Rich properties of systems with strongly correlated electrons, such as transition metal (TM) oxides, is largely connected with an interplay of different degrees of freedom in them: charge, spin, orbital ones as well as crystal lattice. Specific and often very important role is played by orbital degrees of freedom. They can lead to a formation of different superstructures (an orbital ordering) which are associated with particular types of structural phase transitions — one of very few examples where the microscopic origin of these transitions is really known; they largely determine the character of magnetic exchange and the type of magnetic ordering; they can also strongly influence many other important phenomena such as insulator-metal transitions (IMT), etc.

In this comment I will try to shortly summarize the main concepts and discuss some of the well-known manifestations of orbital degrees of freedom, but will mostly concentrate on a more recent development in this field. More traditional material is covered in several review articles [1, 2, 3]. Although I tried to cover the main new development in this area, the choice of topics of course is influenced by my own interests; other people probably would have stressed other parts of this big field.
1 Basic notions

Five-fold degenerate $d$-levels of TM ions ($l = 2, 2l + 1 = 5$) are split in cubic crystal field (CF), typical for many TM compounds, into a triply-degenerate $t_{2g}$ levels (orbitals $xy$, $xz$ and $yz$) and doubly-degenerate $e_g$ ones ($z^2 = 3z^2 - r^2$ and $x^2 - y^2$ orbitals), see fig. 1. Further lowering of CF to a tetragonal or orthorhombic one splits both $t_{2g}$ and $e_g$ levels, whereas a trigonal (rhombohedral) distortion splits only $t_{2g}$ levels. The shape of corresponding electron wave functions is shown in fig. 2, the notation $(x^2 - y^2, xy, etc.)$ actually describes the shape of electronic density of a corresponding orbital. Of course, also linear combinations of the basic orbitals are possible, e.g.

$$|\theta\rangle = \cos(\theta/2)|z^2\rangle + \sin(\theta/2)|x^2 - y^2\rangle.$$  \hspace{1cm} (1)

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**Figure 1**: Schematic form of the crystal field splitting of $d$-levels of transition metal in octahedral coordination.

**Figure 2**: Typical shape of different orbitals: (a) $z^2 = 3z^2 - r^2$-orbital; (b) $x^2 - y^2$-orbital; (c) $xy$-orbital.
Such states, relevant for doubly-degenerate $e_g$ orbitals, can be conveniently described by the pseudospin $T = \frac{1}{2}$ ($T^z = \frac{1}{2}$ for the $z^2$ orbital and $T^z = -\frac{1}{2}$ for the $x^2 - y^2$ one) and represented on a diagram of fig. 3. Note that in cubic CF the axes $x$, $y$ and $z$ are equivalent, i.e. the orbital $|z^2\rangle = |3z^2 - r^2\rangle$ should be equivalent to $|x^2\rangle = |3x^2 - r^2\rangle$ and $|y^2\rangle = |3y^2 - r^2\rangle$. These later ones correspond to the angles $\theta = \pm 2\pi/3$ in Eq. (1) and in fig. 3 which consequently has a $2\pi/3$ symmetry. This finally leads to a specific frustration in orbital sector even in simple lattices such as cubic ones, e.g. in perovskites [1, 4].

Figure 3: Different orbitals, described by Eq. (1), in $T_x - T_z$-plane.

The $t_{2g}$ orbitals, e.g. the one shown in fig. 2(c), have two specific features differentiating them from $e_g$ ones:

1. In contrast to $e_g$ orbitals for which the real relativistic spin-orbit coupling $\lambda \mathbf{L} \cdot \mathbf{S}$ is in the leading order absent ($e_g$-states $|z^2\rangle = |l^z=0\rangle$, $|x^2 - y^2\rangle = \frac{1}{\sqrt{2}}(|l^z=+2\rangle + |l^z=-2\rangle$), and the orbital moment is quenched), it is in general nonzero for $t_{2g}$ states.

2. The shape of $t_{2g}$ wave functions is such that e.g. in 3d lattices they can give rise to 2d and even 1d bands. Thus in perovskite lattices $xy$-orbitals have significant overlap and hopping only in $xy$-planes, but practically negligible overlap in $z$-direction, see fig. 4, and as a result the corresponding tight-binding bands would be two-dimensional, with the dispersion in $k_x, k_y$, but not $k_z$. Even more drastic consequences can we have in other lattices. Thus the corner-sharing TM tetrahedra of B-sites in spinels (topologically equivalent to a pyrochlore lattice), shown in fig. 5, have significant direct overlap of say $xy$ orbitals along metal chains in $xy$-planes, $xz$ orbitals —

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along $xz$-chains, etc. In effect we would have a collection of 1d bands. This feature (reduced dimensionality) on one hand can lead to specific ordering phenomena like Peierls transition [5], see below; and, on the other hand, they can strongly enhance quantum effects in orbital sector ([6], see also [3] and references therein). Note that in principle one of $e_g$-orbitals, $x^2 - y^2$, also has this property (almost no overlap in the third, $z$ direction), thus the occupation of this type of orbital can also lead to a two-dimensional band (this is crucial for High-$T_c$ cuprates), although these effects are more pronounced for $t_{2g}$ systems.

Figure 4: The $xy$-orbitals in a simple cubic (or perovskite) lattice. One can see that there exists strong overlap in $xy$-plane but practically no overlap in the $z$-direction.

Specific role of orbitals in TM compounds is largely connected with the famous Jahn-Teller (JT) theorem (which, as Teller himself wrote in the preface to the book [7], was actually suggested to him by Landau). In a simplest form sufficient for our purposes it states that the high-symmetry state with an orbital degeneracy is unstable with respect to a spontaneous decrease of symmetry lifting this degeneracy (we ignore here specific quantum “vibronic” effects [7, 8] which can be very important for isolated JT impurities, but which are less significant for concentrated systems which we consider here). This spontaneous lifting of symmetry leads to an occupation of particular orbitals (an orbital ordering (O.O.),), and simultaneously to a structural phase transition with the reduction of symmetry (cooperative Jahn-Teller effect). One can not exist without the other, and it is a definite misunderstanding when people sometimes are trying to discuss these phenomena as two sepa-
Another question is, which particular effect are we probing by one or another experimental technique. Different techniques are more sensitive and may be predominantly determined either directly by an orbital occupation, or by the corresponding lattice distortion. Thus e.g. the resonant X-ray scattering at the K-edge ($1s \rightarrow 4p$ transition) \[14\] is apparently mostly determined by lattice distortions \[12, 13, 14\], although there may exist in principle also a direct electronic contribution \[15\], apparently weaker in this channel. At the same time the $L_{2,3}$ absorption ($2p \rightarrow 3d$) directly probes an orbital occupation. But in no way does it mean that these (orbital ordering and Jahn-Teller distortion) are two different phenomena and that one can exist without the other, or that they can have e.g. different temperature dependence; this is

\[1\] There exist different mechanisms of an O.O. and of the corresponding structural distortion: it may be just the electron–lattice, or JT interaction (interaction of orbitals with lattice distortions \[9\]), or it can be a purely electronic (exchange) interaction \[10, 11\], or even a direct quadrupole–quadrupole interaction (relevant for similar phenomena in rare earths compounds). But in any case, even if the main driving force of an O.O. is purely electronic, of course the lattice would react and there will appear a corresponding lattice (JT) distortion.
definitely never the case.

After this general short introduction I will discuss several (not all, of course) specific situations and phenomena in which orbitals apparently play an important role. I will start with the rather well known cases.

2 Orbital ordering in insulators with “simple” lattices

Typical examples of orbital effects in TM compounds are met in systems with one electron or one hole in the doubly degenerate $e_g$ orbitals — the system containing Mn$^{3+}$ ($t^32g^1e_g^1$), Cr$^{2+}$ ($t^32g^1e_g^1$), Cu$^{2+}$ ($t^62g^3e_g^1$), low-spin Ni$^{3+}$ ($t^62g^1e_g^1$). These ions give rise to a strong JT effect, and all of them have a low-symmetry ground state with an O.O., in which an orbital degeneracy is lifted. The best known examples are the colossal magnetoresistance manganites, with the prototype material LaMnO$_3$, or many Cu$^{2+}$ compounds including High-$T_c$ cuprates.

Which mechanism is responsible for an O.O. in these systems, is still not completely clear. Evidently an electron–lattice (JT) interaction [9, 7] is rather strong there. However the electronic (superexchange) mechanism [10, 11] usually also leads to the same type of orbital ordering as the JT mechanism, and many ab-initio calculations [16, 17] reproduce this O.O. even without lattice distortion. The relaxation of the lattice decreases the energy still further, but according to these calculations already purely electronic mechanism gives about 60% of the total energy gain.

The problem is that typically both the mechanisms, JT and the electronic one, give rise to the same structure. To evaluate the relative importance of one or another mechanism of an O.O., it would be very helpful to find the cases where these mechanisms would stabilise different states. One such possibility is discussed in [18]. A more detailed discussion of these “classical” cases of O.O. one can find in the general references [11, 2, 3] cited above.

An important question is how one can get the information about an orbital occupation and O.O. Until recently the main, and practically the only experimental method to find out an orbital occupation was the study of crystal structure: by measuring the local distortion of MeO$_6$ octahedra one could get pretty reliable information about the detailed type of orbital occupation at a particular site. Typical situation is the local elongation of
ligand octahedra, although in general distortions may be more complicated, e.g. containing three types of Me–O distances: two long, two intermediate and two short ones. From these data one can get the type of occupied orbitals \([11, 21, 22]\). If we denote three Me-O distances as \(l\), \(m\) and \(s\), the angle \(\theta\) characterizing the orbital state (1) is given by the expression

\[
\tan(\theta) = \frac{\sqrt{3}(l - s)}{2m - l - s},
\]

(2)
or by the corresponding equation with the change \(\theta \rightarrow \theta \pm \frac{2\pi}{3}\).

The other methods traditionally used to study orbital occupation are those using ESR, and an indirect information about an O.O. one can obtain from magnetic properties of corresponding systems. Also spectroscopic studies are rather informative in this respect (“ligand field spectroscopy”).

An important new development is connected with the use of the resonant X-ray scattering (RXS), initiated by Murakami et al. \([11]\). As mentioned above, depending on the specific version of the method used, one again can be more sensitive to corresponding distortion \([12, 13]\), but there are also the ways to probe orbital occupation directly, see e.g. \([12, 23]\). One has already studied by this method many systems containing Mn, Cu etc. One new and puzzling phenomenon was observed in many of these studies; in many cases the intensity of a signal which was attributed to an O.O., changed rather strongly below magnetic ordering temperature, even in cases where the O.O. occurs at much higher temperatures, so that it has to be already saturated at \(T_N\). This behaviour was found in manganites \([11]\) in which this increase of intensity below \(T_N\) is about 30%, and in KCuF\(_3\) \([24]\), where the effect is even much stronger: the signal has increased at around \(T_N \sim 30\) K by a factor 2.5, despite the fact that an O.O. exists (and is practically constant) in this system up to the temperature of its melting or decomposition. What is the

\(^2\)Although in the simplest treatment for strong JT ions (partially filled \(e_g\)-levels) both local elongation and contraction of ligand octahedra are equivalent, in practice it is not the case: out of hundreds systems with such JT ions with localized electrons there are practically none with locally compressed octahedra. This can be explained by higher-order coupling and by the anharmonicity effects \([19]\). Thus one has to be very careful with the claims sometimes made in theoretical papers, which consider e.g. an alternation of elongated and compressed octahedra. Note that the situation may be different in systems with delocalized electrons and with partially-filled bands: these bands may well be formed by the “flat” orbitals like \(x^2 - y^2\), with corresponding net tetragonal contraction of the sample. This rule is also not true for \(t_{2g}\) electrons, for which both signs of distortions (and also trigonal distortions of different sign) are possible in different situations, see e.g. \([11, 20]\).
explanation of this effect, is completely unclear at present. One possibility is that there may be a direct contribution of magnetic ordering (via spin-orbit coupling or via interference of different scattering channels) to the signal which was attributed to an O.O. Whether this possibility may be realised in practice, is an open question.

To finish with the discussion of the conventional effects connected with an O.O., one should mention that it largely determines the character of an exchange interaction and the type of magnetic ordering in corresponding systems. This is the essence of the famous Goodenough–Kanamory–Anderson (GKA) rules, see e.g. [22, 25]. In short, the main ones of them are: there is a strong antiferromagnetic coupling if on corresponding sites the (singly-) occupied orbitals are directed towards each other. If however an occupied orbital is directed towards an empty (or doubly-occupied) one, there will be a weaker ferromagnetic coupling.

The interplay between an orbital occupation and magnetic ordering in principle gives rise to the possibility of a change of an O.O. at the magnetic transition, but for $T_N \ll T_{O,O}$ this effect is apparently too weak to explain the anomalies at $T_N$ in RXS discussed above.

3 Reduced dimensionality due to orbital ordering

Specific feature of orbital degrees of freedom is an anisotropy of corresponding electron distribution. Consequently, particular orbital occupation can lead to the appearance of a strong anisotropy in the properties of such systems, even if the original crystal structure is relatively isotropic.

There are many examples of this phenomenon. Thus, in undoped manganites with perovskite structure the magnetic ordering is of layered type (A-type ordering — ferromagnetic planes stacked antiferromagnetically) [26]. Even more striking is the example of KCuF$_3$: in this practically cubic crystal, due to an orbital ordering (alternation of hole orbitals $x^2 - z^2$ and $y^2 - z^2$) magnetic properties are those of a quasi-one-dimensional antiferromagnet [27, 10, 11]. Despite cubic lattice, this material is one of the best one-dimensional antiferromagnets.

Orbital ordering can also strongly modify electronic structure and properties of some systems, such as conductivity. Thus, in certain doped man-
ganites, e.g. in Nd$_{1-x}$Sr$_x$MnO$_3$ for $x \sim 0.6$, predominantly $x^2 - y^2$ orbitals are occupied, forming corresponding partially filled band. Consequently this material has much higher conductivity in the $xy$-plane than perpendicular to it. Apparently two-dimensionality of most High-$T_c$ cuprates, although largely due to their layered structure, is substantially enhanced by the location of charge carriers (here holes) mostly in $x^2 - y^2$ bands.

Yet another recent example is the new spin-Peierls system TiOCl: due to a particular orbital occupation this material, that structurally is a layered system, electronically becomes quasi-one-dimensional, which finally leads to a spin-Peierls transition in it.

4 Orbitally-driven Peierls state

TiOCl is not the only example of quasi-1d behaviour caused by orbital ordering. Even more striking example is provided by some spinels with TM on B-sites and with partial occupation of $t_{2g}$-levels. In some of such systems quite spectacular superstructures were observed recently: an “octamer” ordering in CuIr$_2$S$_4$ or “chiral” structural distortion in MgTi$_2$O$_4$. The natural explanation of such strange structures can be found in the concept of an orbitally-driven Peierls state. As illustrated in fig. 5, in this crystal structure different $t_{2g}$ orbitals overlap only with corresponding orbitals of neighbouring sites along particular directions: $xy$-orbital with $xy$ along $xy$-chain, $xz$ with $xz$ in $xz$-chains, etc. As a result the electronic structure consists in a simplest approximation of three degenerate 1d-bands. In both CuIr$_2$S$_4$ and MgTi$_2$O$_4$ there occurs with decreasing temperature a metal–insulator transition with the cubic–tetragonal lattice distortion. This distortion splits three degenerate bands, so that either only one or two of them are partially occupied, figs.6(b), 7(b). In both cases the corresponding bands turn out to be $\frac{1}{4}$ or $\frac{3}{4}$-filled, and as a result the system undergoes a Peierls-like transition — tetramerization along respective directions. It is driven by orbital ordering (one may call it an ODW — Orbital Density Wave). Simultaneously it also leads to a formation of spin singlets on dimers with orbitals directed towards one another (double bonds in figs.6(a), 7(a)). One can see that the resulting superstructures exactly coincide with those observed experimentally in CuIr$_2$S$_4$ and octamers in CuIr$_2$S$_4$, see figs. 6 and 7.

One can argue that similar phenomenon should occur also in some other
Figure 6: Schematic band structure and orbital ordering in MgTi$_2$O$_4$ leading to the formation of “chiral” superstructure (by [5]).
Figure 7: Schematic band structure and orbital ordering in CuIr₂S₄ leading to the formation of octamers (by [5])
systems, e.g. in NaTiO$_2$ [5]. It may be also relevant for the transition to a spin-gap state in La$_4$Ru$_2$O$_{10}$ [31], and possibly even to an old problem of Verwey transition in magnetite [32, 5]. Thus, in La$_4$Ru$_2$O$_{10}$ the appearance of a singlet ground state below structural phase transition was originally interpreted in [31] as a transition of each Ru$^{4+}$ ($d^4$) from $S = 1$ ion into a nonmagnetic $S = 0$ state. However this seems to be rather unlikely, as it would require the splitting of $t_{2g}$ levels larger than the Hund’s rule coupling $J_H$, which for Ru is of order 0.6 eV. Most probably singlet states in this system are again those on Ru dimers, stabilized by corresponding orbital ordering. This picture is supported by recent LDA + U calculations [33], and it seems to agree with the results of recent inelastic neutron scattering [34].

An example of a more complicated singlet Peierls-like state is provided by LiVO$_2$ — the system with a quasi-two-dimensional triangular lattice, fig. 8. A structural transition accompanied by an opening of a spin gap in this system may be explained by an orbital ordering with the formation of three orbital sublattices in it [35], of the type $(xy, xz)$, $(xy, yz)$ and $(xz, yz)$, see fig. 9. One sees that as a result of this ordering there will appear strong antiferromagnetic coupling in some triangles of V (shaded triangles in fig. 9); this would lead to the formation of singlets on these triangles (three spin 1 V$^{3+}$ ions combine into a singlet). One can say that this is a “next level of complexity” — singlets not on dimers, as in Peierls or spin-Peierls case, but on trimers.

![Figure 8: Crystal structure of LiVO$_2$, showing the formation of quasi-two-dimensional triangular lattice of magnetic ions V$^{3+}$ ($t_{2g}^3$).](image)

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5 Possible role of orbitals in insulator-metal transitions

In previous sections we saw that orbital degrees of freedom play an important role in the IMT and in corresponding structural modifications in some spinels. However one can argue that this factor has broader significance, and presumably orbitals play an important role in IMT in many other systems as well. The study of this question is now only at the beginning, thus my discussion here would have mostly a qualitative character and would rely only on a few examples.

Among the best known systems with IMT are vanadium oxides, notably V$_2$O$_3$ and VO$_2$, see e.g. [36]. As to V$_2$O$_3$, the idea of the importance of an O.O. in it was suggested long ago [37] and was revived in [38] to explain neutron scattering results [39] that the magnetic correlations in the metallic phase are quite different from those expected from the long-range magnetic order in the insulating phase. O.O was also invoked initially to explain the results of RXS in V$_2$O$_3$ [40]. And although the initial model of [37] is apparently faulted [41], and the results of [40] can be explained without invoking O.O. [42], still direct X-ray absorption measurements [43] show that indeed there is a change of an orbital occupation accompanying IMT, although it is much weaker than the one considered in [37] [38] [40].

The case of VO$_2$ is more interesting from our point of view. The IMT in
VO₂, occurring at about 70°C, is accompanied by the structural transition from the rutile (R) to the monoclinic (M1) phase, in which V chains along c-axis of R structure are dimerized, and simultaneously there occurs a “twisting” — tilting of V dimers, caused by the antiferroelectric-type shifts of V ions towards oxygens in ab-plane. As suggested already long ago by Goodenough [44], this “twisting” shifts and depopulates antibonding π* -band made of V orbitals lying mostly in ab-plane, so that only the 1d band made of one type of t₂g orbitals of V, which have strong direct overlap along c-chains, is occupied. This 1d half-filled band, in its turn, leads to a Peierls distortion (dimerization of c-chain), and finally the material becomes insulating.

We see that in this picture the change of orbital occupation at the IMT plays crucial role in the transition itself. This picture is now confirmed by a number of ab-initio calculations [45], and very recently it was proven by the direct X-ray absorption measurements [16]. Thus at least in VO₂ the orbital reorientation is extremely important for the IMT.

One can even qualitatively understand why orbital effects are stronger in VO₂ than in V₂O₃. There exist a strong tendency of d¹ ions to form spin singlets in many TM compounds. Besides VO₂, similar phenomenon is also observed in Ti₂O₃ [22] and in the Ti Magnéli phases, e.g. in Ti₄O₇ [47]. But this tendency is much less prominent for d², d³, etc, configurations. And apparently the tendency to form singlet pairs is greatly enhanced by corresponding orbital ordering: it is most favourable for that to put one electron at each site of the pair into orbitals directed towards one another.

As I said, the question of the role of orbitals at IMT’s is just started to be investigated, and it is not a priori clear how important is this factor in general; it may indeed be system-dependent. But one can give some arguments that it can help to explain one general open problem which seems to be quite common for many IMT’s in TM compounds and which did not attract yet sufficient attention:

In most of the TM systems with IMT the energy gap E₂g which opens in the insulating phase is much larger than the corresponding Tc. Thus e.g. in V₂O₃ and in VO₂ E₂g is ~ 0.5–0.6 eV, whereas Tc is respectively 150 K and 370 K; in Fe₃O₄ E₂g ~ 0.3 eV and Tc = 119 K, etc. This large discrepancy is not an exception but rather a rule for IMT in this class of compounds. This is in strong contrast to the situation e.g. in superconductors or in systems with CDW or SDW, where one typically has the values of the gap of the order of the theoretical ones for BCS superconductors, 2Δ/Tc = 3.5. Such values we should expect also for Peierls transitions (which is actually the case in several
low-dimensional materials \[48\]) or in spin-Peierls systems \[49\]. Apparently this large discrepancy at IMT in TM compounds is a consequence of strong electron correlations in these systems, and it can serve as a signature of their importance.

However why is it the case, is not really clear. In simple treatments of the Mott-Hubbard transitions, to get small \(T_c\) one would require an extremely fine tuning of the parameters (electron hopping \(t\) or bandwidth \(W = 2zt\) and the Hubbard repulsion \(U\)) which determine whether the material would be a metal or an insulator: typically both \(W\) and \(U\) are of order of several eV, and one indeed needs their almost exact cancellation to get \(T_c\) of order of 100 K, or 0.01 eV. More sophisticated calculations, e.g. DMFT \[50\], sometimes (re)produce small \(T_c\) and large values of \(E_g/T_c\), although one usually has to invoke some extra factors such as frustrations. Physical picture used in this approach is that of “preformed” gap of order of \(U\) (between lower and upper Hubbard bands), whereas in the metallic phase close to IMT there exists also a small coherent peak at the Fermi-level. But again, the widths of this peak which determines the energy scale of IMT is small only when we have fine tuning of \(W\) and \(U\).

One possible factor which can help to resolve this problem is an eventual change of spin and orbital correlations at the IMT. In real systems not only does the gap close at the IMT, but also magnetic and orbital order, or correlations, change significantly. Above we discussed the orbital change in VO\(_2\). In V\(_2\)O\(_3\) probably the role of orbitals is less important, but, on the other hand, spin correlations change a lot \[39\], possibly even becoming ferromagnetic above \(T_c\) \[51\]. Orbital modification, e.g. in VO\(_2\), can make the effective bandwidth smaller in the insulating case (simply speaking, for example making the energy bands one-dimensional instead of three-dimensional ones above \(T_c\), or removing the crossing of different bands). Then one can have the situation that \(W > U\) above \(T_c\), but becomes (much) smaller below it. If so, we would not need such a “fine tuning” of \(W\) and \(U\), as is required in the simple nondegenerate Hubbard model.

Change of spin correlations (in its turn also connected with the change of orbital occupation) can also facilitate strong IMT with opening of a large gap, because it can lead to a change of an effective value of the Coulomb (Hubbard) repulsion \(U\) \[43\]. Indeed, typically spin ordering or correlations in the insulating state are antiferromagnetic. Then the virtual transition of an electron to a neighbouring site, determining the value of \(U_{\text{eff}}\), is just the usual \(U\) in the Hubbard model. However, as is often the case, magnetic correlations
in the metallic phase are smaller or even become ferromagnetic; then such virtual transition would “cost” the energy $U - J_H$ (or several $J_H$ in case of many-electron ions), where $J_H$ is the intra-atomic Hund’s rule exchange (of order $0.8-0.9 \text{eV}$ for 3d ions). Thus effectively the value of $U$ may strongly decrease above $T_c$, which can be traced back to the presence and modification of orbital occupation at the IMT. This effect again makes the conditions for the IMT less stringent, and can at least partially explain large values of energy gaps in the insulating phase.

6 Orbital in frustrated lattices

As I already said, an orbital exchange may be frustrated even in simple lattices such as square or cubic ones. These frustrations would become even more prominent in the lattices with geometric frustrations, such as triangular, kagome or pyrochlore lattices. Frustrated systems attract now considerable attention, but mostly from the point of view of their spin properties. However orbitally-degenerate frustrated systems also present significant interest. The system which was most widely discussed in this context is LiNiO$_2$, containing low-spin Ni$^{2+}$ ions with the configuration $t^6$ $e_g^1$ on a two-dimensional triangular lattice, similar to that in LiVO$_2$ shown in fig. 8. This state has both $S = \frac{1}{2}$ and the double orbital degeneracy on this lattice. This system was first studied as one of the best candidates for the Anderson’s RVB state, but later it was suggested that there exists in it also an orbital liquid state. Experimentally indeed there exist in this system neither long-range magnetic order, nor structural transition required by orbital degeneracy.

Theoretical treatment of this situation has shown that there exists a large orbital degeneracy in this system, which however can be lifted by the order-from-disorder mechanism. Magnetic interactions, however, were shown to be predominantly ferromagnetic in the Ni layer. Similar system NaNiO$_2$ indeed shows the behaviour obtained theoretically: there exists in it a structural transition with an O.O. at $T_{str} = 480K$, and at lower temperatures - a magnetic ordering with ferromagnetic layers coupled antiferromagnetically. The absence of a long-range magnetic ordering in LiNiO$_2$ may be explained by interlayer frustrations, which is probably responsible for the spin-glass transition observed in LiNiO$_2$ at about 8 K. However the absence of JT transition in it is not yet explained.
Recently a short-range orbital order in LiNiO$_2$ was detected by EXAFS \cite{59} and by PDF \cite{60}.

7 Some extra remarks

In this short article I described certain phenomena in which orbital degrees of freedom play an important role. At the end I want also to make a few other, somewhat speculative comments about certain other possible manifestations of orbitals in the structure and properties of systems with strongly correlated electrons.

1) One may argue that the very formation of certain crystal structures is at least partially determined by orbital degrees of freedom. The best known example is probably given by many Cu$^{2+}$ compounds. It is well known that because of the extremely strong JT effect, Cu$^{2+}$ always exists either in a strongly distorted (elongated) ligand octahedron, or this elongation is so strong that one or two apex ligands “go to infinity”, leaving Cu$^{2+}$ in a 5-fold pyramid or 4-fold square coordination. These coordinations are very typical for Cu$^{2+}$ and for many compounds containing it, including such important ones as High-$T_c$ cuprates. The very existence of e.g. YBCO superconductor structure is largely connected with this factor.

2) Another, less clear but rather suggestive case, is the structure of hexagonal manganites $RMnO_3$, $R =$ small rare earth (RE) or Y and Sc.$^3$ Mn$^{3+}$ ions in these systems are 5-fold coordinated (located in the centre of oxygen trigonal bipyramid). Interestingly, Mn is the only TM element forming this crystal structure: all the others, including e.g. Fe$^{3+}$ ($d^5$) (orthoferrites) or Cr$^{3+}$ ($d^3$) (orthochromites) form (distorted) perovskite structure even for small RE. Why is that, is not completely clear, but one factor may be that Mn$^{3+}$ in an octahedral coordination, typical for perovskites, is a strong JT ion. Probably the combination of JT distortion with strong tilting, required for small RE, is not very favourable (although one can still stabilize $R MnO_3$ with small RE in a perovskite structure). Thus it is feasible that, instead of trying to lift the JT degeneracy, the system simply chooses another crystal structure — that of hexagonal YMnO$_3$, in which this degeneracy is absent. Indeed, the CF splitting of 3d-levels in trigonal bipyramid coordination is

\footnote{These systems attract now considerable attention because they are one of the best known example of multiferroics — materials that combine magnetic ordering with ferroelectricity \cite{61}}
into two doublets and an upper singlet, and 4 electrons of Mn$^{3+}$ occupy two lowest doublets, so that no orbital degeneracy is left.

3) Yet another, also rather speculative example of a possible role of orbital degeneracy in apparently unrelated phenomena may be met in TM compounds in which there exist a spontaneous charge, or valence disproportionation. An example of this phenomenon is given e.g. by ferrates like CaFeO$_3$ [62], in which there occurs charge disproportionation $2$Fe$^{4+}$ $\rightarrow$ Fe$^{3+}$ + Fe$^{5+}$ (of course, this process is never complete, and actually the charge modulation is much less than the one that would follow from this formula, but the quantum numbers of the resulting states indeed coincide with those of Fe$^{3+}$ and Fe$^{5+}$).

Another system in which similar phenomenon apparently takes place is perovskite nickelates RNiO$_3$ with the low-spin Ni$^{3+}$ [63]. The appearance of two inequivalent Ni’s was established at least for small RE and Y [64], and possibly in all these systems there occurs charge disproportionation of the type $2$Ni$^{3+}$ $\rightarrow$ Ni$^{2+}$ + Ni$^{4+}$ (another option is that both Ni ions are Ni$^{2+}$, but the extra hole is located at every second [111] layer of oxygens [63]).

Interestingly enough, in both these cases the starting, homogeneous state would correspond to the situation with orbital degeneracy: high-spin Fe$^{4+}$ ($t^3_{2g}e^{1}_{g}$) and low-spin Ni$^{3+}$ ($t^6_{2g}e^{1}_{g}$) are both strong JT ions. It is not actually clear if this factor is really important in causing charge disproportionation, but one may argue that this disproportionation is one way to get rid of orbital degeneracy: instead of doing it via JT distortion, the system does it by simply getting rid of the degenerate electron! (the resulting states Fe$^{3+}$, Fe$^{5+}$, or Ni$^{2+}$, Ni$^{4+}$ are all nondegenerate).

There are many other effects connected with orbital degrees of freedom in TM compounds. I can not dwell on all of them here and will only list some of them with short comments and some references:

(a) Apparently orbitals play an important role in double exchange in manganites and similar materials. Thus, their inclusion helps to explain the absence of ferromagnetism and the appearance of unusual magnetic structures in overdoped manganites — leading to a marked asymmetry in their properties for underdoped (hole-doped) and overdoped (electron-doped) systems [65].

(b) In connection with the colossal magnetoresistance manganites, the question arises what is the orbital state and the role of orbitals in “optimally doped” ferromagnetic metallic state. Experimentally at low temperatures there are no indication of JT distortion, even local [66].
planation is that here we are dealing with an orbital liquid, stabilized by doping [67]. However also a more exotic possibility was discussed in this context [68] — that with ordering of complex orbitals, of the type of (1) but with complex coefficients, e.g.

\[
\left| z^2 \right| + i\left| x^2 - y^2 \right| \div \sqrt{2}.
\]

This state has cubic symmetry and causes no lattice distortion, but it has a magnetic octupole moment.

(c) Orbitals may play a role in charge ordering (CO), often observed in doped TM compounds. One such example, that of CuIr₂S₄, was already mentioned above. Possibly O.O. is also relevant for the low-temperature behaviour of magnetite: recent LDA + U calculations [69] gave such O.O. for the crystal structure obtained in [70].

(d) In connection with the problem of CO, one has to mention the possibility of two types of it: the conventional site-centered ordering, and a bond-centered one (called Zener polaron state in [71]). Charge/octamer ordering in CuIr₂S₄ can be viewed both as a site-centered charge and orbital ordering and as a bond-centered formation of spin singlets at certain bonds; the same is true for the insulating state of VO₂ and in Magneli phases of Ti and V. Similar coexistence of site-centered and bond-centered CO, facilitated by corresponding O.O., apparently may be present in slightly underdoped manganites, and the resulting state may be ferroelectric — a new mechanism of ferroelectricity in magnetic systems [72]. This factor can also be important in the low-temperature phase of magnetite Fe₃O₄, and it can explain its multiferroic behaviour [73].

In this mini-review I tried to show that the orbital degrees of freedom, especially in case of orbital degeneracy, give rise to multitude of consequences. Many of them are already well known, but this field is definitely far from closed and still produces new and new surprises.

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