Orbital polarization in LiVO$_2$ and NaTiO$_2$

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Abstract. – We present a band structure study of orbital polarization and ordering in the two-dimensional triangular lattice transition metal compounds LiVO$_2$ and NaTiO$_2$. It is found that while in NaTiO$_2$ the degeneracy of $t_{2g}$ orbitals is lifted due to the trigonal symmetry of the crystal and the strong on site Coulomb interaction, in LiVO$_2$ orbital degeneracy remains and orbital ordering corresponding to the trimerization of the two-dimensional lattice develops.

It is well known that transition metal compounds with orbital degeneracy will in some way restructure to remove that orbital degeneracy in the ground state. Well known is the example of a two-fold orbitally degenerate case of divalent Cu in octahedral symmetry with one hole in a $e_g$-like orbital. A similar case is trivalent Mn in $O_h$ symmetry as in the now well known colossal magnetoresistance materials. In these so called strong Jan Teller systems local lattice distortions determine the type of orbital ordering. It is also well established that the relative spatial orientation of occupied orbitals on neighboring ions determines not only the magnitude but also the sign of the exchange interactions governing the magnetic structure of the system [1]. In the early 3$d$ transition metal compounds only the $t_{2g}$ orbitals are occupied leaving us with three-fold degeneracy in the cases of Ti$^{3+}$ and V$^{3+}$ with one and two 3$d$ electrons respectively assuming also $O_h$ symmetry. In contrast to the $e_g$ orbitals the bonding to the neighboring O 2$p$ orbitals is much weaker, bandwidths are much smaller and therefore the removal of the orbital degeneracy may be more subtle. It has for example recently been suggested that the orbital degeneracy in LiVO$_2$ can be lifted by a particular kind of orbital ordering driven by the nearest neighbor exchange interactions [2]. The orbital ordering proposed there is one which simultaneously removes the frustration in the spin Hamiltonian of this triangular two-dimensional lattice and results in a non magnetic singlet ground state. Another much discussed two-dimensional triangular lattice spin system is NaTiO$_2$ with spin 1/2 per Ti ion, which in case of uniform Heisenberg interaction would be a frustrated magnetic system, making it one of the few remaining possible examples of a resonating valence bond (RVB) ground state [3]. However also here the orbital degeneracy could have been lifted by

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Fig. 1. – The fragment of the crystal structure of NaTiO$_2$ and LiVO$_2$. $x$, $y$, $z$ are along the cubic crystal axes, the $z'$ axis is the trigonal threefold rotation axis.

orbital ordering resulting in a non-uniform Heisenberg spin Hamiltonian and a subsequent removal of the frustration. In this paper we present a detailed band structure study of these two systems both with and without the inclusion of the on site $d$-$d$ Coulomb interaction in a so called LDA+U approximation. We find that although LiVO$_2$ behaves as suggested by Pen et al. [2] NaTiO$_2$ should not be considered as orbitally degenerate and remains a candidate for an RVB ground state [3].

LiVO$_2$ and NaTiO$_2$ crystallize in an ordered rock salt-like structure with alternating [111] planes of Li(Na),O,V(Ti),O ions as shown in fig. 1. Each of these layers forms a triangular two dimensional lattice and since the layers containing the magnetic ions are so well separated the exchange interactions between layers is very small compared to that within a layer. Peculiar in these compounds is a change from a high temperature paramagnetic phase and a Curie-Weiss susceptibility with a large negative effective Curie temperature (which corresponds to strong antiferromagnetic coupling between local moments) to a low temperature nonmagnetic system without any sign of long-range order [4, 5]. This is usually explained by the frustration of the triangular lattice antiferromagnet leading to the possibility of an RVB ground state with a quantum liquid of randomly distributed spin singlet pairs [3]. However such models do not take into account orbital degeneracy and the possibility of orbital ordering, which can qualitatively change the type of exchange interactions as discussed above.

While the nearest neighbors of the transition metal ion (oxygen atoms) are arranged in an almost perfect octahedron with $O_h$ symmetry, the overall symmetry of the crystal structure is trigonal, and in that case the $t_{2g}$ level is split into a nondegenerate $A_{1g}$ and double degenerate
Fig. 2. – Left panel – the total densities of states from LDA calculations. Right panel – the partial densities of states from LDA calculations: dotted line – $A_{1g}$, solid line – $E_g$. The Fermi energy is the zero energy.

$E_g$ levels. (Note: in further discussion $e_g$ and $E_g$ have different meanings). The $t_{2g}$-orbitals can be represented as the set $(d_{xy}, d_{yz}, d_{zx})$ in the coordinate system with axes pointing towards the O-neighbors (fig. 1). In this coordinate system the $A_{1g}$ and $E_g$-orbitals have the following form [6]:

$$A_{1g} : (d_{xy} + d_{yz} + d_{zx})/\sqrt{3} \quad E_g : \frac{1}{\sqrt{2}}(d_{zx} - d_{yz}) \quad \frac{1}{\sqrt{6}}(-2d_{xy} + d_{yz} + d_{zx})$$ (1)

The resulting orbital order will strongly depend on how this trigonal splitting will affect the resulting orbital polarization of the partially filled $t_{2g}$ band. If the centre of gravity of the $A_{1g}$ band is lower than $E_g$, then in the case of the $d^1$ configuration the degeneracy will be lifted, but the $d^2$ configuration will be still degenerate provided that the Hunds rule exchange is larger than this splitting which is certainly expected to be the case. If the $E_g$ level is lower than $A_{1g}$, then the $d^2$ configuration in the high spin state will be nondegenerate.

In order to look into this problem we have performed band structure calculations for LiVO$_2$ and NaTiO$_2$ by LMTO method [7] in standard Local Density Approximation (LDA) [8] and also in LDA+U approach [9] which allows to take into account Coulomb correlations between 3$d$ electrons of transition metal ions. We used the crystal structures and atomic positions as given by [10, 11]. The total DOS obtained in LDA and presented in the left panel of fig. 2 shows the O 2$p$ band between -8 and -4 eV, (Ti,V) 3$d$ band of $t_{2g}$ symmetry crossing the Fermi level between -1 and 1 eV, and of $e_g$ symmetry around 3 eV well above the Fermi energy. As
one can see, indeed the $t_{2g}$-$e_g$ crystal field splitting is larger than the bandwidth and V $3d$ subbands of the $t_{2g}$ and $e_g$ symmetry are separated by a gap. We should mention that the $e_g$ band width is even smaller than that of $t_{2g}$, this is because the $e_g$-$e_g$ hopping of the neighboring transition metal ions goes through oxygen atoms and the angle of Me-O-Me bond is nearly $90^\circ$, so the $e_g$-$e_g$ hybridization is small. In spite of the fact that there is a trigonal distortion of the lattice the $t_{2g}$ band is not splitted due to the trigonal symmetry into $A_{1g}$ and $E_g$ subbands and a more delicate quantitative analysis is needed to clarify this problem.

In the right panel of fig. 2 the partial DOS for decomposition of the $t_{2g}$ band into orbitals of the $A_{1g}$ and $E_g$ symmetry are presented. One can see that the situation can not be described in the simple terms of $A_{1g}$-$E_g$ "splitting": both curves have the same width and they are approximately in the same energy region. We can estimate the actual splitting of the $A_{1g}$ and $E_g$ levels by calculating the values of the centres of gravity of these bands.

In the case of NaTiO$_2$ with one $d$ electron the center of gravity of the $A_{1g}$ band is 0.1 eV lower than that of the $E_g$ band. As a result the occupied part of $t_{2g}$ band has slightly more $A_{1g}$ character than $E_g$, and the occupancy of orbitals are .25 and .20 per spin-orbital for $A_{1g}$ and for each $E_g$ correspondingly. This means that the degeneracy of the $t_{2g}$ orbitals is essentially lifted but the splitting is still much less than the band widths. This small splitting is non the
Fig. 4. – The $t_{2g}$ holes from LDA+U calculations for LiVO$_2$. Only V atoms for one triangle in a hexagonal plane are drawn. The view is from the point directly above V-triangle.

less important since as we will see below if we turn on the $d$-$d$ Coulomb interaction in LDA+U the $A_{1g}$ band will be occupied and the $E_g$ unoccupied now with a splitting mainly due to U. However the choice as to which band is occupied and which one not is dictated by the small crystal field splitting. The above result would also indicate that the $A_{1g}$-$E_g$ local excitation energy would be only 0.1 eV or so and would contribute to charge conserving excitonic-like excitations. In this LDA+U calculation the $d$-$d$ Coulomb interaction was found to be 3.6 eV (taking into account the screening of $t_{2g}$ electrons by $e_g$ electrons [12]) which is much larger than the $t_{2g}$ band width and leads to the localization of a single $d$ electron in the $A_{1g}$ orbital.

The LDA+U calculations were carried out for both antiferromagnetic and ferromagnetic cases. For the AFM case we choose the simplest magnetic order with four nearest neighbors out of the six in the basal plane having anti-parallel spin orientation and other two parallel. Independent of the spin ordering a single $d$ electron in the $t_{2g}$ shell of the Ti ion turned out to be localized in the $A_{1g}$ orbital. The occupation numbers for the majority spin are 0.9 for $A_{1g}$ and 0.1 for $E_g$ for both FM and AFM cases. The Ti(3$d$) projected density-of-states obtained from LDA+U calculations is shown in fig. 3(a). So we can say from the fig. 3(a) that the LDA+U solution for NaTiO$_2$ is almost fully orbitally polarized. One can see from eq. 1 that the $A_{1g}$ orbital ($d_{3z^2-r^2}$ in fig. 3(a)) is symmetric in the hexagonal Ti-Ti plane and the occupation of this orbital leads to the isotropic exchange. This indicates that NaTiO$_2$ would still behave like a frustrated spin system.

In the case of LiVO$_2$ the centre of gravity of the $A_{1g}$ band is only 0.025 eV lower then the centre of gravity of the $E_g$ band, and the resulting occupancies are 0.37 and 0.36 for $A_{1g}$ and for each $E_g$-orbitals correspondingly. In this situation orbital degeneracy is not lifted, since we now have two electrons one in a $A_{1g}$ and one in a $E_g$ orbital, because the Hund's rule exchange
strongly favours the high spin state. As a result the appearance of some kind of orbital order can be expected. In [2,13,14] the formation of local spin singlets on trimers containing V-atom triangles was suggested as the model explaining the low-temperature nonmagnetic behavior of LiVO$_2$. Those spin singlets were stabilized by a specific orbital order [2].

The LDA+U method is based on a mean-field approximation and can not fully reproduce the essentially many-electron singlet wave function, especially the correct energy difference of singlet-triplet configurations. However a single Slater determinant trial wave function can still describe the basic relationship between spin and orbital degrees of freedom. To imitate trimer spin singlets we performed LDA+U calculations with spin-order of the type "up-down-zero" on every triangle (closed circles on the fig. 1). The self-consistent calculations resulted in the orbital order of the same type as proposed in [2] from model calculations [fig. 3(b)]: on every V atom the occupied orbitals are $xz$ and $yz$ if in a local coordinate system $z$ axis is directed towards the oxygen atom sitting just above the center of V-triangle, and x and y axes are directed towards other oxygens of an octahedron(fig. 1). We should also mention the fact that the LDA+U calculations give the correct semiconducting state for LiVO$_2$ [fig. 3(b)] instead of a metallic state from "normal" LDA (left panel of fig. 2).

In fig. 4 the angular distribution of the $t_{2g}$ hole is presented as was obtained from the LDA+U calculations. It indicates the same orbital order proposed in [2] (fig. 1(a) in [2]): $xz$ and $yz$ orbitals are occupied, the $t_{2g}$ hole is in $xy$ orbital in a local coordinate system of every V atom.

Both LiVO$_2$ and NaTiO$_2$ were regarded as candidates for realization of Anderson’s “resonating valence bond” systems with a quantum liquid of randomly distributed spin singlet pairs. Our results show that while in LiVO$_2$ more complicated trimer spin singlets with corresponding orbital order are formed, no orbital order due to the crystal field lifting of the orbital degeneracy is present in NaTiO$_2$, and its magnetic properties are most probably explained by a nondegenerate model, so that it is indeed a good candidate for Anderson’s RVB state. What then is the nature of the structural phase transition observed in NaTiO$_2$ at $T_c$=250, remains an open question.

Summarizing, we have shown that the degeneracy of the $t_{2g}$-orbitals in NaTiO$_2$ is lifted because of the trigonal symmetry of the crystal and the large $d$-$d$ Coulomb interaction and no orbital ordering occurs. In LiVO$_2$ orbital degeneracy remains in spite of the same trigonal distortion as in NaTiO$_2$, and in effect the orbital ordering consistent with the trimerization of the two-dimensional lattice takes place.

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