# Orbital Ordering in a Two-Dimensional Triangular Lattice

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We discuss the role of orbital ordering in a two-dimensional triangular lattice. Usually, this lattice is considered as "frustrated." We show that a peculiar type of orbital ordering can remove this frustration if we allow for orbital degeneracy. We pay special attention to the $d^2$ case, for which we present mean field calculations for possible orbital orderings and an exact diagonalization study of a three-site cluster within a degenerate Hubbard model. The results support the possibility of an orbitally ordered singlet ground state. In particular, it provides new insight to the magnetic phase transition and the low temperature phase of $LiVO_2$. [S0031-9007(97)02453-8]

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Transition metal (TM) compounds are well known for their large diversity and richness in physical phenomena. The flurry of activity in the field of high-$T_c$ superconductors has as yet not culminated in an understanding of their origin, but has opened up a Pandora's box of new effects in sometimes old "well understood" compounds: the colossal magnetoresistance in $La_{1-x}Ca_xMnO_3$ [1], the spiral spin fluctuations in the paramagnetic phase of $V_2O_3$ [2], the temperature dependent high energy scale spectral weight transfer in $V_2O_3$ [3], and the peculiar charge ordering in $La_2Sr_{2-x}NiO_4$ [4] and related materials. This richness of properties is due to the strongly correlated nature of the $3d$ states in these systems, often rendering them magnetic, and to the strong hybridization with the extended ligand valence states.

Another very important aspect is the orbital degeneracy of open $3d$ shells. In a localized system such orbital degeneracy will be lifted at low temperatures in one way or another: this is the well-known Jahn-Teller effect [5]. In concentrated systems it often leads to structural phase transitions accompanied by a certain ordering of occupied orbitals. Such orbital ordering may be driven by other factors than lattice distortions, e.g., by exchange interactions [6]; of course, the lattice always follows to some extent. The strongest effects of this kind are observed in TM compounds with a twofold $e_g$ orbital degeneracy [e.g., those containing $Mn^{3+}(d^4)$, $Co^{2+}(d^7)$, or $Cu^{2+}(d^9)$ in octahedral coordination]. Some well-known examples are the $Mn^{3+}$ spinels, $LaMnO_3$, and $KCuF_3$ [6].

In this Letter, we discuss the very interesting situation that may exist in systems with partially filled $t_{2g}$ shells, in which orbital ordering can drive the system into a spin-singlet state without any long-range magnetic order. Specifically, we describe in this Letter a new class of orbitally ordered systems involving threefold degenerate orbitals in a triangular two-dimensional lattice. This model is relevant for a class of $d^1$ and $d^2$ TM compounds, including $LiVO_2$, $NaTiO_2$, and titanium halides, which are often regarded as model systems for the triangular lattice Heisenberg antiferromagnet. These materials contain quasi-two-dimensional hexagonal TM cation layers, the cation $3d$ states being split into doubly degenerate $e_g$ and triply degenerate $t_{2g}$ levels, due to a ligand field of approximate $O_H$ symmetry.

The triangular lattice Heisenberg antiferromagnet is interesting because of the frustration present in this system. Especially, it has attracted much attention since Anderson [7] pointed out the possibility of a "resonating valence bond" (RVB) ground state for the $S = \frac{1}{2}$ case. This quantum liquid of randomly distributed spin singlet pairs could be a way to overcome the frustration that is present in the Néel state of the triangular antiferromagnet. For larger spins one could expect some kind of long-range magnetic order, e.g., triangular order of the Yafet-Kittel type [8]. This occurs in $LiCrO_2$ which has a $(t_{2g})^3$ configuration (i.e., a half-filled level, without orbital degeneracy).

However, in case of orbital degeneracy, which is not considered in the Heisenberg model, the situation may be drastically different. An orbital ordering may occur which makes the exchange interaction strongly nonuniform, thereby invalidating the standard Heisenberg model. We will illustrate this by considering a hexagonal plane, each site consisting of a threefold degenerate $t_{2g}$ level. In this particular crystal structure, the exchange interactions are mainly due to direct $t_{2g}$-$t_{2g}$ overlap [8]. An estimate of the superexchange interactions via oxygen shows that these are, for reasonable parameter values, about an order of magnitude smaller than the direct exchange. We describe the system by a degenerate Hubbard model; unlike the Heisenberg model, it takes into account the dependence of exchange interactions on the particular orbital occupation. The Hamiltonian is

$$H = -\sum_{i}(U_u + J_H) + \sum_{i,\alpha,\sigma} U_e c^{i\dagger}_{\alpha\sigma} c^{i\dagger}_{\alpha\bar{\sigma}} c^{i}_{\alpha\sigma} c^{i}_{\alpha\bar{\sigma}} + \sum_{\substack{i,\alpha,\beta,\sigma,\sigma' \\ \beta\neq\alpha}} (U_u c^{i\dagger}_{\alpha\sigma} c^{i\dagger}_{\beta\sigma'} c^{i}_{\alpha\sigma} c^{i}_{\beta\sigma'} + J_H c^{i\dagger}_{\alpha\sigma} c^{i\dagger}_{\beta\sigma'} c^{i}_{\alpha\sigma'} c^{i}_{\beta\sigma}) + \sum_{\substack{\langle i,j\rangle \\ \alpha,\beta,\sigma}} t_{ij}(\alpha,\beta) c^{i\dagger}_{\alpha\sigma} c^{j}_{\beta\sigma}, \tag{1}$$

where $c^{i\dagger}_{\alpha\sigma}$ and $c^{i}_{\alpha\sigma}$ are the usual creation and annihilation operators for an electron on site $i$, in orbital $\alpha \in \{d_{xy}, d_{yz}, d_{zx}\}$ with spin $\sigma$. $U_e$ and $U_u$ are Coulomb integrals for orbitals of equal and unequal spatial symmetry, and $J_H$ is the intra–atomic Hund's rule exchange energy. The last (intersite) term of $H$ contains the nearest-neighbor hopping integrals $t_{ij}(\alpha, \beta)$. The constant first term of $H$ is defined such that if the hopping term is zero, the ground state energy is zero. For simplicity, we will consider only the $\sigma$-bonding matrix elements (Fig. 1); other ($\pi$-bonding) matrix elements are about three times smaller [9]. Because the exchange interactions are proportional to $t^2$ in lowest order, they are determined primarily by the pairs of strongly overlapping orbitals.

In a nearest-neighbor Heisenberg model, one would assume a uniform antiferromagnetic (AFM) exchange, leading to a frustrated system. This is a good starting point for systems with threefold occupied $t_{2g}$ levels, like $\mathrm{Cr}^{3+}$ compounds. However, for a twofold occupation an orbital degeneracy is present. The frustration can now be removed by an orbital ordering: the two most obvious possibilities are shown in Fig. 1. We will show now that these two configurations have, to lowest order in perturbation theory, the lowest possible mean field energy. We go only one step beyond the Heisenberg model, still assuming a large Hund's rule coupling but now allowing different orbital occupations, with occupation dependent intersite exchange couplings. Only if two orbitals with $\sigma$ overlap are both occupied, we have, according to the Goodenough-Kanamori-Anderson (GKA) rules [8], a strong AFM exchange coupling between $S = 1$ spins: $J = t^2/U$. If only one electron participates in the $\sigma$ bond, the exchange is much weaker and ferromagnetic (FM) and we assume $J = 0$. Also for two empty orbitals with $\sigma$ overlap, we have $J = 0$. Using this nonuniform exchange, we can still apply the Heisenberg model to calculate the mean field energy.

To account for the correct energy zero, it is convenient to calculate the energies of the FM and AFM spin orderings for the two orbital orderings of Fig. 1. In the case of Fig. 1(a), the magnetic couplings are present in two directions only, and the situation is equivalent to a square Heisenberg lattice. For $N$ sites, the mean field energy of the AFM (Néel) state is $E^{(a)}_{\mathrm{AFM}} = -4NJ$, while the FM state, in which electron hopping is not possible, is at $E^{(a)}_{\mathrm{FM}} = 0$. In Fig. 1(b), a three orbital sublattice is formed, and the $N/3$ triangles are magnetically decoupled. For the given orbital ordering, a single triangle can be described by a three-site Heisenberg Hamiltonian. It is straightforward to calculate the energy difference between the AFM and FM configurations: $E(S_{\mathrm{tot}} = 0)$-$E(S_{\mathrm{tot}} = 3) = -6J$. However, unlike the situation in Fig. 1(a), electrons can still hop *between* clusters in both the FM and AFM states. Taking into account this "electronic" contribution to the total energy, which is $-2t^2/U$ per site, we obtain again $E^{(b)}_{\mathrm{AFM}} = -4NJ$.

We see that the frustration can be removed by different orbital orderings. However, we note that the $\sqrt{3}\,a \times \sqrt{3}\,a$ ordering of Fig. 1(b) is particularly favorable because only bonds within the clusters are doubly occupied. This facilitates a further energy lowering due a lattice distortion by increasing the $d$-$d$ hybridization in all doubly occupied bonds. Indeed, there is experimental evidence for a unit cell tripling in $\mathrm{LiVO_2}$ [10].

To study the characteristics of such triangles in $\mathrm{LiVO_2}$, and to verify if the orbital ordering as shown in Fig. 1

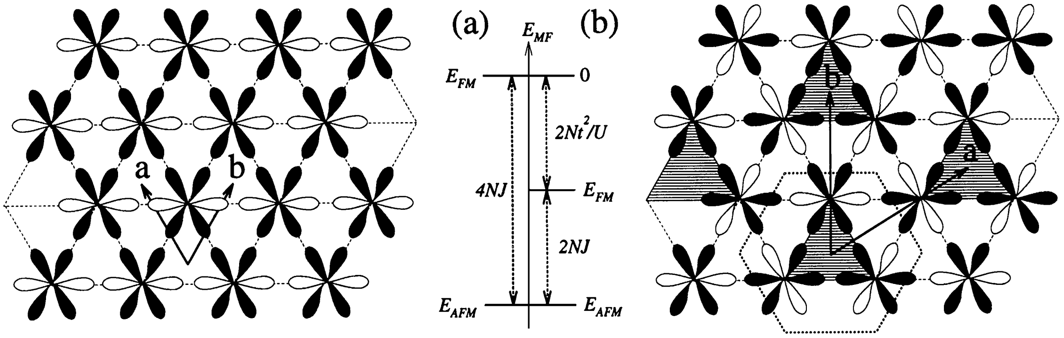

FIG. 1. Schematic view of $t_{2g}$ orbitals in a hexagonal plane. Only in-plane lobes are drawn. Dashed lines represent $\sigma$ bonds. The filled and open shapes for occupied and unoccupied orbitals depict two different orbital orderings (a) and (b). In (b), a $\sqrt{3}\,a \times \sqrt{3}\,a$ superlattice is formed, spanned by the vectors $\vec{a}$ and $\vec{b}$. The energy diagram shows the mean field energies for AFM and FM spin configurations.

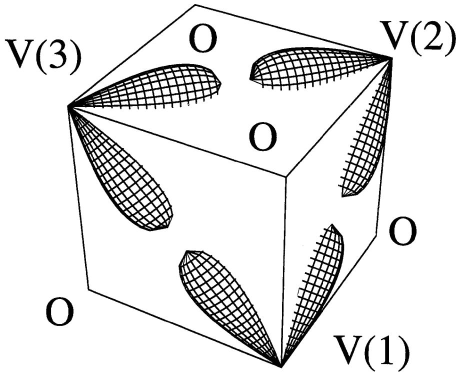

FIG. 2. The triangular V ion cluster in a cubic approximation. Only strongly overlapping lobes of $t_{2g}$ orbitals are drawn. The positions of O ions are also indicated.

is also favorable on a local scale, we have carried out an exact diagonalization of $H$ for three sites. For $V^{3+}$ we estimate $U_e \approx 5.1$ eV, $U_u \approx 3.6$ eV, and $J_H \approx -0.8$ eV, by fitting V ($d^2$) atomic term energies [11], and assuming an $F_0$ Slater integral of 4 eV [12,13]. The calculation for this cluster, as depicted in Fig. 2, involved 7056 basis states. We treat the magnitude of the largest hopping integrals as a parameter $t$ ranging from 0 to 1 eV. From this study we determined the energy, type of orbital ordering, and spin configuration for the lowest energy states as a function of $t$. The energies of these states (with total spins of 0, 1, and 2) are shown in Fig. 3.

We find that the lowest singlet state has the orbital ordering as discussed before, i.e., with all electrons in strongly hybridizing orbitals. The ordering of the other states of Fig. 3 is quite different. The lowest $S = 1$ state has one "spectator" electron that does not participate in the bonding. One of the strongly hybridizing orbitals is unoccupied now, leading to a *ferromagnetic* exchange for the corresponding bond. The frustration in this bond is now removed and the triplet is therefore more stable than the singlet for small $t$. The lowest $S = 2$ and $S = 3$ states have two and three spectator electrons, respectively. For $t < 1$ eV, the energy of the lowest $S = 3$ state is comparable to that of the lowest $S = 0$ and $S = 1$ states. However, we do not consider it in Fig. 3 for the following reason. A lattice of $S = 3$ clusters would be extremely unfavorable because the frustration between triangles is not removed in this case. The periodic continuation of the $S = 3$ state would yield a FM state, while we have strongly AFM intersite exchange interactions. Consequently, this state would be pushed up strongly in energy (outside the energy range of Fig. 3) if interactions between clusters were taken into account. Therefore the $S = 3$ state is not a possible candidate for the ground state of the full lattice.

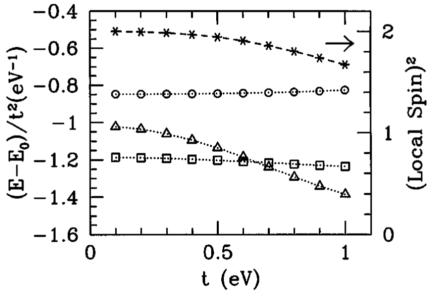

FIG. 3. Properties of the V triangle as a function of the $d$-$d$ hybridization: energies of the lowest $S_{\text{tot}} = 0$ (△), $S_{\text{tot}} = 1$ (□), and $S_{\text{tot}} = 2$ (∘) states, and expectation value of the local spin squared (*).

It is obvious that the orbital ordered singlet state becomes favorable for large $t$, i.e., if the AFM intersite exchange $J_A$ is much larger than the on-site FM exchange $J_H$. However, it is stabilized with respect to the triplet state already at a moderate $t$ value, for which the *local* spin squared ($\langle|\vec{S}_{\text{loc}}|^2\rangle$, as shown in Fig. 3) is still close to the free ion value of 2. To understand this, we calculate the singlet and triplet energies $E_S$ and $E_T$ in second order degenerate perturbation theory in $t$. By using a basis set of six-electron spin eigenfunctions, and considering exchange interactions between individual electrons instead of between $S = 1$ entities, we can account for the finite Hund's rule coupling and a possible lowering of the local spin moment. Assuming a uniform Coulomb interaction $U$, we have an AFM (pairwise) exchange constant $J_A = 4t^2/(U - J_H)$. We can now estimate $E_S = -3J_A/2 + (3J_A^2)/(4J_H)$. The $J_A^2$ term (of order $t^4$) is due to mixing with another $S_{\text{tot}} = 0$ state that is only $2J_H$ higher in energy. This mixing becomes apparent in Fig. 3 by the slight lowering of the local moment. Note that for $J_H \rightarrow \infty$ we obtain the Heisenberg ground state energy. For the lowest triplet state one coupling is ferromagnetic, yielding $E_T = -(5/4)J_A - t^2/(U + J_H)$. Here a $t^4$ term is absent because the lowest triplet state does not couple to $S_{\text{tot}} = 1$ states with higher on-site exchange energy. Therefore, $E_S$ decreases more quickly with $t$ than $E_T$, and eventually becomes smaller. We can roughly estimate the value for $t$ in undistorted $LiVO_2$ at 0.5 eV [9], which is somewhat smaller than the $t$ value for which $E_S < E_T$. However, we should bear in mind that for all values of $t < t_c$, the energy difference between singlet and triplet is very small. As noticed before, a lattice distortion accompanying trimer formation increases $t$, thereby stabilizing the singlet. We conclude that the orbital ordering of the singlet state is not unfavorable on a local scale, and compatible with the ordering in Fig. 1(b).

The scenario described above explains the main properties of $LiVO_2$, which exhibits a first order phase transition [14,15] at around $T_t = 500$ K. The most peculiar property is a change from a high temperature paramagnetic phase with a Curie-Weiss susceptibility $\chi \propto (T + \Theta)^{-1}$ (with a very large negative $\Theta = -1800$ K, corresponding to a large AFM coupling), to a low temperature nonmagnetic system without any sign of long-range order [10]. The high temperature susceptibility is consistent with a local moment of $S = 1$, as expected for a $d^2$ configuration in the presence of a strong on-site Coulomb interaction. Recent x-ray absorption experiments [16] confirmed this observation, and also suggested there is little, if any, change in the local electronic structure on going through the phase transition and a retention of the local moment below $T_t$.

Goodenough [8,17] interpreted the phase transition in terms of the formation of trimers below $T_t$. In this model, the nonmagnetic behavior is attributed to molecular orbital formation in the basal plane, which would quench the local spin moment. The trimerization model is supported by x-ray diffraction [10] and extended x-ray-absorption fine structure [18]. Furthermore, $^{51}$V NMR experiments [19] revealed the development of a large and asymmetric electric field gradient at the V site below $T_t$, which was also explained qualitatively by a symmetry lowering. However, the molecular orbital limit is definitely not consistent with the retention of a local $S = 1$ state found experimentally [16].

The treatment as presented above seems to work very successfully for the $d^2$ case. We can use this approach to treat other similar systems, e.g., $NaTiO_2$. It has the same crystal structure, but contains $Ti^{3+}$ ions in a $d^1$ configuration. Anderson [7] showed that for an isotropic Heisenberg interaction and without orbital degeneracy, the ground state will most probably be of the RVB type. $NaTiO_2$ shows a phase transition at 260 K [20,21], accompanied by a structural distortion and a drop in the susceptibility. An important observation is that the entropy change at the transition exceeds $R \ln 2$ which one would have if only spin degrees of freedom ($S = \frac{1}{2}$) participate in the transition. In our opinion this can be explained by some kind of orbital ordering. If we assume the same type of ordering as in Fig. 1(b), but now with the "white" orbitals singly occupied, we would have a FM intersite exchange, according to the GKA rules. However, this is not consistent with the absence of FM ordering in the low temperature phase [20]. Another possible ordering is the one with one-dimensional chains [white orbitals in Fig. 1(a)]. This leads to a strong AFM exchange along the chains, in better agreement with the low magnetic susceptibility. Although the lowest order mean field energies for the two orderings are again equal, the latter might be more favorable due to the possibility of singlet pair formation and a spin Peierls distortion of the one-dimensional chains. The transition could now be one in which singlet pairs are already present at high $T$, but form an ordered lattice at low $T$. The situation then looks like that of RVB, but now with a strong orbital component in the fluctuating bonds at high $T$.

Summarizing, we have shown that orbital ordering may remove frustration present in magnetic systems. We demonstrated it on a particular model of a triply degenerate hexagonal lattice, but similar situations may occur in other cases, if some form of frustration is present. Our results explain quite naturally the main properties of $LiVO_2$ which undergoes a phase transition into a spin-singlet phase at low temperature, while the local spin configuration of each V ion remains essentially unchanged. It would be interesting to investigate also other systems having a similar orbital and crystal structure (Ti dihalides, $NaTiO_2$) or materials with other types of orbital degeneracy. Another interesting issue is the character of elementary excitations in such systems. Orbital degrees of freedom may either give rise to new collective modes (orbital waves—"orbitons") or may strongly renormalize other elementary excitations (phonons, magnons).

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