

# Crystal field splitting in correlated systems with the negative charge transfer gap

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**Abstract.** Special features of the crystal field splitting of  $d$ -levels in the transition metal compounds with the small or negative charge-transfer gap  $\Delta_{CT}$  are considered. We show that in this case the Coulomb term and the covalent contribution to the  $t_{2g} - e_g$  splitting have different signs. In order to check the theoretical predictions we carried out the ab-initio band structure calculations for  $\text{Cs}_2\text{Au}_2\text{Cl}_6$ , in which the charge-transfer gap is negative, so that the  $d$ -electrons predominantly occupy low-lying bonding states. For these states the  $e_g$ -levels lie below  $t_{2g}$  ones, which demonstrates that at least in this case the influence of the  $p-d$  covalency on the total value of the crystal field splitting is stronger than the Coulomb interaction (which would lead to the opposite level order). We also show that the states in conduction band are made predominantly of  $p$ -states of ligands (Cl), with small admixture of  $d$ -states of Au.

## 1. Introduction

One of the most important factors determining properties of the transition metal (TM) oxides is the splitting of  $d$ -levels when the TM ions are put in a crystal. This crystal-field (CF) splitting largely determines magnetic and orbital state of respective ions, and thus their properties. In general there are two mechanisms, which have to be taken into account in the calculation of the CF splitting.

One is the Coulomb interaction of  $d$ -electrons with charges of surrounding ions - mainly nearest-neighbor anions like  $O^{2-}$  in oxides or  $F^-$  and  $Cl^-$  in fluorides and chlorides. Since the Coulomb repulsion with anions depends on the shape of the electron density, the resulting corrections to the energy spectrum will be different for different  $d$ -orbitals.

The second mechanism which also leads to the CF splitting is the covalency, the hybridization between  $d$ -states of the TM ions and ligand  $p$ -states. The  $p-d$  hybridization (hopping integrals  $t^{pd}$  in Eq. (1)) strongly depends on the symmetry of the local environment and will be very different for  $d$ -orbitals pointing to the ligands ( $e_g$  orbitals in the case of a octahedral surrounding) or looking in between of them ( $t_{2g}$  orbitals in the octahedra), which would lead to their splitting. Here and below we will discuss the octahedral symmetry.

We show below that the role of these two mechanisms may strongly differ in conventional TM compounds and in the materials with the negative charge-transfer (CT) gaps [1, 2], with a (e.g. oxygen) holes in the ground state.

## 2. The basic model

The standard model describing transition metal (TM) ions in a crystal is

$$\begin{aligned}
 H = & \epsilon_{d0} \sum_{i\alpha} d_{i\alpha\sigma}^\dagger d_{i\alpha\sigma} + \epsilon_p \sum_{j\beta} p_{j\beta\sigma}^\dagger p_{j\beta\sigma} \\
 & + \sum_j t_{ij\alpha\beta}^{pd} (d_{i\alpha\sigma}^\dagger p_{j\beta\sigma} + h.c.) \\
 & + \sum_{(\alpha\sigma) \neq (\beta\sigma')} U_{\alpha\beta}^{dd} n_{i\alpha\sigma} n_{i\beta\sigma'}.
 \end{aligned} \tag{1}$$

Here  $d_{i\alpha\sigma}^\dagger$ ,  $d_{i\alpha\sigma}$  are the creation and annihilation operators of  $d$ -electrons at a site  $i$  in the orbital state  $\alpha$  with spin  $\sigma$ ,  $p_{j\beta\sigma}^\dagger$ ,  $p_{j\beta\sigma}$  describe different  $p$ -electrons at the  $j$ -th ligand surrounding given TM site. The system is also characterized by the on-site Coulomb (Hubbard) interaction  $U^{dd} = U$ , and by the charge-transfer energy  $\Delta_{CT}$ , defined as the energy of the transition

$$d^n p^6 \rightarrow d^{n+1} p^5, \tag{2}$$

which in the electron representation used in the Hamiltonian (1) is

$$\Delta_{CT} = \epsilon_{d0} + nU - \epsilon_p = \epsilon_d - \epsilon_p. \tag{3}$$

Here we introduced the renormalized energy of  $d$ -levels

$$\epsilon_d = \epsilon_{d0} + nU \quad (4)$$

- the effective  $d$ -energy levels to which an electron is transferred from  $p$ -states of a ligand in the “reaction” (2). [3] Further on in this paper by  $d$ -levels shown e.g. in Figs. 1 and 3 we have in mind these renormalized  $d$ -levels (4).

In principle one should include in this Hamiltonian some other terms, such as the intra-atomic Hund’s rule exchange  $J_H$ , Coulomb repulsion for ligand  $p$ -electrons  $U_{pp}$ , etc. For our purposes, however, the simplified model (1) is sufficient.

### 3. Positive charge-transfer energy, $\Delta_{CT} > 0$

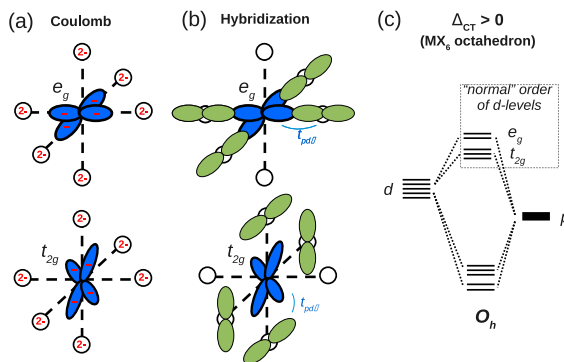
In a most typical situation for the TM compounds, when the ligand  $p$ -levels lie deep below  $d$ -levels of the TM ions, both the Coulomb and the hybridization contributions to the CF splitting lead to the same sequence of  $d$ -levels. This case is characterized by a large positive CT gap  $\Delta_{CT}$ , defined in Eq. (3). As explained above and as is clearly seen in Fig. 1(a), the Coulomb repulsion of  $d$ -electrons with negatively-charged ligands is stronger for  $e_g$ -electrons with the lobes of the electron density directed towards the ligands than for  $t_{2g}$ -orbitals pointing in between the anions. This leads to the CF splitting shown in Fig. 1(c) such that  $e_g$ -orbitals lie *above*  $t_{2g}$ . This sequence of  $d$ -levels is referred as “normal”.

The same “normal” sequence of  $d$ -levels is also caused by the  $p - d$  hybridization, i.e. by covalent contribution. Since the hopping matrix elements  $e_g - p$  ( $t_{pd\sigma}$ ) are larger than hoppings between  $t_{2g}$ -orbitals and  $p$ -orbitals of ligands ( $t_{pd\pi}$ ), the  $e_g$ -levels are pushed up stronger than  $t_{2g}$ , see Figs. 1(b), (c). [4]

Relative importance of these two contributions to the total value of the CF splitting depends on the compound, but in the usual situation of  $\Delta_{CT} > 0$  they at least work in the same direction.

In the early stage of the development of the CF theory it was argued that an account of the real shape of ligand orbitals may change the sign of the Coulomb contribution, obtained in the point-charge model. [5] However, it was shown later that in order to consider ionic term in a correct way the  $d$ -electron wave functions must be orthogonalized to the ligands. [6] As a result, the total ionic contribution to the CF splitting has the same sign as the covalent term in the case of  $\Delta_{CT} > 0$ . [7]

Note that for the *bonding* levels (the lower levels in Fig. 1(c)) the covalency contribution gives the sequence of levels opposite to the “normal”: the levels with the  $e_g$ -symmetry have stronger bonding-antibonding splitting and lie *below* those with the  $t_{2g}$ -symmetry. But for large positive CT gap these states are predominantly made of the combination of  $p$ -states of ligands with a proper symmetry, with only a small admixture of  $d$ -states, and one rarely discuss these states, which lie deep below the Fermi energy. All interesting phenomena take place in the partially-filled antibonding states, which have predominantly  $d$ -character and which are responsible e.g. for magnetism, orbital



**Figure 1.** (color online) Charge-transfer gap  $\Delta_{CT} > 0$ . There are two contributions to the resulting CF splitting caused by (a) the Coulomb interaction and (b) the  $p-d$  hybridization (or covalency). The  $e_g$ -orbitals (the  $x^2 - y^2$  is shown as an example) pointing to the ligands have larger hybridization and stronger repulsion from them and as a result lie above the  $t_{2g}$ -levels (the  $yx$ -orbital is sketched). The ligands forming octahedra are shown as open circles,  $d$ -orbitals are painted in blue and ligand  $p$ -orbitals in green. For the Coulomb contribution the charges (not the signs of the wave-functions) are indicated. The levels with predominantly  $d$ -character are marked by the dashed “box”.

ordering etc. But this changes drastically in case of the negative CT gap  $\Delta_{CT} < 0$ , which we now consider.

#### 4. Negative charge-transfer energy, $\Delta_{CT} < 0$

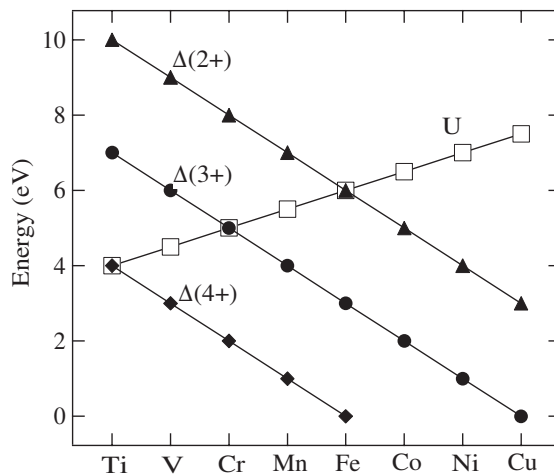
The situation is quite different for the systems with small and especially negative CT gaps. In this case the Coulomb and covalent contributions to the splitting of  $d$ -levels have different signs. The negative CT gap is met in the compounds based on the late TM ions with unusually high valence, or high oxidation state [2], like  $\text{Fe}^{4+}$  or  $\text{Cu}^{3+}$ , see Fig. 2, compiled by Mizokawa on the basis of the data of [8, 9].

The negative CT energy means that it is favorable to transfer an electron from the ligand  $p$ -shell to a  $d$ -level, i.e. to perform the “reaction” (2) already in the ground state. Such a process is sometimes called self-doping. [11, 10] On the language of energy levels a regime with the negative CT energy corresponds to the situation when the initial *renormalized*  $d$ -levels  $\epsilon_d$  in (4) lie below the ligand  $p$ -levels.

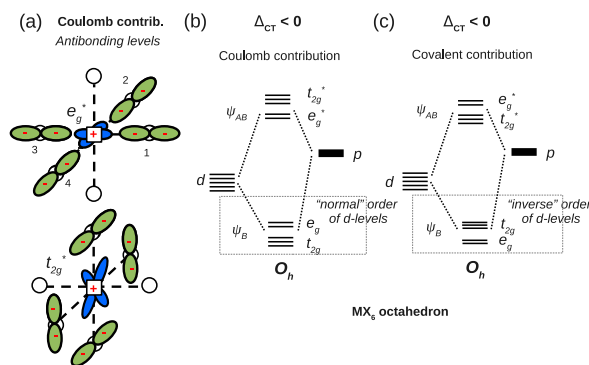
We start with an analysis of the covalent contribution to the CF splitting, Fig. 3(c). In contrast to the case of  $\Delta_{CT} > 0$  it is now the lower bonding orbitals that have predominantly  $d$ -character with a small admixture of  $p$ -states

$$\Psi_B = \alpha|d\rangle + \beta|p\rangle, \quad \alpha^2 + \beta^2 = 1, \quad \alpha \gg \beta. \quad (5)$$

For these bonding states the covalency leads to the splitting such that the  $t_{2g}$ -levels lie above  $e_g$ -ones, i.e. this covalency contribution leads to an “inverted” CF splitting for  $d$ -electrons.



**Figure 2.** The charge-transfer (CT) gap  $\Delta_{CT}$  and the on-site Coulomb repulsion  $U$  values for different 3d-ions, after T. Mizokawa. [9]



**Figure 3.** (color online) Charge-transfer (CT) gap  $\Delta_{CT} < 0$ . The crystal-field splitting caused by the Coulomb interaction (b) and due to the covalency (c) are shown. Examples of the antibonding orbitals are sketched in the panel (a). Ligands forming octahedra are shown as open circles,  $d$ -orbitals are painted in blue and ligand  $p$ -orbitals in green. For the Coulomb contribution the charges (not the signs of the wave-functions) are indicated. The levels with predominantly  $d$ -character are marked by the dashed “box”.

These bonding states are actually completely filled. The electrons of partially-filled levels will actually be in the antibonding orbitals  $t_{2g}^*$ ,  $e_g^*$ . Due to a stronger  $pd\sigma$  hybridization of orbitals having  $e_g$ -symmetry with the ligand  $p$ -shell, the bonding-antibonding splitting of  $e_g$ -orbitals is larger than that of  $t_{2g}$ -orbitals. As a result the order of antibonding levels is “normal”, the same as in Fig. 1 ( $t_{2g}^*$ -levels are below  $e_g^{the*}$ -subshell). But, in contrast to the case of a positive CT gap, here the wave function of the antibonding states will be

$$\Psi_{AB} = \alpha^*|d\rangle + \beta^*|p\rangle, \quad (\alpha^*)^2 + (\beta^*)^2 = 1, \quad \alpha^* \ll \beta^*, \quad (6)$$

i.e. these states have predominantly  $p$ -character. In effect the resulting state would be the state with the self-doping described above, i.e. with a large fraction of oxygen holes.

The Coulomb contribution, however, would lead to the opposite sequence of  $d$ -levels, compared to the covalent term. For the  $d$ -levels themselves it would have the same sign as for the case of  $\Delta_{CT} > 0$ , and due to a stronger repulsion from ligands the  $e_g$ -levels (bonding) would be pushed *above*  $t_{2g}$ , opposite to the influence of the hybridization.

One has to somewhat specify these arguments. In the case of  $\Delta_{CT} < 0$  the ground state should be better taken not as  $d^n p^6$ , but rather as  $d^{n+1} p^5$ , according to (2). This will change the magnitude of the Coulomb terms, the ting effect: still  $e_g$ -electrons would repel stronger from the ligands (with smaller charge, e.g.  $O^{1.5-}$  instead of  $O^{2-}$ ). Thus in the case of the negative CT gap the contributions of the Coulomb interaction and of the  $p-d$  covalency to the CF splitting of  $d$ -states is opposite.

The same can be said about the antibonding levels. As follows from Eq. (6), the antibonding levels have predominantly  $p$ -character, but the combinations of ligand  $p$ -electrons with  $e_g$ -symmetry shown in Fig. 3(a), (e.g. the  $\sigma$  combination  $p_\sigma = \frac{1}{\sqrt{4}}[p_{1x} - p_{2y} - p_{3x} + p_{4y}]$ , which hybridizes with  $d_{x^2-y^2}$ -orbital) would have stronger attraction to a positively-charged  $d$ -ion than the  $t_{2g}^*$ -orbitals, made out of the  $\pi$ -combination of ligand orbitals. As a result the antibonding  $t_{2g}^*$ -levels due to this factor would lie higher than  $e_g^*$  (Fig. 3(b)).

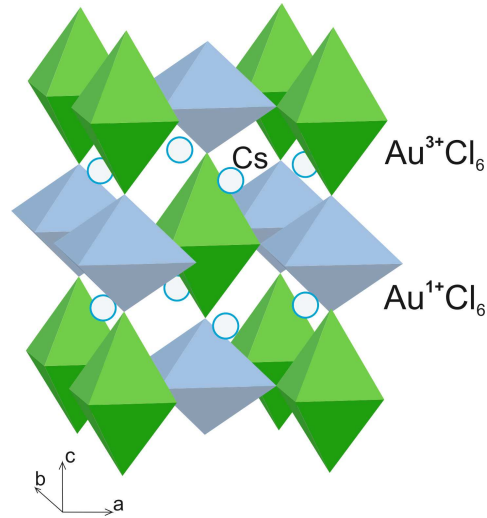
Thus we see that, in contrast to the “normal” case of positive CT gap, where both contributions to the CF splitting, the Coulomb contribution and the covalency, lead to qualitatively the same order of levels (antibonding  $e_g$ -levels are above  $t_{2g}$ , and vice versa for bonding states), for negative CT gaps the situation is different: these two contributions lead to the *opposite* level order. Therefore by studying the actual order of these levels, experimentally or theoretically, one can get some information about which of these contributions is in fact stronger. We undertook such a study on the example of a system with the negative CT gap -  $\text{Cs}_2\text{Au}_2\text{Cl}_6$ .

## 5. Crystal field in $\text{Cs}_2\text{Au}_2\text{Cl}_6$

$\text{Cs}_2\text{Au}_2\text{Cl}_6$  should formally contain the  $\text{Au}^{2+}(d^9)$  ions. However, it is well-known in chemistry that this valence state of gold is unstable and is practically never observed experimentally: Au is known to exist in a valence  $\text{Au}^{1+}$  or  $\text{Au}^{3+}$ . This also happens in this material: there occurs a spontaneous charge disproportionation (CD) into  $\text{Au}^{1+}$  (Au2) and  $\text{Au}^{3+}$  (Au1), so that there appears in this compound two inequivalent Au positions, with checkerboard ordering in a cubic perovskite lattice. [12, 13], see Fig. 4. In effect even the formula of this material is usually written not as  $\text{CsAuCl}_3$ , as for usual perovskites, but as  $\text{Cs}_2\text{Au}_2\text{Cl}_6 = \text{Cs}_2\text{Au}^{1+}\text{Au}^{3+}\text{Cl}_6$ .

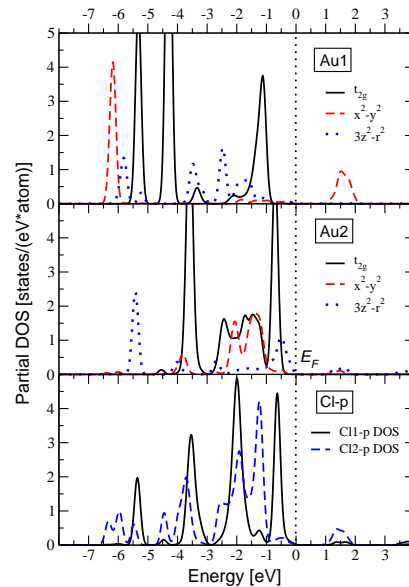
We carried out the ab-initio band structure calculations of this material, have shown that it has negative CT gap, and analyzed the CF splitting.

The ab-initio band-structure calculations of  $\text{Cs}_2\text{Au}_2\text{Cl}_6$  were performed within the frameworks of the Density Functional Theory (DFT) and the Generalized Gradient Approximation (GGA). We used the PW-SCF code with the ultrasoft version of



**Figure 4.** The crystal structure of  $\text{Cs}_2\text{Au}_2\text{Cl}_6$ .

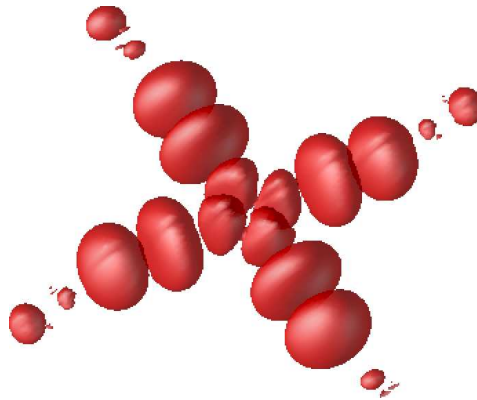
pseudopotentials [14, 15]. A maximum cut-off energy for the plane waves was chosen to be 200 eV. The Brillouin-zone (BZ) integration in the course of self-consistency interactions was performed over a mesh of 72 k-points. The structural data for ambient pressure were taken from Ref. [16]. The Wannier functions were constructed using the formalism described in Ref. [17].



**Figure 5.** Partial density of states for  $\text{Cs}_2\text{Au}_2\text{Cl}_6$  at ambient pressure. Au1 represent atom, which should have oxidation state 3+, while Au2 - 1+ (according to valence bond sum analysis of the crystal structure). The Cl-p partial density of states is the normalized per one Cl for two classes of “apical” Cl1 and “plane” Cl2 in the octahedra. The Fermi level is taken as zero.

The partial densities of states (PDOS) are presented in Fig. 5. One may clearly see





**Figure 6.** The charge-density corresponding to the antibonding orbital of  $x^2 - y^2$ -symmetry centered on Au1 site, nominally  $Au^{3+}$ . The central part corresponds to the contribution of the real  $Au-5d$   $x^2 - y^2$  orbital, while the rest is a  $\sigma$  combination of the  $Cl-p$  orbitals.

that indeed the lowest states in the valence band have largest contributions from the  $Au - d$ , not  $Cl - p$  states, so that the CT energy is indeed negative in this compound. The states closest to the top of the valence band, as well as the states in the conduction band, are mainly of  $p$ -character.

The total occupation of Au2  $5d$ -shell is 9.6, which is close to the  $d^{10}$  configuration, expected for  $Au^{1+}$ . However the number of  $d$ -electrons for Au1 is 9.3, much larger than 8 electrons expected from the naive ionic picture for the 3+ oxidation state of Au. Thus one should represent this states not as  $Au^{3+}$  ( $d^8$ ), but rather as  $d^9 \underline{L}$  or even  $d^{10} \underline{L}^2$ , where  $\underline{L}$  denotes ligand hole. This is due to the self-doping effect described above.  $Au^{3+}$  ions turned out to be Jahn-Teller active, but non-magnetic, with the configuration  $t_{2g}^6 e_{g\uparrow}^1 e_{g\downarrow}^1$  (or rather  $d^{10} \underline{L} \uparrow \underline{L} \downarrow$ ).

As it was shown in previous two sections, a larger hybridization leads to a larger bonding-antibonding splitting, independent on the sign of the  $\Delta_{CT}$ . The Cl octahedron surrounding Au1 is elongated along  $z$ -axis. Then the bonding-antibonding splitting for the orbital of  $x^2 - y^2$ -symmetry should be the largest among all of Au  $5d$ -orbitals. This is exactly what we see in the upper panel of Fig. 5. The Coulomb contribution to the crystal-field splitting would stabilize just the opposite sequence of levels, see Fig. 3(b). This means that at least in this system the Coulomb contribution to the total value of the CF splitting is much less than the covalent term.

It is important to mention that the conduction band is basically formed by the  $\sigma$  combination of  $Cl-p$  states with  $x^2 - y^2$  symmetry. These are actually the antibonding  $e_g^*$  orbitals of the type (6), shown in Fig. 3(a). The charge density for this orbital, obtained using the Wannier function projection technique, is shown in Fig. 6. The detailed calculations show that about  $\sim 20$  % of the charge-density corresponding to this orbital has a  $5d$ -character, while the main part  $\sim 80$  % comes from the  $Cl-p$  orbitals.

A similar analysis can be performed for the compressed along the  $z$ -axis  $Au_2O_6$



octahedra. Here again the covalent contribution dominates and pushes down the bonding orbital of  $3z^2 - r^2$ -symmetry, which has the largest hybridization with the Cl- $p$  states.

The question which naturally arises is how general is the conclusion reached above, that the covalency contribution to the CF splitting is (much) larger than the Coulomb contribution. Generally speaking, one could think that the covalency contribution to the  $t_{2g} - e_g$  splitting, which is

$$\Delta_{CF}^{cov.} \sim \frac{t_{pd\sigma}^2 - t_{pd\pi}^2}{\Delta_{CT}}, \quad (7)$$

could become small for very large  $|\Delta_{CT}|$ . It is not surprising that this contribution dominates for systems with small or slightly negative CT gap (apparently  $\text{Cs}_2\text{Au}_2\text{Cl}_6$  belongs to this class). Different approaches [7, 18], however, demonstrate that it is also the case for the values of parameters typical for “normal” TM compounds, such as  $\text{KNiF}_3$  [7] or  $\text{NiO}$ . [18] Nevertheless, one can not exclude that in some cases (e.g. for the early 3d metals) the situation could be different and the Coulomb contribution would become comparable or larger than the covalency one.

## 6. Summary

In this paper we analyzed possible features of the crystal field splitting in different situations, and argued that for the negative charge-transfer gaps, in contrast to the “normal” situation with  $\Delta_{CT} > 0$ , different contributions to the crystal field splitting, the Coulomb contribution and that of the covalency with the ligands, act in opposite direction: the Coulomb contribution always pushes the  $t_{2g}$  levels below the  $e_g$  ones, whereas the  $p - d$  hybridization would lead to the opposite order of the bonding levels (which for negative charge transfer gap have predominantly  $d$ -character). The study of a concrete example of  $\text{Cs}_2\text{Au}_2\text{Cl}_6$  demonstrates that this system indeed has negative charge-transfer gap, so that the states in the conduction band are largely made of  $p$ -states of Cl. The bonding states of  $d$ -character lie  $\sim 2$ -6 eV below the Fermi energy, and in this region the  $e_g$  levels lie below  $t_{2g}$  ones. Thus in this particular system the  $p - d$  hybridization dominates and determines the sequence of levels. We discuss in conclusion whether the opposite situation could be possible, in which case the sequence of  $d$ -levels would be determined by the Coulomb contribution and might be different from the usual one.

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