Orbital structure and magnetic ordering in stoichiometric and doped crednerite CuMnO$_2$

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The exchange interactions and magnetic structure in layered system CuMnO$_2$ (mineral crednerite) and in nonstoichiometric system Cu$_{0.94}$Mn$_{0.06}$O$_2$, with triangular layers distorted due to orbital ordering of the Mn$^{3+}$ ions, are studied by ab initio band-structure calculations, which were performed within the GGA $+U$ approximation. The exchange interaction parameters for the Heisenberg model within the Mn planes and between the Mn planes are estimated. We explain the observed in-plane magnetic structure by the dominant mechanism of the direct $d$-$d$ exchange between neighboring Mn ions. The superexchange via O ions, with 90$^\circ$ Mn–O–Mn bonds, plays a less important role for the in-plane exchange. The interlayer coupling is largely dominated by one exchange path between the half-filled $3z^2 - r^2$ orbitals of Mn$^{3+}$. The change of interlayer coupling from antiferromagnetic in pure CuMnO$_2$ to ferromagnetic in doped material is also explained by our calculations.

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I. INTRODUCTION

Magnetic systems with geometric frustrations attract considerable attention nowadays. Due to competition of different exchange paths often rather complicated magnetic structures are realized, which are very sensitive to external influences and can be changed, e.g., by small modifications of composition.

There exist many magnetic materials containing the triangular layers as a main building block [1]. Among them there are well-known systems like NaCoO$_2$ [2]; delafossites AMeO$_2$ ($A =$ Cu, Ag, Pd, . . . ; Me–transition metals), such as multiferroic CuFeO$_2$ or AgCrO$_2$ [3,4]; compounds with unusual charge states like Ag$_2$NiO$_2$ [5]; ferroaxial multiferroic FeRb(MoO$_3$)$_2$ [6]; and even some organic systems with spin-liquid ground states [7,8]. A regular triangular lattice with equal triangularities is frustrated, which can lead to complicated ground states, especially in the presence of strong magnetic anisotropy. Such frustrations could in principle be lifted due to lattice distortion, for example caused by orbital ordering [9,10] (which, on the other hand, can itself lead to frustration in some not even geometrically frustrated lattices [9,11]). However, in certain cases frustrations can remain even after such orbital ordering.

Apparently, an example of this type is delafosfite CuMnO$_2$ (mineral crednerite). The crystal structure of CuMnO$_2$ is shown in Fig. 1. Two features, disclosed by the experimental studies of stoichiometric CuMnO$_2$ [12,13] and similar systems with an excess of Cu, Cu$_{0.94}$Mn$_{0.06}$O$_2$ [14], are quite nontrivial and require explanation. First, the presence of the Jahn-Teller Mn$^{3+}$ ($t^2_{2g}e^1_g$) ions in this system leads to a change of the crystal structure (with corresponding ferro-orbital ordering) from the usual for delafosfite rhombohedral $R$$_3$$m$ to a monoclinic $C2/m$ structure already at room temperature. In this structure different directions in the triangular $ab$ plane become inequivalent: there exist for each Mn two short and four long Mn–Mn distances in the plane. This in principle could lift frustration, if the antiferromagnetic (AFM) exchange $J_1$ on the long Mn–Mn bonds would be stronger than the exchange $J_2$ on the short ones: then the topology of the plane would essentially become that of a square lattice [Fig. 2(a)].

However, experimentally it turned out that this is not the case: apparently, the exchange at short bonds is stronger, which, with the uniaxial magnetic anisotropy of Mn$^{3+}$ (spins are oriented predominantly along the long Mn–O bonds), still leaves the system frustrated [the stacking of the antiferromagnetic chains along the short Mn–Mn direction is frustrated for equivalent long bonds which couple such chains; see Fig. 2(b)]. According to Ref. [12] this degeneracy is lifted below magnetic transition: at $T < T_N = 65$ K the structure changes from monoclinic to triclinic $C1$ due to magnetostriction (note that in this group the interlayer direction is $b$, see Fig. 1).

The first question is why indeed the exchange coupling along the short Mn–Mn bond is stronger. At first glance it seems very natural: exchange interaction is expected to be stronger for the shorter bond. However, besides the direct Mn–Mn exchange due to the overlap of the $d$ orbitals of Mn, usually also the superexchange via oxygen plays an important role, especially for the heavier 3d elements, and one could expect that for the ferro-orbital ordering like that found in CuMnO$_2$ this contribution could be stronger for longer Mn–(O)–Mn bonds (see details below). Why this is not the case is a priori not clear.

Another surprising phenomenon was found in non-stoichiometric crednerite with a small excess of copper, Cu$_{0.4}$Mn$_{0.6}$O$_2$, with part of the in-plane Mn substituted by Cu. It was found in Ref. [14] that, whereas the in-plane magnetic ordering (and magnetostrictive distortions) remains practically the same as for pure CuMnO$_2$, the interlayer exchange coupling changes to the opposite: if it was antiferromagnetic in CuMnO$_2$, it becomes ferromagnetic in Cu$_{0.4}$Mn$_{0.6}$O$_2$ [16]. Interlayer coupling is not often treated seriously in the study of such layered frustrated systems; it is usually considered rather as a nuisance (although of course everyone understands that some such interlayer coupling is required to make a real three-dimensional long-range magnetic ordering). Here, however, we have to seriously address the question of such interlayer coupling and its dependence on the exact composition of the material.

To explain the observed features, one has to know the values of exchange interaction between different Mn–Mn pairs, both
The results of our calculations, first of all, confirm that the experimentally observed magnetic structure is the theoretical ground state and also confirm the results of the previous first-principles calculations [18] for the stoichiometric case. The analysis shows that the hopping between the $3z^2 - r^2$ and $xy$ orbitals and the direct hopping between $xy$ orbitals should give the main contribution to the $J_2$ exchange, and this AFM exchange turns out to be much stronger than $J_1$, leading to the magnetic structure observed experimentally. The interlayer ordering from the calculations also coincides with that observed experimentally. For the nonstoichiometric CuMnO$_2$ the in-plane ordering remains the same, whereas the interlayer ordering changes to the opposite, in agreement with the findings of Ref. [14]. We discuss the physical mechanism of this change.

## II. Calculation details

The calculations were carried out by the pseudopotential method in the PWSCF code [19] in the framework of the density-functional theory (DFT). We used the Vanderbilt ultrasoft pseudopotentials for all ions; $3d$, $4s$, and $4p$ for Cu and Mn and $2s$ and $2p$ states for O were considered as valence. The plane-wave cutoff energy for these pseudopotentials was taken be 40 Ry. The strong electronic correlations were included on Mn sites via the GGA + $U$ approximation [20]. Effective $U_{	ext{eff}} = U - J_H$ for the Mn 3$d$ states was chosen to be 4.1 eV [21]. We checked that main conclusions do not depend on the choice of $U_{	ext{eff}}$, and we also present the results for $U_{	ext{eff}} = 3.6$ eV.

The integration in the course of self-consistency iterations was performed over a mesh of 256 $k$ points in a whole part of the Brillouin zone, switching off the symmetry of the space group to allow any possible orbital order. We used the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [22].

In order to estimate the exchange interaction parameters within the Mn triangular layers and the interlayer exchange we calculated the total energies of different magnetic configurations and used the Heisenberg model in the form

$$H = \sum_{ij} J_{ij} S_i S_j,$$

where summation runs twice over each pair. The in-plane exchange constants $J_1$ and $J_2$ (see Fig. 2) were recalculated from the total energies of three magnetic structures: (1) fully ferromagnetic, (2) Mn ions along the short (long) Mn–Mn bond ordered ferromagnetically (antiferromagnetically), and (3) Mn ions along the short Mn–Mn bonds antiferromagnetically coupled. The unit cell contains 4 f.u. In the low-temperature (LT) phase the exchange parameters $J_1$ along two long Mn–Mn bonds were assumed to be the same, since the difference of the bond lengths is quite small, $\sim 0.02$ Å. For the calculation of the exchange constants along the $b$ axis the unit cell was doubled in this direction and the magnetic ordering in plane was chosen as in the experiment (ferromagnetic chains are going along the longest Mn–Mn bond).

The lattice parameters (unit cell and atomic coordinates) used in the calculations were taken from the experimental data of Refs. [12–14] for 300 K [high-temperature (HT) phase] and for 10 K (LT phase).
III. RESULTS AND DISCUSSION

The first-principles calculations of the stoichiometric CuMnO₂ were performed for the HT and LT phases. The magnetic moment on Mn³⁺(d⁷) is close to 3.7 μ₀ in both phases (3.68 μ₀ in the LT and 3.74 μ₀ in the HT phase). The occupancy of the 3d shell for the interlayer linearly coordinated Cu⁺ was found to be 9.73 in the LT and 9.71 in the HT phase. This is close to the d¹⁰ configuration expected from the simple ionic consideration. The Mn³⁺ ion has 5.58 (5.54) electrons in the LT (HT) phase. The deviation from the nominal filling d⁴ is related to the hybridization effects as discussed below.

According to the GGA + U calculations CuMnO₂ is a metal at the HT phase in the ferromagnetic configuration, while at lower temperatures in the experimental [12] AFM magnetic structure the energy gap opens, E₉ = 0.2 eV, and the system becomes insulating. We found that such magnetic order, with the AFM stripes in the Mn plane and the AFM arrangement along the crystallographic b axis [Fig. 2(b)], is the ground state in the LT phase with the lowest total energy.

The partial Cu 3d, Mn 3d, and O 2p densities of states for the LT phase are presented in Fig. 3. One can see that the Mn d states are lower and broader than the Cu 3d ones, which are closer to the Fermi level. A substantial hybridization between the Mn 3d and O 2p states is noticeable. Because of the hybridization the occupation of the 3d shell of Mn is larger than the nominal, but the spin moment is consistent with the d⁷ configuration (3.7 μ₀).

The structural distortions caused by the Jahn-Teller character of the Mn³⁺ and orbital ordering result in the structure with two types of inequivalent Mn–Mn pairs in the MnO₂ plane: those along the a direction, with the short Mn–Mn distance of 2.88 Å, and the long bonds in two other directions, with the Mn–Mn distance of ∼3.14 Å (they become inequivalent in the magnetically ordered phase; see Fig. 2). In effect one may expect that the exchange coupling in the ac plane can be characterized by two exchange constants: J₂ (short Mn–Mn bonds) and J₁ (long Mn–Mn bonds). The direct calculation in the GGA + U approximation shows that J₁ = −1.5 K (FM) and J₂ = 16.5 K (AFM).

The MnO₂ octahedra in the basal triangular layer have a common edge, so that the Mn–O–Mn angle is close to 90°. There exist in this geometry several contributions to the nearest-neighbor magnetic coupling. First, there is a direct hopping between the Mn orbitals, especially t₂g ones, with the lobes directed toward one another [see Fig. 4(a)]. This contribution must be antiferromagnetic. The direct exchange is known to be quite efficient for the first few 3d transition-metal ions, but it gradually decreases going from left to right in the periodic table, and already for Cr and Mn the superexchange may become larger [17].

Let us consider contributions to the superexchange via O ions, some of which are illustrated in Figs. 4(b) and 4(c) (see more details, e.g., in Ref. [17]). For such a Mn–O–Mn 90° bond, according to Goodenough-Kanamori-Anderson rules (GKA) [23,24], the superexchange between the half-filled t₂g orbitals via oxygens will be also antiferromagnetic, ~ t₉₂g/U₂p(1/2 + Δ/2Δ₂p), where Δ is the charge-transfer energy [energy of the excitation, in our case, Mn³⁺(d⁷)O²⁻(2p⁰) → Mn²⁺(d⁵)O⁻(2p⁵)], and U₂p is the repulsion of oxygen p electrons.

Potentially, though, the most important contribution to the Mn–Mn exchange via oxygens could be the t₂g–e₉ exchange, which, for the hopping to the half-filled e₉ orbital, is antiferromagnetic, and could be quite strong, ~ t₉₂g/e₉(1/2 + Δ/2Δ₂p).
In the pair of the MnO$_6$ octahedra forming the long Mn–Mn bond the single half-filled $e_g$ orbital ($2z^2 - x^2 - y^2$) will lie in the plane defined by a common edge and two Mn ions and will take part in such an exchange process as shown in Fig. 4(c). Thus, this contribution will be stronger for the longer Mn–Mn bond. This is what we had in mind in Sec. I, where we mentioned that superexchange may lead to the situation in which $J_1$ would be stronger than $J_2$, but this not the case and direct exchange obviously dominates.

It has to be mentioned again that, actually, it is a priori not clear whether the direct $d$-$d$ exchange on a short Mn–Mn bond or the superexchange via oxygens on the long bonds would be stronger. In the second case we would have expected that the magnetic ordering would be simple two-sublattice antiferromagnetism in an effective square lattice formed by the long Mn–Mn bonds [Fig. 2(a)]; it can also be viewed as the stripe ordering in the original triangular lattice, but with stripes of parallel spins running along short bonds, not along long ones, as in Fig. 2(b)]. Note that such a situation is indeed realized on some triangular lattices, e.g., in NaVO$_2$ [25] (in this case the orbital ordering and the direct $d$-$d$ exchange relieve geometric frustration).

There exist also other contributions to the nearest-neighbor exchange, e.g., those involving one occupied and one empty orbital; according to the GKA rules, these processes would give ferromagnetic contribution, but weaker by the factor of $\frac{1}{4}$ or $\frac{1}{8}\pi$. Still, there are many such exchange channels, so that the total contribution of these processes can be significant.

The results of our ab initio calculations give an answer to the question raised above; it turns out that the antiferromagnetic exchange $J_2$ on the short Mn–Mn bond is stronger than the superexchange contributions on the long bonds. Apparently, the rather short Mn–Mn distance (2.88 Å) on a short bond makes direct $t_{2g}$ exchange dominant, but the superexchange between $e_g$ and $t_{2g}$ orbitals via oxygen should also be important.

In order to estimate the interlayer exchange interaction parameters and also to simulate the doped system Cu$_{1+x}$Mn$_{1-x}$O$_2$ we used the supercell with eight inequivalent Mn ions. Two different magnetic configurations were calculated. In both structures Mn ions constituting short in-plane Mn–Mn bonds were antiferromagnetically coupled, while the interlayer spin order was taken different, either ferromagnetic or antiferromagnetic [16]. The calculated exchange constant $J_{\text{inter}} = 0.8$ K (AFM) reproduced the observed interlayer ordering for undoped CuMnO$_2$ [13,18]. The main contribution to the interlayer exchange is given by the process illustrated in Fig. 5.

The strongest exchange path goes from the occupied (half-filled) $3z^2-r^2$ orbital of the Mn ion in one layer, where the local $z$ axis is directed along the long Mn–O bond, via corresponding oxygen $2p$ orbitals and eventually diamagnetic Cu$^{1+}$ sitting in between layers, and then to the similar $3z^2-r^2$ orbital of one particular Mn in the next layer [see Fig. 5(a)]. This exchange coupling is antiferromagnetic, which provides the antiferromagnetic coupling between layers observed for CuMnO$_2$ [12]. Note that the Mn ions connected by this exchange path do not belong to one unit cell; i.e., one must be careful in comparing the obtained magnetic ordering with the experimental one (which is defined in Ref. [12] in terms of relative orientation of crystallographically equivalent Mn ions in neighboring layers).

As it was mentioned above, the same (as for pure CuMnO$_2$) supercell consisting of the eight Mn ions was used to simulate the magnetic properties of the nonstoichiometric Cu$_{1+x}$Mn$_{1-x}$O$_2$ with $x = 0.04$. Since the exact position of the doped Cu$^{2+}$ in the Mn$^{3+}$ plane is unknown, the virtual crystal approximation was used: an extra 0.32 holes were added in the calculations of the aforementioned supercell. This corresponds to the uniform distribution of this hole over a whole cell.

The occupations of the 3$d$ shell of the Cu and Mn ions in the doped system are slightly different from the stoichiometric case, being 9.71 and 5.55, respectively. The magnetic moment on Mn in the triangular plane is 3.69 $\mu_B$. The occupations for different 3$d$ orbitals are the same as in pure CuMnO$_2$. The interlayer exchange for $x = 0.04$ was found to be $J_{\text{inter}} = -1.8$ K, ferromagnetic, instead of an antiferromagnetic interlayer coupling of $+0.8$ K for the undoped compound. The intralayer exchanges are $J_1 = -6.4$ K and $J_2 = -14.6$ K. Thus, our calculations fully reproduce experimentally observed changes of the sign for the interlayer exchange coupling [14]. This can be explained in the following way: when we substitute some Mn ions by Cu$^{2+}$ (formally trivalent Cu$^{3+}$ is rather difficult to obtain, and it cannot be formed at these conditions, which is confirmed by our calculations), we induce two changes. One is that Cu$^{3+}$ itself is magnetic and has a different orbital occupation, so that for some ions the same exchange path from the $3z^2-r^2$ orbital of the Mn in the lower plane would connect to Cu$^{2+}$ in the neighboring plane, for which the $3z^2-r^2$ orbital will be completely filled. The $d$ hole will be, as always, on the $x^2-y^2$ orbital. Due to different orbital occupation this exchange would be ferromagnetic, in accordance with the GKA rules.

Another consequence of the substitution of Mn$^{3+}$ by Cu$^{2+}$ is that to guarantee electroneutrality one Mn ion per each...
Cu should become Mn$^{4+}$. These Mn$^{4+}$ ions, e.g., in the upper layer, would couple to Mn$^{3+}$ in the lower layer also ferromagnetically [see Fig. 5(b)]. Besides, as just explained, each Cu$^{2+}$ in the triangular layer, as well as each Mn$^{4+}$, would couple ferromagnetically to both the layer above and the layer below. Thus, effectively each extra Cu$^{2+}$ would make four interlayer bonds ferromagnetic instead of antiferromagnetic. Apparently, all these factors combine to lead to the inversion of the interlayer magnetic ordering in nonstoichiometric crednerite with the excess of Cu, and the fact that already a very small amount of excess copper, only 4% in Cu$_{1.04}$Mn$_{0.96}$O$_2$ studied in Ref. [14], is sufficient to lead to this inversion of interlayer ordering is probably connected with the factors discussed above: that effectively every extra Cu changes sign of the exchange of four interlayer bonds to the opposite, so that the effective doping is not 4%, but is rather $\sim$16% (i.e., 16% of the strongest interlayer bonds change sign).

There may be also other factors contributing to the same effect. Notably, it is known, e.g., on the example of CMR manganites, that the substitution of Mn by other ions with different valence can modify the in-plane magnetic ordering in a rather large region around the dopant [26]. It is not excluded that also here the in-plane ordering could be modified close to Cu$^{2+}$ and especially to Mn$^{4+}$, which should be created simultaneously. The interaction of this distorted region in a given plane with the next plane with its, say, original ordering could also have the opposite sign from the interaction of two “virgin” planes. The eventual presence of magnetic distortions due to doping in CuMnO$_2$ should be checked by special experiments (the simplest indication of that would be certain broadening of magnetic reflexes in nonstoichiometric crednerite as compared to those in pure CuMnO$_2$ or ESR measurements).

It is worth mentioning that the results obtained in the present investigation do not strongly depend on the value of on-site Hubbard repulsion $U_{\text{eff}}$. In order to check $U$ dependence we performed additional calculations with smaller $U_{\text{eff}} = 3.6$ eV. The decrease of the $U_{\text{eff}}$ leads to the increase of the AFM contributions to the intralayer exchange coupling, which are known to be $\sim U^2/3$. As a result, both in-plane exchanges become more AFM: $J_1$ equals 21.0 and 17.2 K, while $J_2$ is $\sim$0.2 and $\sim$5.1 K for pure CuMnO$_2$ and nonstoichiometric cases, respectively. For $U_{\text{eff}} = 3.6$ eV the interlayer exchange coupling changes its sign, going from CuMnO$_2$ ($J_{\text{inter}} = 0.6$ K) to Cu$_{1.04}$Mn$_{0.96}$O$_2$ ($J_{\text{inter}} = -1.1$ K) as for $U_{\text{eff}} = 4.1$ eV.

The results obtained in the present paper agree with the conclusions of Ref. [27], where it was shown that the magnetic properties of CuMnO$_2$ strongly depend on what kind of dopant is used: magnetic Cu$^{2+}$ with a not completely filled 3$d$ shell or nonmagnetic Ga$^{3+}$. In the first case the interlayer coupling changes to the opposite, while in the second it remains the same (antiferromagnetic). This demonstrates that this change is not due to a modification of the crystal structure but is connected with the substitution of Mn$^{3+}$ by magnetic Cu$^{2+}$, with the generation of another magnetic ion Mn$^{4+}$, as explained above.

IV. CONCLUSION

In conclusion, on the basis of ab initio band-structure calculations we obtained a physical picture which explains experimentally observed stripy antiferromagnetic order in stoichiometric crednerite CuMnO$_2$, as well as in the system with an excess of Cu, Cu$_{1+x}$Mn$_{1-x}$O$_2$. Ferro-orbital ordering present in this system plays a very important role in determining the exchange constants and finally the magnetic structure. We argue that the in-plane magnetic ordering is mainly provided by the direct exchange interaction between the $t_{2g}$, while superexchange between $e_g$ and $t_{2g}$ orbitals on different sites is expected to be smaller. The interlayer exchange is mainly given by the exchange path involving the half-filled $e_g$ orbitals of Mn$^{4+}$. Substitution of a part of Mn$^{3+}$ by Cu$^{2+}$, with corresponding creation of compensating Mn$^{4+}$ ions, leads to the inversion of the interlayer coupling for already rather small doping, which explains the puzzling experimental observation of Poienar et al. in Ref. [14].

The obtained results once again demonstrate the importance of orbital ordering for magnetic structures, this time in a frustrated system. It also shows that such systems are very sensitive to even small variations of conditions, e.g., small doping, and their properties can be effectively modified even by small perturbations.

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These notions require some explanation; they are not self-evident for triangular lattices with antiferromagnetic ordering in the layer. By antiferromagnetic or ferromagnetic interlayer ordering, one has in mind the orientation of Mn ions in a corresponding unit cell, lying in different layers and connected by the lattice vector (010).