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# Unusual valence, negative charge-transfer gaps and self-doping in transition-metal compounds\*

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## Abstract

In this paper I discuss the electronic structure and properties of a specific, rather unconventional class of transition metal (TM) compounds, e.g. TM oxides, which formally have unusually high values of the oxidation state, or valence, of TM. In contrast to the typical situation, in this case the charge-transfer gap (excitation energy for the transfer of electrons from the ligands to the TM) is very small and may even become negative. As a result a profound modification of an electronic structure and of all the properties may take place: there appear holes in the oxygen  $p$ -bands (“self-doping”); the material may become the metal of a specific type; there may occur insulator–metal transitions of a specific type; magnetic properties may be quite different from the ones expected normally; the character of elementary excitations may change drastically. I give general discussion of such situation and consider several examples of corresponding systems and their specific properties.

## 1 Introduction

In this paper the specific class of transition metal compounds will be discussed—the systems with the negative charge transfer gap. This article is neither a fully original paper with some concrete new results, nor a review of a certain established field. Rather it is an attempt to formulate a problem to single out a specific class of materials which have much in common and which may have rather

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\*This paper is devoted to the memory of Prof. R. Dagys and was originally published in a memorial volume of Lithuanian Journal of Physics (Lietuvos fizikos žurnalas), **37**, 65 (1997)

unique properties. Thus this paper has in a sense a conceptual character. My aim is to attract attention to the compounds with the negative charge transfer gaps, to discuss some of their properties, to show the connection of this problem to some other phenomena actively discussed nowadays such as insulator–metal transitions, Kondo-insulators or High- $T_c$  Superconductivity. The treatment is necessarily rather qualitative, and some of the analogies I use may seem rather far-fetched. But I hope that this treatment may stimulate more active investigation of these compounds, in the course of which some of the ideas put forth below may be either confirmed or refuted.

For me personally, with my purely theoretical background, one of the first expositions to the idea that the local properties of transition metals *at the atomic level* may be crucial for such phenomena as insulator–metal transitions came from the discussions with R. Dagys. That is why I think that this article, in which these ideas play very important role, can be appropriate for this issue.

## 2 Transition-metal insulators

As is well known, transition metal compounds (for concreteness we shall speak below about oxides) have two main groups of electrons determining their properties. These are the electrons of partially filled  $d$ -shells of TM, and  $p$ -electrons of oxygen [1]. In the standard chemical language we usually speak about certain valence, or oxidation state, of TM, assuming that oxygen ions are  $O^{2-}$ . Thus in ionic picture we have TM ions with partially filled  $d$ -shell ( $d^n$ ) and oxygen ions with filled  $2p$ -shell (configuration  $p^6$ ).

The  $d$ -orbitals have relatively small radius and are rather localized. In this case it is very important to take into account Coulomb interaction of these electrons, in particular  $d$ – $d$  repulsion on the same site (Hubbard interaction) [2]  $U n_{di\uparrow} n_{di\downarrow}$ , where  $n_{di\sigma} = d_{i\sigma}^+ d_{i\sigma}$ ,  $d_{i\sigma}^+$  are the creation operators of  $d$ -electrons on the site  $i$  with the spin  $\sigma$  (we ignore for a moment orbital index). Just this interaction, when strong enough, makes typical stoichiometric TM oxides insulators (Mott–Hubbard mechanism).

Another important group of electrons in these compounds are  $p$ -electrons of oxygen. Coulomb interaction of these electrons can in a first approximation be neglected (although sometimes it may be important, especially in cases of large concentration of holes). However one should definitely include the hybridization (covalent mixing) of  $p$ -electrons with  $d$ -electrons of transition metals; this hybridization determines many properties of these materials [1, 3].

An important parameter is the relative position of TM  $d$ - and oxygen  $p$ -levels,  $\epsilon_d$  and  $\epsilon_p$ , respectively. Thus the simplest generic model describing TM compounds should have the form

$$H = \sum \epsilon_d d_{i\sigma}^+ d_{i\sigma} + \sum \epsilon_p p_{j\sigma}^+ p_{j\sigma} + \sum (t_{pd} d_{i\sigma}^+ p_{j\sigma} + \text{h.c.}) + U \sum n_{di\uparrow} n_{di\downarrow}. \quad (1)$$

Sometimes it is also necessary to take into account some extra factors (orbital structure of  $d$ - and  $p$ -shells, anisotropy of  $p$ - $d$  hopping,  $p$ - $p$  and  $p$ - $d$  interaction, direct  $p$ - $p$  hopping); however for the illustration the model (1) is sufficient.

The model (1) can describe different situations:

*a.* If  $p$ - $d$  mixing (the third term in (1)) is small enough, the system (for one electron per site) is insulating. Depending on the ratio of the parameters  $U$  and  $\epsilon_d - \epsilon_p$  one may discriminate between two kinds of such insulators [4]. If

$$\Delta = (\epsilon_d + U) - \epsilon_p > U, \quad (2)$$

an insulator is of a Mott–Hubbard type: the lowest excited states corresponding to the creation of charged excitations are the transitions of  $d$ -electrons from one TM ion to another,  $d^n + d^n \rightarrow d^{n+1} + d^{n-1}$ . To a first approximation then the energy gap for a conductivity will be  $E_g^{(\text{MH})} \sim U$ .

Another situation exists if the oxygen  $p$ -levels are not deep enough. Then the lowest charge excitations correspond to a transfer of an electron from oxygen into TM  $d$ -shell,  $p^6 + d^n \rightarrow p^5 + d^{n+1}$ . These excitations are lower than the Mott–Hubbard ones when  $\Delta < U$ . With our definition of parameters (1) the gap in this case is  $E_g^{(\text{Ch.tr.})} = \Delta$ . Such materials are called charge-transfer insulators. Corresponding phase diagram is schematically illustrated in fig. 1.

Often one describes these materials using not electron, but hole representation. One can use in this case the same Hamiltonian (1) but taking as a ground state with zero energy the configuration  $d^{n+1}p^6$  and treating  $d_{(\sigma)}^+p_{j\sigma}^+$  as hole creation operators,  $\epsilon_d$  and  $\epsilon_p$  as hole energy levels and  $U$  as  $d$ - $d$  hole repulsion. Then the configuration  $d^n p^6$  corresponds to one  $d$ -hole with the energy  $\epsilon_d$ ,  $d^{n-1}$ —to two  $d$ -holes with the energy  $\epsilon_d + U$ , and  $p^5$ —to a hole on oxygen with the energy  $\epsilon_p$ . Mott–Hubbard insulators then have a gap  $E_g = U$ , and charge transfer insulators —  $E_g = \epsilon_p - \epsilon_d = \Delta$ ; a borderline between them again corresponds to  $U \simeq \Delta$ .

Most of the transition metal oxides belong to one of these two categories. They are insulators. Partially filled  $d$ -shells determine their magnetic properties; an exchange interaction is mostly due to a hopping via intermediate oxygen (superexchange mechanism) [3]. Details of the resulting magnetic structure depend on the type of  $d$ -orbitals occupied, on the geometrical arrangement of corresponding ions etc.; it follows the so called Goodenough–Kanamori–Anderson rules [1, 3, 5].

### 3 Negative charge transfer gaps

As it is clear from the previous discussion, there may exist situations when oxygen  $p$ -levels lie high enough in energy, so that the charge-transfer gap  $\Delta$  may become very small or even negative. All the properties of corresponding systems could change drastically. One can encounter such a situation in cases when the formal valence state of the transition metal is unusually high. In principle the valence of

the TM can vary in wide range, from 2+ up to sometimes 6+. Thus, there exist V oxides from VO ( $V^{2+}$ ) to  $V_2O_5$  ( $V^{5+}$ ); there are Cr compound ranging from  $Cr^{2+}$  ( $KCrF_3$ ) to  $Cr^{6+}$  ( $CrO_3$ ,  $K_2CrO_4$ ).

Usually materials at the beginning of the TM series (V, Ti, Cr), at least for ordinary valence, are believed to belong to the insulators of Mott–Hubbard type. With increase of valence they may cross to charge-transfer regime (for higher valence the relevant  $d$ -levels lie deeper). In principle they may also enter a regime with very small  $\Delta$  (we suspect that  $CrO_2$  is such a case).

Heavier TM oxides usually belong to charge-transfer compounds. This is now well established especially by high-energy spectroscopy (XAS, XPS). It is shown e.g. that the holes introduced by hole doping (for instance in  $Ni_{1-x}Li_xO$  [6]) are mostly introduced into oxygen  $p$ -states. This fact plays also crucial role in High- $T_c$  Superconductors for which the basic structure elements are  $CuO_2$ -planes [7, 8].

One may argue that with the increasing valence of heavier TM ions (Fe, Co, Ni, Cu) charge-transfer energy would decrease and may become negative. In this case, instead of having an electronic configuration, corresponding to the formal valence state, e.g.  $d^n p^6$ , the system may prefer to have configuration  $d^{n+1} p^5$ . One may say that TM ions “resist” having too high a valence and prefer to retain lower valence (higher occupation of  $d$ -shell) at the expense of creating holes on oxygens.

The resulting situation may be illustrated on a following scheme (fig. 2). In fig. 2 we show the relative position of relevant electronic states in different regimes. The case 2a) corresponds to a Mott–Hubbard insulator: the chemical potential  $\mu$  lies between  $d$ -levels with different occupations and the lowest charge-carrying excitations are those across the Mott–Hubbard gap, creating extra electrons and holes in  $d$ -subbands ( $d$ -levels  $\epsilon_d$  and  $\epsilon_d + U$  would become the lower and upper Hubbard bands). The case 2b) corresponds to a charge-transfer insulator. Here lowest excitations are those across the charge-transfer gap  $\Delta$ . We have shown here also the split-off states (Zhang–Rice singlets [9, 10]) which can be created when the hole is introduced into oxygen  $p$ -band (acceptor doping) and which probably play crucial role in High- $T_c$  Superconductors.

The “motion” along the line AB in fig. 1 (decrease of  $\Delta$ ) corresponds here to the modification of an electronic structure shown in figs. 2c, 2d. We may have here the situation strongly resembling the mixed-valent one, where we have partially filled oxygen band overlapping and strongly hybridizing with the correlated  $d$ -states.

The notion of a negative charge-transfer energy (“negative  $\Delta$ ”) was introduced in a most apparent form by Fujimori et al. [12] during the study of  $NaCuO_2$ . This material which formally corresponds to  $Cu^{3+}$  ( $d^8$ ) was shown to have rather the configuration  $d^\alpha p^\beta$  with  $\alpha \sim 8.8$ ,  $\beta \sim 5.2$ —i.e. close to the configuration  $Cu^{2+}(d^9)O^-(p^5)$  (if one takes into account that there are two oxygen per one copper, the average “valence” of oxygen will be changed). There are other materials of the same class: probably to them belong  $LaCuO_3$ ;  $RNiO_3$  (R—rare

earth);  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ; possibly the material with the “colossal” magnetoresistance  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ , etc. Properties of these compounds vary widely:  $\text{NaCuO}_2$  is a diamagnetic insulator [11, 12];  $\text{LaCuO}_3$  is paramagnetic metal (or small gap insulator—there is still some controversy about it, see e.g. [13]).  $\text{LaNiO}_3$  is paramagnetic (Pauli) metal, whereas the compounds  $\text{RNiO}_3$  with  $\text{R} = \text{Pr}, \text{Nd}, \text{Sm}$  have insulator–metal transitions with the strange magnetic ordering in the insulating phase [14, 15].  $\text{LaCoO}_3$  at low temperatures is magnetic insulator with rather unusual magnetic properties; it has gradual insulator–metal transition at high temperatures [1]. However, doping by Sr (which formally produces  $\text{Co}^{4+}$ ) makes this system a ferromagnetic metal [16, 17]. The same is true for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ , see [1, 18].  $\text{CrO}_2$ , which may also belong to this class [18], is metallic and is one of the few ferromagnetic TM oxides. Thus we see that the compounds belonging to this class have a wide variety of properties.

## 4 Self-doping

As is clear from figs. 1, 2, the situation with the small or negative  $\Delta$  should lead to drastic modification of all the properties. In this case the  $p$ -band lies very close or even higher than the initially empty  $d$ -levels so that part of oxygen  $p$ -electrons should go to  $d$ -levels and there should appear holes in  $p$ -band, fig 2*d*. One may call this situation *self-doping*: here holes appear in  $p$ -band not due to externally introduced impurities, but due to a special position of intrinsic energy levels of the system.

Of course there always exists a hybridization between  $p$ -sites of ligands and  $d$ -states of the transition metal ions, so that the resulting bands have mixed character. Thus one should not literally treat the holes as belonging solely to oxygens. Actually the wave function describing the ground state of the system may be schematically written as

$$|\Psi\rangle = \alpha |d\rangle + \beta |p\rangle \quad (3)$$

and in case of negative charge-transfer gap the weight of the configuration  $|d^{n-1}p^5\rangle$  exceeds that of  $|d^n p^6\rangle$ ,  $|\beta|^2 > |\alpha|^2$ . Keeping in mind the  $d$ – $p$  hybridization, we can nevertheless say that in this case one should start not from the configuration  $|d^n p^6\rangle$  corresponding to the formal oxidation state of TM, but rather from the configuration  $|d^{n-1}p^5\rangle$  with the holes in  $p$ -band. This extreme limit is of course also an approximation, one should later on take into account the hybridization and interaction of  $p$ -holes with the remaining  $d$ -configurations, but for these compounds this state is definitely a better starting point than the original configuration  $d^n p^6$ .

This approach is now rather widely used in theoretical treatments of the High- $T_c$  Superconductors, for which the  $d$ – $p$  model (1) (often called in this field the Emery model) is the usual starting point, see below. However the applicability of this approach and even the necessity to use this model for the description of wider

class of TM compounds, especially those with small or negative charge-transfer gap, is not yet widely appreciated, and many phenomena connected with the corresponding physics are not investigated well enough.

The situation with self-doping looks somewhat similar to that in small- or zero-gap semiconductors (grey tin; HgTe) or semimetals (Bi, graphite). However there are also important differences. In contrast to ordinary semimetals, here we have crossing of energy levels of electrons with quite different character: one forming more or less ordinary energy band (oxygen  $p$ -band), and another intrinsically strongly correlated (localized  $d$ -electrons). Consequently electron–electron interactions, both between the  $d$ -electrons and between  $d$ - and  $p$ -electrons plays here very important role. In this respect the situation here resembles more that in heavy-fermion or mixed-valence compounds, especially those with small gaps (Kondo-insulators [19], like “gold” SmS, SmB<sub>6</sub>, CeNiSn etc). Relevant energy scales here, however, are strongly different from the Kondo-systems, especially the  $d$ – $p$  hybridization is much stronger than in rare earth compounds. This change of energy scale may in principle lead to different physical behaviour, although an analogy of our problem with that in valence-fluctuating rare earth compounds may be very productive.

## 5 Properties of negative charge-transfer gap compounds

The appearance of oxygen holes may lead to several important consequences. These holes are rather mobile: the effective bandwidth of the  $p$ -band (actually, of course, hybridized  $p$ – $d$  band, which however in this case has largely  $p$ -character) is typically  $\sim 0.5$  eV. Thus one could in principle expect that the material would become a metal.

However this is not at all evident and need not in general be the case. Thus, in the undoped case one would have equal number of  $p$ -holes and of extra electrons on  $d$ -shell. In this situation they may prefer to form excitonic-like bound states, so that the resulting state would still be an insulator (although with a gap of a collective nature). This is probably the case of NaCuO<sub>2</sub>. This state has much in common with the above mentioned Kondo-insulators [19]—rare-earth compounds with equal number of conduction electrons and localized spins, which also have an energy gap of collective origin [20].

In NaCuO<sub>2</sub> the formation of this insulating ground state is probably facilitated by the crystal structure of this compounds, which consists of one-dimensional CuO<sub>2</sub>-chains with the CuO<sub>4</sub>-plaquettes sharing common edge [11, 12], see fig. 3. However other crystal structures—e.g. perovskite LaCuO<sub>3</sub> with three-dimensional network of CuO<sub>6</sub>-octahedra sharing common corners—may be more favourable for a metallic state [12] (although it is not really proven, see the discussion in [13]).

If the resulting ground state would be a metal, it may be rather unusual: it will be a metal of a mixed-valence type, where one of the components— $d$ -orbitals admixed into a conduction band—is strongly correlated whereas another one—oxygen  $p$ -electrons—may be treated as uncorrelated. What is the nature of the corresponding insulator-metal transition due to closing of the charge-transfer gap, is a completely open problem.

One can have here in principle two possibilities, with even or odd number of electrons per elementary cell. They are illustrated in figs. 4, 5 (cf. fig. 2); for simplicity we speak here about electrons.

In fig. 4 we show possible evolution of spectra when  $d$ -level with even number (e.g. two)  $d$ -electrons moves towards empty conduction band<sup>1</sup>. We see that here we have insulators both for  $\epsilon_c \gg \epsilon_d$  (for oxides it would mean  $\epsilon_p^{hole} \gg \epsilon_d^{hole}$ ) and in the opposite limit  $\epsilon_d \gg \epsilon_c$ , where both electrons are in a conduction band. In this case we have good chances to have insulator also in between, which would correspond to a Kondo-insulator (one  $d$ -electron per one electron in a conduction band)—although it is not proven and may in principle depend on the specific details such as crystal structure etc. The situation illustrated in fig. 4 corresponds to a low-spin state. If the initial configuration would correspond to a high-spin state (parallel spins in fig. 4a)) there should occur magnetic–nonmagnetic transition somewhere in between.

Fig. 5 corresponds to an odd number of electrons per unit cell. Here fig. 5a (deep  $d$ -level) describes the (magnetic) insulator of a Mott-Hubbard type. However an opposite limit ( $\epsilon_d \gg \epsilon_c$ ) would correspond to a metal with all the electrons in a partially filled conduction band and an empty  $d$ -level. Thus we should have somewhere in between (when  $\Delta = \epsilon_c - \epsilon_d$  changes sign and becomes negative) an insulator–metal transition. There is at present no theory of such transitions, e.g. it is not clear whether they would be I-st or II-nd order, whether magnetic order disappears simultaneously with the insulator–metal transition, etc.

The situation with the negative charge-transfer gap may lead to a specific modification of the local electronic configuration (crystal-level scheme) of the TM ion itself. In particular the configurations which are usually unstable may be stabilized in this case [21]. Let us consider this situation on the specific example of the compounds containing  $\text{Co}^{3+}(d^6)$ , e.g.  $\text{LaCoO}_3$  [22]. Usually two competing configurations are considered for this case: the high-spin ( $S = 2$ ) and the low-spin ( $S = 0$ ) ones, see fig. 6 a), b). If we now treat the situation with the negative charge-transfer gap, we should have locally the configuration which is rather  $d^7p^5$ . The ion with the configuration  $d^7$  should definitely be in the high-spin state with  $S_d = \frac{3}{2}$ , see fig. 6c). However there will be an oxygen hole nearby which is schematically illustrated in fig. 6c). The hybridization of oxygen  $p$ -electrons with the predominantly  $e_g$ -states of the TM

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<sup>1</sup>For oxides this would correspond to a hole representation: empty  $d$ -level approaching full conduction band, see fig. 2.



is rather strong, and it always decreases the total energy if corresponding mixing is allowed. From fig. 6c) it is clear that for that the spin on oxygen should be antiparallel to the spin of the TM (here Co). Thus the total spin of this state will be  $S_{tot} = \frac{3}{2} - \frac{1}{2} = 1$ , i.e. the configuration  $\text{Co}^{3+}\text{O}$  ( $d^7p^5$ ) will have neither high-, nor low-spin state, but an intermediate spin  $S = 1$ . Recent band-structure calculation using LDA+U method which permits to take into account electron correlations, indeed confirmed that an intermediate spin state may be the ground state of  $\text{LaCoO}_3$  at certain conditions [22]. This gives an alternative explanation of the intriguing properties of  $\text{LaCoO}_3$  [1] which were usually interpreted in a framework of the model of the low-spin–high-spin transition.

Another interesting group of problems emerge when we think of the possible magnetic structure of these materials. As is mentioned above, in ordinary cases (Mott–Hubbard or charge-transfer insulators with filled oxygen  $p$ -shells) we can describe magnetic interactions as mostly due to superexchange. The rules which determine magnetic structure (Goodenough–Kanamori–Anderson rules [1, 3]) are well known and are very successful.

In case of negative charge-transfer energy the situation may be modified drastically. If we have, besides  $d$ -electrons ( $d$ -spins), also holes (spins) on oxygen, then one may expect different exchange mechanisms entering the game. If oxygen holes are delocalized and form bands, there may appear  $d$ – $d$  interaction of the RKKY-type via  $p$ -band. Or, if a band is sufficiently narrow, double-exchange mechanism [23] (tendency to form ferromagnetic alignment of localized spins provided by mobile holes) may be efficient; it may produce e.g. ferromagnetic metallic state (this may be the situation in  $\text{CrO}_2$ ,  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  and in  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ). If, on the other side, oxygen holes could be treated as localized, there should be strong  $p$ – $d$  exchange interaction which would also give a ferro- (or rather ferri-) magnetic state: the spins of TM ions will be parallel, and antiparallel to the spins of oxygens sitting in between [24], see fig. 7 <sup>2</sup>.

The role of orbital degrees of freedom in negative- $\Delta$  systems is also far from trivial. It is known in particular that in case of orbital degeneracy the system becomes unstable (Jahn-Teller effect), and in concentrated case it experiences the cooperative Jahn-Teller transition [25] (an orbital ordering accompanied by the structural phase transition; this is one of the very few cases of structural transitions for which we know its microscopic origin). What would become of these transitions for negative  $\Delta$ , is not known. The change of the occupation of  $d$ -level may remove the degeneracy, or, vice versa, may make degenerate the system which by formal valence is not degenerate. However, the degeneracy removed from  $d$ -orbitals may still be present (it may be “transferred” to the degeneracy of the corresponding oxygen holes). What will be the outcome is definitely inter-

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<sup>2</sup>We consider here the crystal structure like that in perovskites or in  $\text{La}_2\text{CuO}_4$ ; in principle the outcome should be sensitive to the detailed crystal structure.

esting to explore; this may determine many properties of these compounds, both structural and magnetic, and may be crucial, e.g. for the “colossal” magnetoresistance in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ .

There is also an important connection of the situation in negative- $\Delta$  compounds and in doped cuprates (High- $T_c$  Superconductors). In these latter materials the holes introduced by doping form singlet bound states with  $\text{Cu}^{2+}$  spins (Zhang-Rice singlets [9, 10]) which most probably determine transport and superconducting properties at relatively low doping. In this sense the substances with the formal valence  $\text{Cu}^{3+}$  ( $\text{NaCuO}_2$ ;  $\text{LaCuO}_3$ ) could correspond to a situation where we have these singlets *at each site*, cf. fig. 3. However the very picture of singlet bound states may turn out to be invalid for very high concentration of them: excessive doping may lead not to a “removal” of spins from our system (which is the case with Zhang-Rice singlets and which is usually described by  $t$ - $J$  model [9]) but to *adding* extra spins (we have all  $d$ -electron spins and we add holes—or spins—on oxygen [27]). What will be the properties of such systems is not really clear. We thus see that our problem (description of negative- $\Delta$  compounds) has much in common with the description of overdoped High- $T_c$  Superconductors.

In this connection one more remark is in order. Until now we discussed mostly the stoichiometric compounds with negative charge-transfer gap. However most probably it is just in doped materials that the specific properties of these systems could be most pronounced. Indeed, as we mentioned above,  $p$ - $d$  hybridization is always present in the TM compounds, and as a result the electronic configuration is never really  $d^n p^6$  but always has admixture of other configurations, such as  $d^{n+1} p^5$ . In that sense the difference between the usual compounds and those with negative CTG may be sometimes more quantitative than qualitative, according to Eq. (2) and to the discussion there. It is true that the theoretical discussion in this case should start from the opposite limit of holes in the  $p$ -band, but the outcome may in some cases look similar to the usual treatment. However, for doped compounds we have more chances to have really different behaviour. The case of High- $T_c$  cuprates gives a good example of the new striking phenomena which may be connected with the introduction of holes into oxygen  $p$ -states. One can even speculate: does not the clue to the search of new (high-temperature) superconductors lie in the unusually high valence?

## 6 Conclusion

We see that the TM compounds with the unusually high valence of the TM ions and small or negative charge-transfer gap constitute well-defined special class of compounds, for which we can expect rather wide range of properties.

Experimental studies of these compounds are now under way. However their theoretical understanding is still lacking. The nature of the resulting states is

a completely open problem: at the moment we do not know when to expect metallic or insulating behaviour (or the insulator-metal transition), what will be the magnetic properties, etc. There are clear links of this problem to that of heavily doped High- $T_c$  Superconductors and to the Kondo-insulators, and one may hope that eventual progress in the description of negative- $\Delta$  systems may shed some light on these problems too (and vice versa).

Experimentally there are also a lot of problems to be solved. One has to check whether all the “suspicious” materials mentioned above ( $\text{LaCuO}_3$ ;  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ;  $\text{PrNiO}_3$ ;  $\text{CrO}_2$ ;  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ) belong to the class of compounds with small or negative charge-transfer gap. Probably the most direct tool for this is high-energy spectroscopy and possibly some local spectroscopic probes (NMR, ESR). Special attention should be paid to the properties of doped compounds of this type. Thus for example it would be very interesting to try to dope, e.g. by Sr or Ba, the quasi-one-dimensional compounds  $\text{NaCuO}_2$  or  $\text{KCuO}_2$ , which definitely have negative charge-transfer gap (“Zhang–Rice singlets at each site”). This would be the counterpart of the High- $T_c$  cuprates in which by doping e.g.  $\text{La}_2\text{CuO}_4$  we go formally from  $\text{Cu}^{2+}$  in the direction of “ $\text{Cu}^{3+}$ ”: here it would correspond to moving in the opposite direction, from “ $\text{Cu}^{3+}$ ” toward  $\text{Cu}^{2+}$ . What would be the properties of such system would be very interesting to study.

One can raise many other interesting questions and suggest a lot of other experiments to probe the behaviour of these systems. Here I only want to stress once again that the study of this very specific and interesting class of transition metal compounds presents definite interest both from the fundamental point of view and possibly for certain practical applications.

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## References

- [1] J. B. Goodenough, *Magnetism and the Chemical Bond*, Interscience Publ., New York–London, 1963
- [2] J. Hubbard, *Proc. Roy. Soc.* **A277**, 237 (1964)
- [3] P. W. Anderson, in *Magnetism*, G. T. Rado, H. Suhl (Eds.), vol. 1, New York 1963
- [4] J. Zaanen, G. A. Sawatzky and J. W. Allen, *Phys. Rev. Lett.* **55**, 418 (1985)
- [5] J. Kanamori, *J. Phys. Chem. Sol.* **10**, 87 (1959)
- [6] P. Kuiper et al., *Phys. Rev. Lett.* **62**, 221 (1989)
- [7] V. J. Emery, *Phys. Rev. Lett.* **58**, 2794 (1987)
- [8] A. K. Zvezdin and D. Khomskii, *Pis'ma v ZhETF, Prilozhenie* **46**, 102 (1987) (*JETP Lett. Suppl.* **46**, 87 (1987));  
D. Khomskii and A. K. Zvezdin, *Solid State Comm.* **66**, 651 (1988)
- [9] F. C. Zhang and T. M. Rice, *Phys. Rev. B* **37**, 3757 (1988)
- [10] H. Eskes and G. A. Sawatzky, *Phys. Rev. Lett.* **61**, 1415 (1988)
- [11] K. Hestermann and P. Hoppe, *Z. Anorg. Allg. Chemie* **367**, 261 (1969)
- [12] T. Mizokawa, H. Namatame, A. Fujimori et al., *Phys. Rev. Lett.* **67**, 1638 (1991)
- [13] M. T. Czyzyk and G. A. Sawatzky, *Phys. Rev. B* **49**, 14211 (1994)
- [14] J. B. Torrance et al., *Phys. Rev. B* **45**, 8209 (1992)
- [15] J. L. García-Muñoz, J. Rodríguez-Carvajal and P. Lacorre, *Europhys. Lett.* **20**, 241 (1992); *Phys. Rev. B* **50**, 978 (1994)
- [16] G. H. Jonker and J. H. van Santen, *Physica* **19**, 120 (1953)
- [17] P. H. Raccach and J. B. Goodenough, *J. Appl. Phys.* **39**, 1209 (1968)
- [18] D. Khomskii and G. A. Sawatzky, *Solid State Comm.* in press (1997)
- [19] G. Aeppli and Z. Fisk, *Comments Cond. Matt. Phys.* **16**, 155 (1992)
- [20] D. Khomskii, chapter in the book “Quantum Theory of Solids”, ed. I. M. Lifshits, ser. “Advances in Science and Technology in the USSR”, MIR Publ., Moscow, 1982, pp. 70–129

- [21] R. H. Potze, G. A. Sawatzky and M. Abbate, unpublished
- [22] M. A. Korotin, S. Yu. Ezhov, I. V. Solovyov, V. I. Anisimov, D. I. Khomskii and G. Sawatzky, *Phys. Rev. B* **54**, 5309 (1996)
- [23] C. Zener, *Phys. Rev.* **81**, 440 (1951)
- [24] A. Aharoni, R. J. Birgenau and M. A. Kastner, *IBM J. Res. Develop.* **33**, 287 (1989)
- [25] K. I. Kugel and D. Khomskii, *Usp. Fiz. Nauk* **136**, 621 (1982) (*Sov. Phys.—Uspekhi* **25**, 231 (1982))
- [26] K. I. Kugel and D. Khomskii, *ZhETF* **64**, 1429 (1973) (*Sov. Phys.—JETP* **37**, 725 (1973));  
D. Khomskii and K. I. Kugel, *Solid State Comm.* **13**, 763 (1973)
- [27] V. J. Emery and G. Reiter, *Phys. Rev. B* **38**, 4547 (1988)

P.S. (December 2000)

This small, review-like, paper was written in 1997 and published in the memorial issue of the Lithuanian Journal of Physics **37**, 65 (1997) devoted to the memory of my late friend R. Dagys. As this journal is not widely available, I think it worthwhile to put it on the web, although it is already three years old. The development since 1997 has shown that the problems raised in this paper are still important, and the discussion presented in this paper may still be useful. I did not change the main content of the paper; to somewhat update it, below are two more recent references relevant to the problems discussed in this paper.

M. A. Korotin, V. A. Anisimov, D. I. Khomskii and G. A. Sawatzky, *Phys. Rev. Lett.* **80**, 4305 (1997)

T. Mizokawa, D. I. Khomskii and G. A. Sawatzky, *Phys. Rev. B* **61**, 11263 (2000)

## Figure Captions

- Fig. 1 Schematic phase diagram of the transition metal compounds (by [4])
- Fig. 2 Energy spectrum of *a*) Mott-Hubbard insulator; *b*) charge-transfer insulator with the positive charge-transfer gap  $\Delta$ ; *c*), *d*) the system with small and negative charge-transfer gap
- Fig. 3 The main motive of the crystal structure of  $\text{NaCuO}_2$
- Fig. 4 Evolution of the energy spectrum with the even (e.g. two) number of electrons per unit cell *a*) Mott-Hubbard insulator (low-spin state); *b*) charge-transfer insulator ( $\Delta > 0$ ); *c*) charge-transfer insulator ( $\Delta \sim 0$ ); *d*) the system with the negative charge-transfer gap; in this particular case it is also an insulator.  $\mu$  is the chemical potential
- Fig. 5 Evolution of the energy spectrum with the odd number (here one) of electrons per unit cell *a*) Magnetic Mott-Hubbard insulator; *b*) magnetic charge-transfer insulator; *c*) the situation with the small charge-transfer gap, which can be an insulator or a metal; *d*) the situation with large negative charge-transfer gap, which in this particular case should be a metal with empty *d*-shell. Other notations are the same as in fig. 4
- Fig. 6 Energy levels and electron occupation of the ion with the configuration  $d^6$  (e.g.  $\text{Co}^{3+}$ ): *a*) high-spin state; *b*) low-spin state; *c*) intermediate-spin state.  $t_{pd}$  is the transition metal-oxygen hybridization
- Fig. 7 Possible origin of the ferromagnetic ordering in case of localized oxygen *p*-holes (by [24])

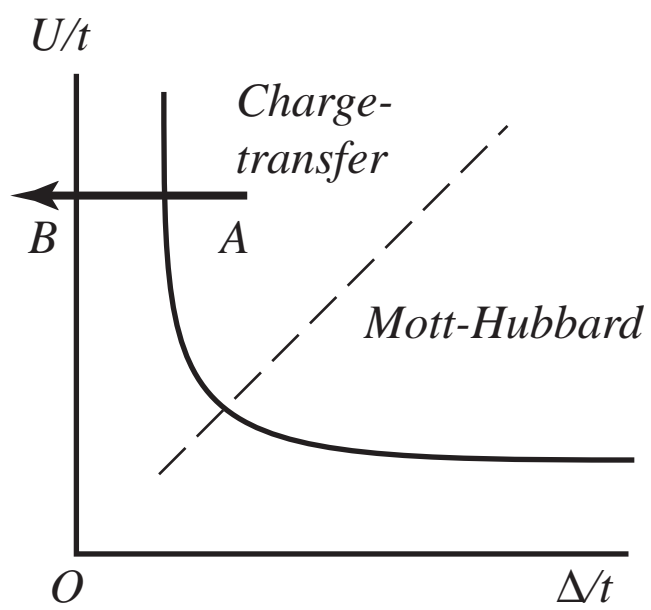


Fig. 1

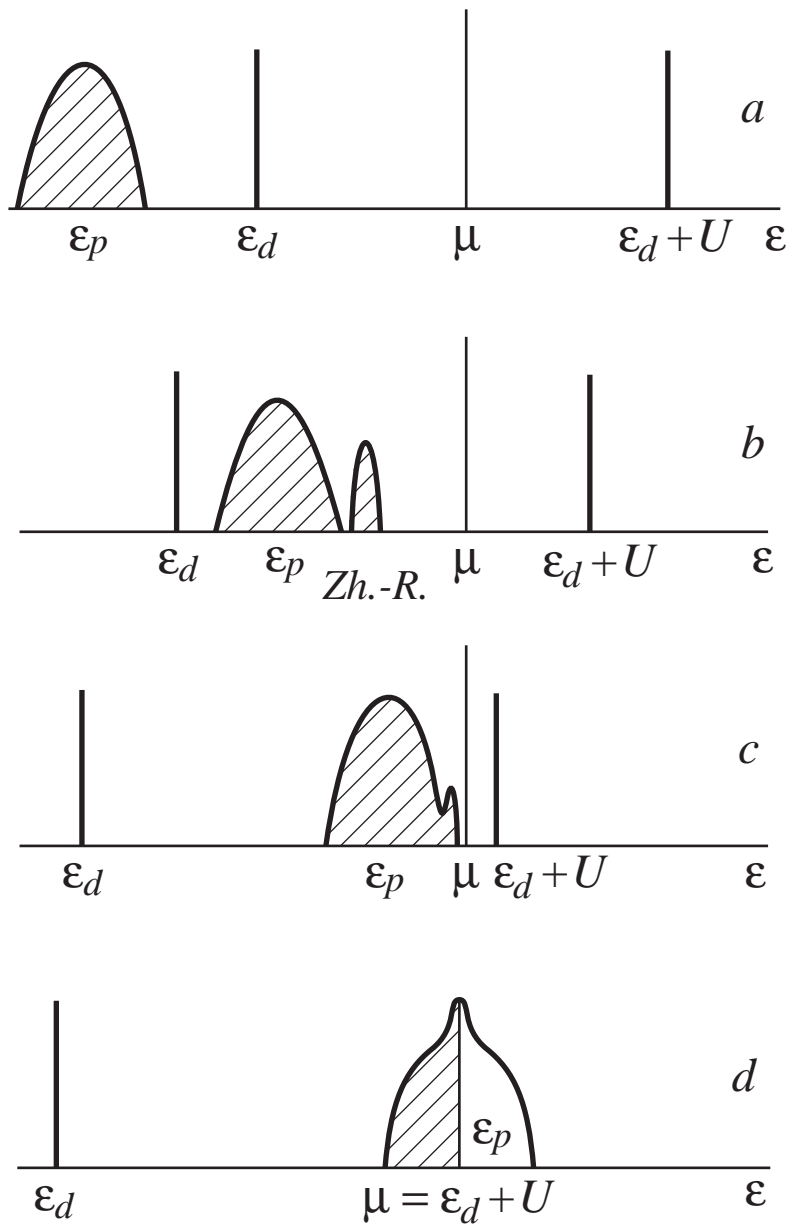


Fig. 2



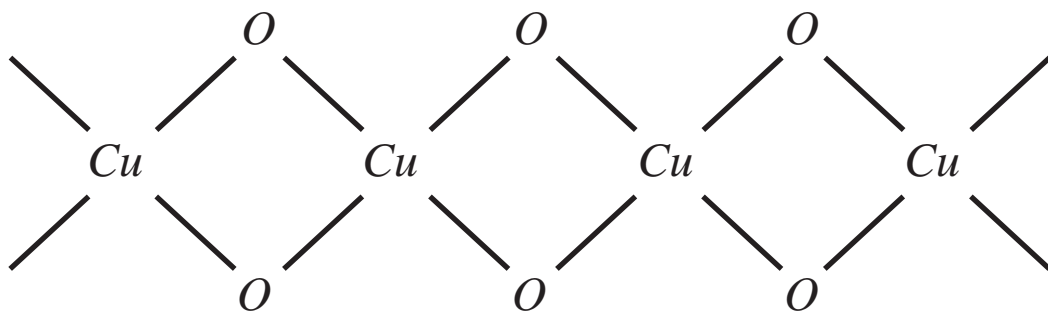


Fig. 3

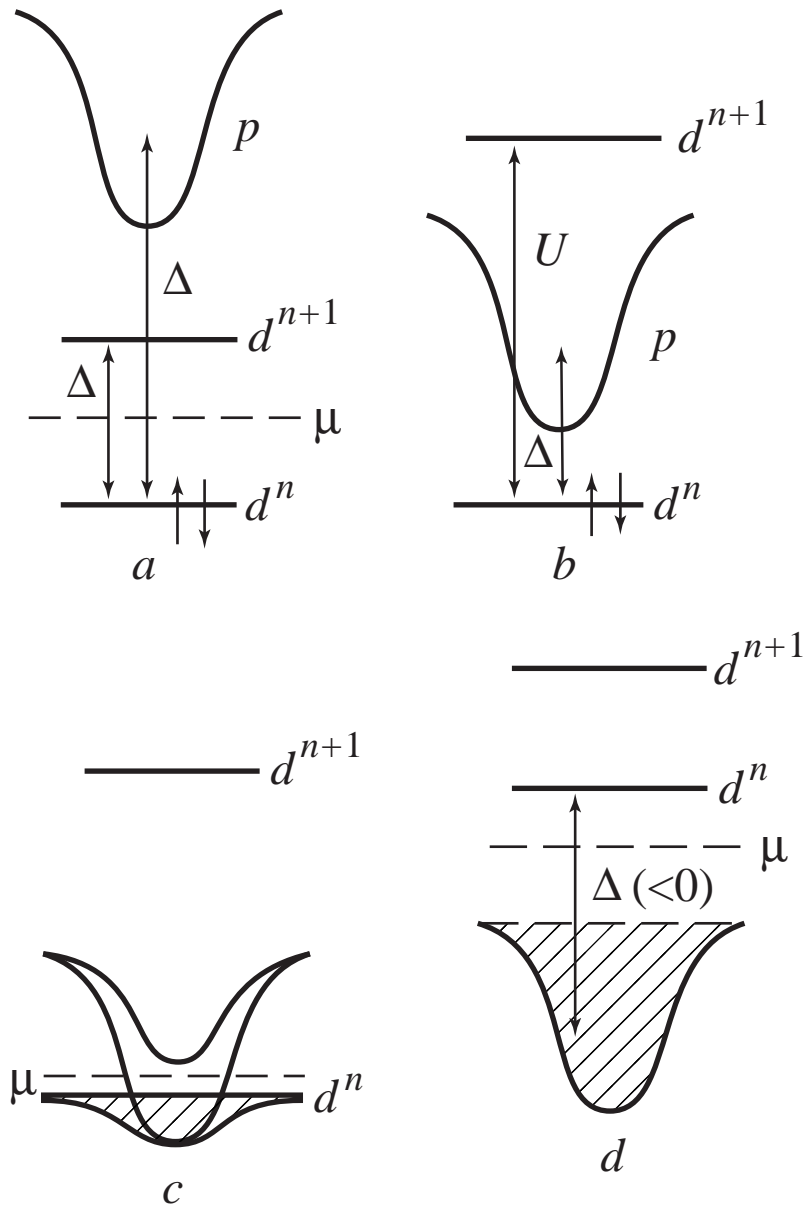


Fig. 4

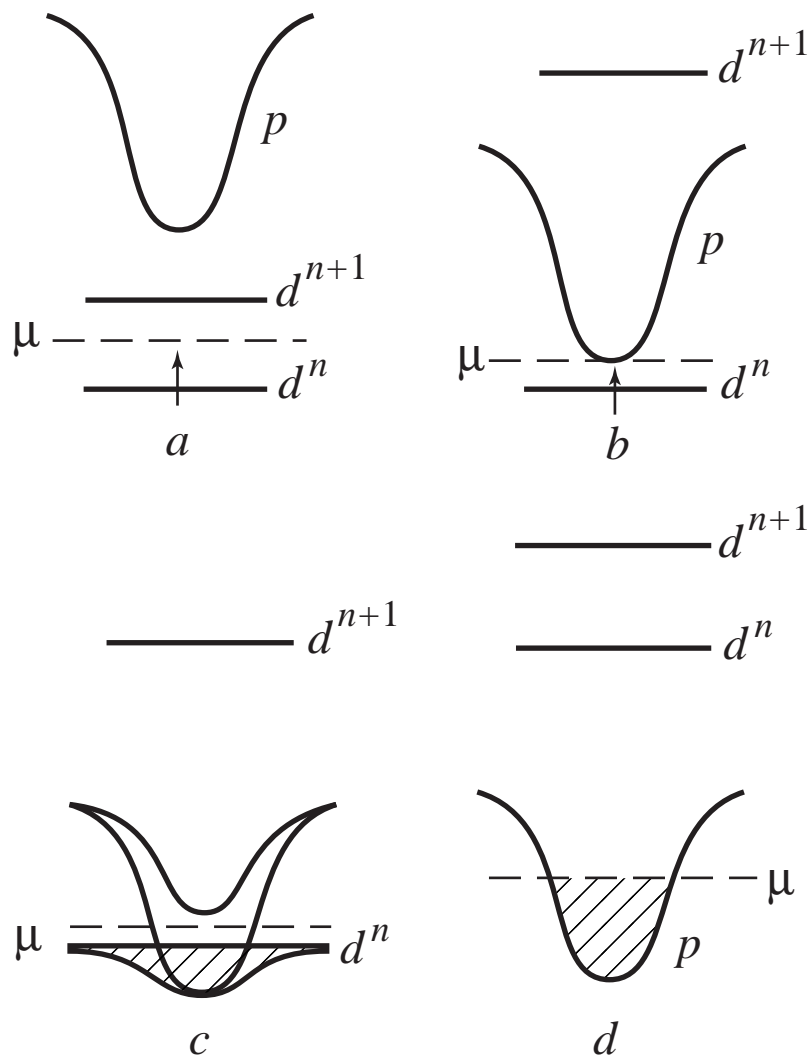


Fig. 5

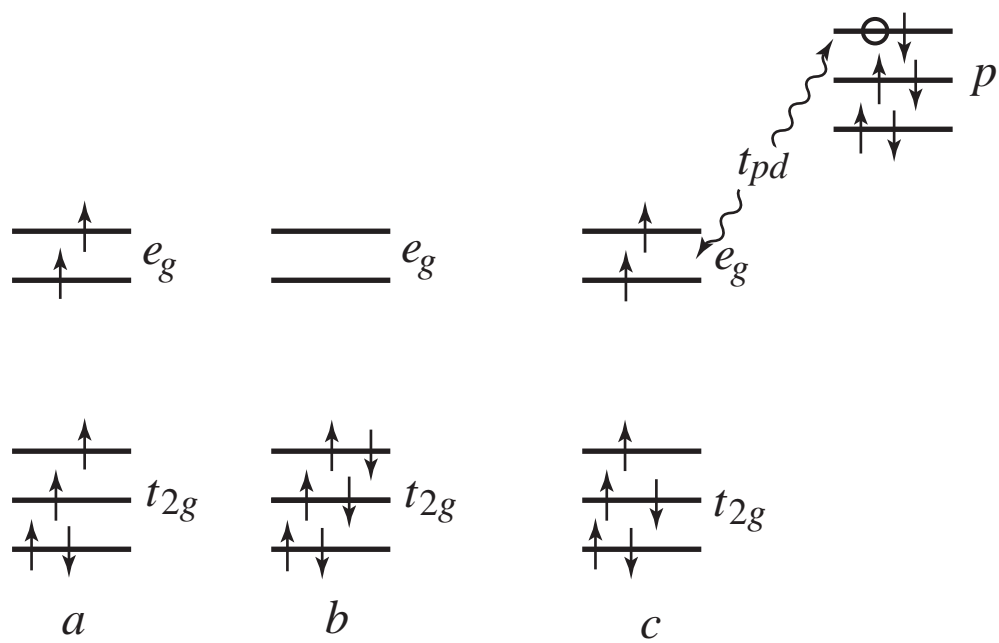


Fig. 6

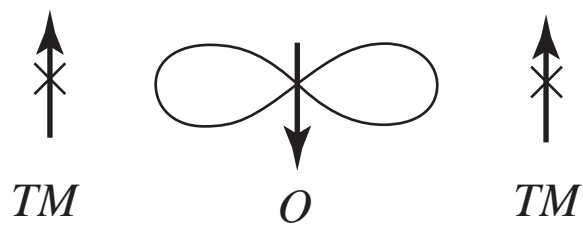


Fig. 7