}^{3+}$  occupies  $3z^2 - r^2$  -orbital, where the local  $z$ -axis is directed along the long Mn-O bonds, see Fig. 1 and red bonds in Figs. 8,10), the contribution of this process would be different for  $J_1$  and  $J_2$ . This is explained in details below.

We start with  $J_1$ . If the local  $z$  axis is directed along the longest  $\text{Mn}^{3+}$ -O bond, then the  $x^2 - y^2$  orbital of  $\text{Mn}^{3+}$  must be empty, while the  $3z^2 - r^2$  orbital is half-filled. The expression for the exchange coupling between the half-filled  $x^2 - y^2$  orbital of  $\text{Mn}^{2+}$  and the half-filled  $xy$  orbital of  $\text{Mn}^{3+}$  is very similar to Eq. (3) with the only difference that here one of the  $t_{pd}$  hoppings is of the  $\sigma$  symmetry. Since according to Ref. 43 the hopping between the  $x^2 - y^2$  and  $p_x$  orbital is  $(\sqrt{3}/2)t_{pd\sigma}$  in the given geometry and  $t_{pd\sigma} \approx 2t_{pd\pi}$  [30]:

$$J_1^{xy/x^2-y^2} = \frac{3}{2} \frac{t_{pd\pi}^2 t_{pd\sigma}^2}{\Delta_{3+}^2 (V + 4J_H)} = 3J_0 \quad (4)$$

(since exchange occurs via two oxygens the prefactor equals  $2(\sqrt{3}/2)^2 = 3/2$ ). The orbitals providing this contribution are shown in Fig. 8(a). The exchange coupling given by Eq. (4) are antiferromagnetic.

The ferromagnetic contribution comes from the interaction between the half-filled  $xy$  orbital of  $\text{Mn}^{2+}$  and the empty  $x^2 - y^2$  orbital of  $\text{Mn}^{3+}$ , which are shown in

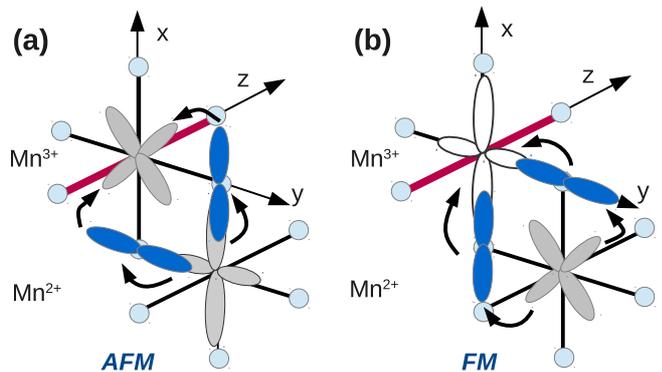


FIG. 8: (color online). Two  $t_{2g}/e_g$  contributions to the superexchange interaction between  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  in the case of the  $J_1$ . The antiferromagnetic contribution is presented in the left panel (a), while ferromagnetic in the right panel (b). The ligands are shown as light blue circles, half-filled Mn  $3d$  orbital in grey, empty  $x^2 - y^2$  orbital in white, ligand  $2p$  orbitals in blue. The long  $\text{Mn}^{3+}$ -O is shown in red.

Fig. 8(b). Finding the difference between total energies of ferromagnetic and antiferromagnetic solutions in the perturbation theory one gets that

$$J_1^{x^2-y^2/xy} = -\frac{3}{2} \frac{t_{pd\pi}^2 t_{pd\sigma}^2 4J_H}{\Delta_{3+}^2 V (V + 4J_H)} = -\frac{12J_0 J_H}{V}. \quad (5)$$

This type of the ferromagnetic terms described by the second Goodenough-Kanamori-Anderson rule [29, 36] are usually quite small because instead of the small  $V$  there appears  $U$ , which is much larger. In effect these contributions  $\sim 1/U^2$  are considerably smaller than the conventional antiferromagnetic superexchange, which is  $\sim 1/U$ . This is one of the reasons why the insulating transition metal oxides are mostly antiferromagnets. [44] Moreover typically the ferromagnets are the systems with the small  $U$  ( $\text{YTiO}_3$ , [45]  $\text{K}_2\text{Cr}_8\text{O}_{16}$ , [46]  $\text{Ba}_2\text{NaOsO}_6$ , [47] and etc.). Since, as was mentioned above, in the present system  $V$  is less than  $U$  this term turns out to be quite efficient. The multiplier  $4J_H$ , which appears in the numerator in Eq. (5) due to the high spin state of Mn ions, additionally increases this contribution.

The  $t_{2g}/e_g$  contributions to the  $J_2$  can be obtained in a similar manner. The antiferromagnetic coupling between the  $x^2 - y^2$  orbital of  $\text{Mn}^{2+}$  and  $t_{2g}$  orbital is exactly the same as in the case  $J_1$  [the difference is only in the notations: here the  $xz$  orbital is the active one, see Fig. 9(a)] and described by Eq. (4).

The ferromagnetic contribution is also similar, but the coefficients in expression for its value will be different. Due to different direction of the long Jahn-Teller  $\text{Mn}^{3+}$ -O bond only one of the lobes of the empty  $x^2 - y^2$  orbital of  $\text{Mn}^{3+}$  ion will be directed towards  $\text{Mn}^{2+}$ , see Fig. 9(b). As a result the ferromagnetic term will be just

$$J_2^{x^2-y^2/xy} = -\frac{3}{4} \frac{t_{pd\pi}^2 t_{pd\sigma}^2 4J_H}{\Delta_{3+}^2 V (V + 4J_H)} = -\frac{6J_0 J_H}{V}. \quad (6)$$

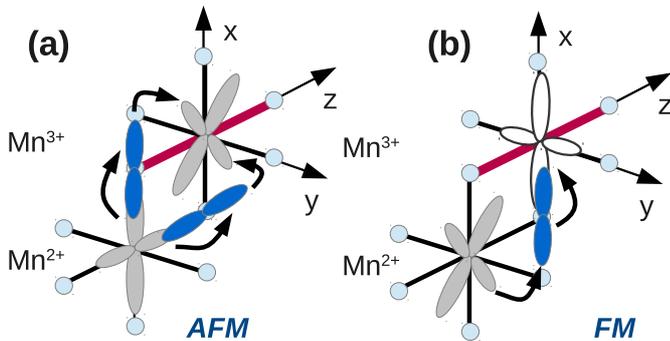


FIG. 9: (color online). Two  $t_{2g}/e_g$  contributions to the superexchange interaction between  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  in the case of the  $J_2$ . The antiferromagnetic contribution is presented in the left panel (a), while ferromagnetic in the right panel (b). The ligands are shown as light blue circles, half-filled Mn  $3d$  orbital in grey, empty  $x^2 - y^2$  orbital in white, ligand  $2p$  orbitals in blue. The long  $\text{Mn}^{3+}\text{-O}$  is shown in red.

In addition to the reduction of the ferromagnetic contribution for this pair (6) as compared to (5), there appears for this bond (due to different direction of the long  $\text{Mn}^{3+} - \text{O}$  bond) also an antiferromagnetic contribution from the hopping between the half-filled  $xz$  orbital of  $\text{Mn}^{2+}$  and the half-filled  $3z^2 - r^2$  orbital of  $\text{Mn}^{3+}$ , shown in Fig. 10:

$$J_2^{3z^2-r^2/xz} = \frac{2t_{pd\pi}^2 t_{pd\sigma}^2}{\Delta_{3+}^2 (V + 4J_H)} = 4J_0. \quad (7)$$

Since an opposite hopping from  $3z^2 - r^2\text{-Mn}^{2+}$  to  $xz\text{-Mn}^{3+}$  is also possible, the prefactor 2 appears in the last equation. Thus one may see that the ferromagnetic  $t_{2g}/e_g$  component of  $J_2$  turns out to be suppressed due to a specific orbital order induced by the Jahn-Teller distortions of the  $\text{Mn}^{3+}\text{O}_6$  octahedra, while the antiferromagnetic one is enhanced.

Combining above mentioned contributions one obtains, that

$$J_1 = \left(4 - \frac{12J_H}{V}\right)J_0, \quad (8)$$

$$J_2 = \left(5 - \frac{6J_H}{V}\right)J_0. \quad (9)$$

Thus  $J_1$  is ferromagnetic if  $V < 3J_H \sim 2.7$  eV. The estimations of  $V$  mentioned in Sec. IV A definitely satisfied this condition, so that  $J_1$ , as well as  $J_2$ , are expected to be ferromagnetic and  $|J_1| > |J_2|$ . However a care should be taken with  $V$  calculated in Ref. 41, 42, since in the present consideration  $V$  is not only the inter-site Coulomb repulsion, but it also includes the effects of the different local environment of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{3+}$  ions. In order to calculate  $V$  directly one may use the constrain calculations as proposed in Ref. 42. This lies beyond the scope of the present paper. Here we only provide the upper limit for the value of  $V$ .

One may extract the unscreened value of  $V$ , recalculating it as the center of the gravity difference for the  $3d$  bands of  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  in the LDA approximation. Since there is a different number of the  $d$  electrons on these two ions there will be different contributions from the on-site Coulomb repulsion  $U$  to these orbital energies. This correction can be written as  $(U - J_H)(n_d - 1/2)$  [22] in the case Mn ions, where  $n_d$  is the number of the  $d$  electrons per ion. Taking into account this correction, we obtained the unscreened value of  $V \sim 2$  eV, so that even in this situation  $J_1$  must be ferromagnetic. However, according to the Koopmans' theorem the orbital energies cannot be considered as excitation energies (in which we are interested), but are subjected to the orbital relaxation and electron correlation effects, which are the essence of the screening processes and which can be quite efficient. [48]

We would like to note that presented above expressions for the exchange integrals can only be used for the qualitative understanding of the exchange processes in the  $\text{Mn}_4$  molecular magnet. The ferromagnetic contributions from the overlap between empty and half-filled orbitals would be reduced by three factors. First of all one needs to take into account the crystal field splitting ( $\Delta_{CFS}$ ) between the  $t_{2g}$  and  $e_g$  shells in an appropriate way, which will modify the denominators in Eqs. (4)-(7) (e.g. in Eq. (4) one will need to substitute  $\Delta_{3+} \rightarrow \Delta_{3+} + \Delta_{CFS}$ ). Second, as is shown in Appendix A there are antiferromagnetic terms related with the correlation contribution to the exchange coupling and these terms are especially important in the case of  $J_2$ . Third, there will also be an additional contribution coming from the antiferromagnetic interaction between the half-filled  $t_{2g}$  orbitals and the “belt” of the  $3z^2 - r^2$  orbital (i.e.  $r^2$  part) through  $p$  orbital. Corresponding hopping is not small and equals  $t_{pd\sigma}/2$ . [43] This will provide additional contributions to Eqs. (4),(5) and (7) and modify Eqs. (8) and (9), but still leave the qualitative description of the exchange processes correct.

Finally it is worth to mention that for the quantitative estimation of different contributions one needs to know exact values of the model parameters such as  $J_H$  and  $V$ .

## B. $J_{bb}$ exchange

The same delocalization and correlation effects will be important for the exchange coupling between two  $\text{Mn}^{3+}$ , i.e. for the  $J_{bb}$  exchange constant. However, the sign and the value of the total exchange interaction may strongly depend on the details of the crystal structure: the Mn-O, Mn-Mn distances and the Mn-O-Mn bond angle. The detailed analysis of the  $J_{bb}$  does not seem to add much here, since first of all it represents the usual superexchange consideration for two  $\text{Mn}^{3+}$  ions, which can be found elsewhere (e.g. in Ref. 23), and, second, the value of  $J_{bb}$  is quite small.

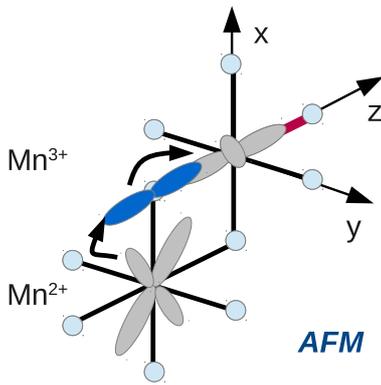


FIG. 10: (color online). The antiferromagnetic  $t_{2g}/e_g$  contributions to the superexchange interaction between  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  in the case of the  $J_2$ . The ligands are shown as light blue circles, half-filled Mn 3d orbital in grey, ligand 2p orbitals in blue. The long  $\text{Mn}^{3+}\text{-O}$  is shown in red.

## V. CONCLUSIONS

In the present paper we performed *ab initio* band structure calculations for the  $\text{Mn}_4(\text{hmp})_6$  molecular magnet within the density functional theory (DFT) using the GGA+U approximation. The exchange parameters for the Heisenberg model were extracted from the total energy calculations of several collinear spin configurations. In contrast to a common belief, one of the exchange constants for two pairs of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  ions (so called  $J_{wb}$ ) turns out to be the largest  $J_1 = -6.3$  K. Two other exchange couplings are  $J_2 = -0.5$  K (another two pairs of  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  ions) and  $J_{bb} = -0.3$  K (between the  $\text{Mn}^{3+}$  ions).

The microscopic analysis based on the fourth order perturbation theory allowed to establish the mechanism of the strong exchange coupling along the  $J_1$  exchange path. Conventional superexchange between two Mn ions in the edge sharing geometry is enhanced in  $\text{Mn}_4(\text{hmp})_6$  by the charge order. The charge disproportionation leads to the situation, in which the lowest virtual excitations, contributing to the superexchange, will be not those across the Hubbard gap  $\sim U$ , but will be those between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ , which cost much smaller energy: the energy  $V$  ( $\ll U$ ) stabilizing the charge ordered state. As a result the exchange coupling between the empty  $x^2 - y^2$  orbital of  $\text{Mn}^{3+}$  and the half-filled  $t_{2g}$  orbitals of  $\text{Mn}^{2+}$ , according to the second Goodenough-Kanamori-Anderson rule [29], turns out to be quite effective and stabilizes ferromagnetic coupling along the  $J_1$  exchange paths.

In addition to charge order, there is an orbital order in  $\text{Mn}_4(\text{hmp})_6$ , which also has influence on the exchange interaction in this system. The direction of the long Jahn-Teller Mn-O bond in the  $\text{Mn}^{3+}\text{O}_6$  octahedra defines the orientation of the empty  $x^2 - y^2$  orbital. This in turn regulates the absolute values of the exchange coupling between different  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  pairs making one of

them ( $J_1$ ) larger than the other ( $J_2$ ).

It is also important that the energy of the first excited state in the exchange process for the ferromagnetic state is reduced by a strong intra-atomic Hund's rule exchange coupling. This is a feature of the  $\text{Mn}^{3+}$  ion with  $d^4$  electronic configurations that has one empty 3d orbital and the energy difference between  $(d \uparrow)^5$  and  $(d \uparrow)^4(d \downarrow)^1$  states is  $4J_H$ . For any other configuration ( $d^3$ ,  $d^2$  etc.) this energy difference between the excited states, according and against Hund's rule, will be smaller.

The exchange constants calculated in the GGA+U approximation were used for the solution of the quantum Heisenberg model for the given geometry. The magnetic susceptibility obtained by the exact diagonalization method reasonably agrees with the experimentally observed data. This additionally supports the results obtained by the DFT methods. The agreement between theoretical and experimental data may be further improved by "educated" fitting, i.e. fitting, which uses exchange constants obtained in the GGA+U approximation as a starting point. The account of the single ion anisotropy on the  $\text{Mn}^{3+}$  sites also makes the agreement better. Although the exchange constants obtained by this fitting are somewhat different from those calculated in the GGA+U ( $J_{bb}^{fit,D} = -0.3$  K,  $J_1^{fit,D} = -3.6$  K,  $J_2^{fit,D} = -0.4$  K,  $D^{fit,D} = -0.2$  K), the general tendency is the same:  $J_1$  is the largest exchange coupling.

One of the questions, which arises is whether it is possible to increase the values of the ferromagnetic exchanges in the  $\text{Mn}_4$  molecular magnets, and what recipes one may provide on the basis of the microscopic model developed in the present study. The substitution of all Mn ions by Co, Ni, Cu ions would result in absence of the empty  $e_g$  orbitals, while changing Mn on Ti or V one reduces the energy gain due to the Hund's rule coupling. From this point of view the pair  $\text{Cr}^{3+}$  ( $t_{2g}^3$ ) and  $\text{Cr}^{2+}$  (Jahn-Teller ion  $t_{2g}^3 e_g^1$ ) could look more promising, if one could stabilize  $\text{Cr}^{2+}$  (which is usually not easy). One may also expect some variations of the exchange constants if the  $\text{Fe}^{4+}$  and  $\text{Fe}^{3+}$  instead of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  ions will be used, since the intersite Coulomb repulsion, which contributes significantly to the energy of the charge ordered state stabilization was reported to be quite small for one of the Fe compounds. [42] The substitution of the rare-earth elements instead of the transition metal ions may lead to a significant gain in the Hund's rule energy, but it will simultaneously decrease the hopping integrals  $t$ .

Alternatively one may try to use not 3d, but 4d or 5d-elements. These typically have low-spin states with (most of) electrons in  $t_{2g}$  shell and with  $e_g$  states often empty and much smaller  $U$  (than 3d counterparts). Then one could expect enhancement of ferromagnetic  $t_{2g} \rightarrow$  empty  $e_g$  contribution. Unfortunately the crystal field splitting between  $t_{2g}$  and  $e_g$  levels for the 4d and 5d are usually larger and also the moment of respective ions are smaller than e.g. those of  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ . [17, 49, 50]

Yet another option, which can be proposed, is the substitution of the oxygen by the another ligand, e.g. sulfur.

The charge transfer energy  $\Delta_{CT}$  for the  $S^{2+}$  ions is much smaller than for  $O^{2+}$ , [38] so that if it were chemically possible to substitute some of the oxygens by sulphurs. This may lead to increase of the exchange coupling.

## VI. ACKNOWLEDGMENTS

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### Appendix A: Correlation contribution to $J_1$ and $J_2$

Very similar analysis can be performed for the correlation contributions to the  $J_1$  and  $J_2$  exchange parameters. Below we briefly discuss them and present some of the formulas.

Since as was mentioned in Sec. IV A the charge transfer energy from O  $2p$  to  $Mn^{2+}$   $3d$  shell ( $\Delta_{2+}$ ) is much larger than from O  $2p$  to  $Mn^{3+}$   $3d$  shell ( $\Delta_{3+}$ ) one may take

into account only a part of the correlation contributions related with the charge transfer energy  $\Delta_{3+}$ , i.e. the processes, when the first excitation occurs to the  $3d$  shell of  $Mn^{3+}$ . We will also neglect the terms describing the exchange coupling via orthogonal  $p$  orbitals, which are of order or  $(t_{pd}^4/\Delta_{3+}^2)(J_H^p/(\Delta_{3+} + \Delta_{2+} + U_{pp})^2)$ , where  $J_H^p$  is the Hund’s rule coupling on the oxygen ion, while  $U_{pp}$  is the Coulomb repulsion between two holes in the  $p$  shell of oxygen.

The correlation contributions from the half-filled  $t_{2g}$  orbitals will be antiferromagnetic and the same for  $J_1$  and  $J_2$ :

$$J_{1,2}^{t_{2g}/t_{2g}} \sim \frac{2t_{pd\pi}^4}{\Delta_{3+}^2} \frac{1}{(\Delta_{3+} + \Delta_{2+} + U_{pp})}. \quad (A1)$$

In the case of  $J_1$  the terms describing the correlation exchange between the empty  $x^2 - y^2$  orbital on the  $Mn^{3+}$  ion and the half-filled  $t_{2g}$  orbitals of the  $Mn^{2+}$  and between half-filled  $t_{2g}$  orbitals on the  $Mn^{3+}$  and the half-filled  $e_g$  orbitals of the  $Mn^{2+}$  have different signs and nearly cancel each other out.

The direction of the Jahn-Teller distortion of the  $Mn^{3+}O_6$  octahedra coincides with one of the  $Mn^{3+}-O$  bond forming the  $Mn^{3+}-Mn^{2+}$  bond in the case of the  $J_2$  exchange coupling. This upsets the delicate balance between ferromagnetic and antiferromagnetic  $t_{2g}/e_g$  terms and makes this contribution antiferromagnetic

$$J_2^{t_{2g}/e_g} \sim \frac{3}{4} \frac{t_{pd\pi}^2 t_{pd\sigma}^2}{\Delta_{3+}^2} \frac{1}{(\Delta_{3+} + \Delta_{2+} + U_{pp})}. \quad (A2)$$

This antiferromagnetic term additionally decreases the ferromagnetic contribution to  $J_2$  given in Eq. (6).

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