Crystal field splitting in correlated systems with negative charge-transfer gap

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Received 9 June 2011, in final form 1 September 2011
Published 18 October 2011
Online at stacks.iop.org/JPhysCM/23/445601

Abstract

Special features of the crystal field splitting of d-levels in the transition metal compounds with small or negative charge-transfer gaps $\Delta_{CT}$ 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 theoretical predictions we carried out \textit{ab initio} band structure calculations for Cs$_2$Au$_2$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 the $t_{2g}$ 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 the conduction band are made predominantly of p-states of ligands (Cl), with a small admixture of d-states of Au. (Some figures in this article are in colour only in the electronic version)

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 within a crystal. This crystal field (CF) splitting largely determines the magnetic and orbital states of the 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 the charges of surrounding ions—mainly nearest-neighbor anions like $\text{O}^{2-}$ in oxides or $\text{F}^-$ and $\text{Cl}^-$ 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 leads to 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 the Hamiltonian) 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 an octahedral surrounding) or pointing in between 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 materials with negative charge-transfer (CT) gaps [1, 2], with ligand (e.g. oxygen) holes in the ground state. The discussion and main conclusions are made for the case of an octahedral environment of the transition metal ions, but can be easily reformulated for other types of surroundings.

2. The basic model

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

$$
H = \epsilon_d \sum_{i\alpha} d_{i\alpha}^\dagger d_{i\alpha} + \epsilon_p \sum_{j\beta} p_{j\beta}^\dagger p_{j\beta} + \sum_{i\alpha\beta\gamma} t_{i\alpha\beta\gamma} (d_{i\alpha}^\dagger p_{j\beta} + h.c.) + \sum_{(\alpha\gamma)\beta(\beta'),(\alpha')} U_{\alpha\beta}^{dd} n_{i\alpha} n_{i\beta'}. \tag{1}
$$

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Figure 1. CT 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 $yz$-orbital is sketched). The ligands forming octahedra are shown as open circles, d-orbitals are shown by dark (blue) and ligand p-orbitals by light (green) shading. 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.

Here $d^\dagger_{i\alpha\sigma}, d_{i\alpha\sigma}$ are the creation and annihilation operators of d-electrons at a site $i$ in the orbital state $\alpha$ with spin $\sigma$. $p^\dagger_{j\beta\sigma}, p_{j\beta\sigma}$ describe different p-electrons at the jth ligand surrounding a 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

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

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

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

(3)

Here we introduced the renormalized energy of d-levels

$$\epsilon_d = \epsilon_{d0} + nU$$

(4)

i.e. the effective d energy levels to which an electron is transferred from the p-states of a ligand in the ‘reaction’ (2).\(^4\) Further on in this paper by the d-levels shown, e.g. in figures 1 and 3, we have in mind these renormalized d-levels (4). In the usual case of Mott insulators the electron hopping $t < (U, \Delta_{CT})$, but in principle this condition may be violated for very small or negative CT energy, see e.g. [2]. The parameters entering the model (1) are system dependent. They can be either determined by self-consistent band structure calculations, or taken from experiment. In the general case 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. They may somewhat renormalize the ‘bare’ values of the CT energy (3). However, as for us this is an empirical parameter determined, e.g., from an experiment, see figure 2 below, the inclusion of these terms would not modify the conclusions, and for our purposes 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 the 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 equation (3). As explained above and clearly seen in figure 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 toward the ligands than for $t_{2g}$-orbitals pointing in between the anions. This leads to the CF splitting shown in figure 1(c), such that the $e_g$-orbitals lie above the $t_{2g}$ ones. This sequence of d-levels is referred to as ‘normal’.

The same ‘normal’ sequence of d-levels is also caused by the p–d hybridization, i.e. by the covalent contribution. Since the hopping matrix elements $e_g$–p ($t_{pd\sigma}$) are larger than the hoppings between the $t_{2g}$-orbitals and the p-orbitals of the ligands ($t_{pd\pi}$), the $e_g$-levels are pushed up more strongly than the $t_{2g}$ ones, see figures 1(b) and (c) [3]. The 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 stages of 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 [4]. However, it was shown later that in order to consider the ionic term in a correct way the d-electron wave functions must be orthogonalized to the ligands [5]. As a result, the total ionic contribution to the CF splitting has the same sign as the covalent term in the case of $\Delta_{CT} > 0$ [6].

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

The situation is quite different for 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 encountered in compounds based on the late TM ions with unusually high valence, or high oxidation state [2], like Fe$^{4+}$ or Cu$^{3+}$, see figure 2, compiled by Mizokawa on the basis of data from [7, 8].

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 [9, 10]. In the language of energy levels a regime with 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, figure 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 with $e_g$-symmetry. But for large positive CT gap these states, which lie deep below the Fermi energy. All the interesting phenomena take place in the partially filled antibonding states, which have predominantly d-character and which are responsible, e.g., for magnetism, orbital ordering, etc. However, this changes drastically in the case of a negative CT gap $\Delta_{CT} < 0$, which we now consider.

Note that for the bonding levels (the lower levels in figure 1(c)) the covalency contribution gives a sequence of levels opposite to the ‘normal’ ones: the levels with $e_g$-symmetry have stronger bonding–antibonding splitting and lie below those with $t_{2g}$-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 discusses these states, which lie deep below the Fermi energy.
These bonding states are actually completely filled. The electrons of partially filled levels will be in the antibonding orbitals $t_2^\sigma$, $e_g^\sigma$. Due to a stronger $p\sigma\sigma$ 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 figure 1 ($t_2^\sigma$-levels are below the $e_g^\sigma$-ones). But, in contrast to the case of a positive CT gap, here the wave function of the antibonding states will be

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

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 make these arguments somewhat more specific. In the case of $\Delta_{CT} < 0$ the ground state should be taken not as $d^p\sigma^p$, but rather as $d^{p-1}\sigma^p$, according to (2). This would change the magnitude of the Coulomb terms, but the resulting effect would still be the same: $e_g$-electrons would still repel more strongly from the ligands (with smaller charge, e.g. $O^{1.3-}$ instead of $O^{2-}$). Thus in the case of a negative CT gap the contributions of the Coulomb interaction and the $p-d$ covalency to the CF splitting of $d$-states are opposite.

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

Thus we see that, in contrast to the ‘normal’ case of a 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 opposite level orders. 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 compound with negative CT gap—$\text{Cs}_2\text{Au}_2\text{Cl}_6$. This system differs from the more conventional transition metal compounds from the point of view of covalency. This is first of all due to a large spatial extension of the Au 5d-orbitals, which results in a strong overlap with the Cl 3p wave functions and hence significant mixing between Au 5d and Cl 3p. Secondly, Au shows a relatively high (for gold) oxidation state in this compound, which should lead to negative values of the CT gap. In addition, $\text{Cs}_2\text{Au}_2\text{Cl}_6$ shows unusual physical properties such as spontaneous charge disproportionation at ambient conditions [11], photoinduced valence transition [18], and very interesting behavior under pressure [15, 19]. Thus a theoretical study of this compound, clarifying in particular the influence of the negative CT gap on the physical properties of this system, presents interest in itself.

5. Electronic structure and crystal field in $\text{Cs}_2\text{Au}_2\text{Cl}_6$

$\text{Cs}_2\text{Au}_2\text{Cl}_6$ should formally contain $\text{Au}^{2+}$($d^6$) 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 $\text{Au}^{3+}$, and in this material a spontaneous charge disproportionation (CD) into $\text{Au}^{1+}$ (Au2) and $\text{Au}^{3+}$ (Au1) occurs, so that there appear in this compound two inequivalent Au positions, with checkerboard ordering in a cubic perovskite lattice [11, 12], see figure 4. In effect even the formula of this material is usually written not as $\text{CsAuCl}_3$, as for usual perovskites, but as $\text{Cs}_2\text{AuCl}_6 = \text{Cs}_2\text{Au}^{1+}\text{Au}^{3+}\text{Cl}_6$.

We carried out ab initio band structure calculations of this material, showed 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 framework of the density functional theory (DFT) and the generalized gradient approximation (GGA). We used the PW-SCF code with the ultrasoft version of pseudopotentials [13, 14]. The maximum cut-off energy for the plane waves was chosen to be 200 eV. 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
or even dedenotes a ligand hole. This is due to the self-doping with rather d 3 this state not as Au +3 , but rather as d 8 −, the number of d-electrons for Au1 is 9.3, much larger than e g active, but non-magnetic, with the configuration t 1g . Au1 represents atoms which should have oxidation state +2 , while Au2 is the 3 + oxidation state of Au. Thus one should represent the Cl p-states, so that the CT energy is indeed negative the valence band have the largest contributions from the Au d, of p-character. However, as was shown in the previous two sections, a larger hybridization leads to a larger bonding–antibonding splitting, independent of the sign of ΔCT. The Cl octahedron surrounding Au1 is elongated along the z-axis. Then the bonding–antibonding splitting for the orbital of x 2 −y 2 -symmetry should be the largest among all of the Au 5d-orbitals. This is exactly what we see in the upper panel of figure 5. The Coulomb contribution to the crystal field splitting would stabilize just the opposite sequence of levels, see figure 6. 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. A similar analysis can be performed for the Au2O 6 octahedra compressed along the z-axis. 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.

6. Discussion of the results

Our ab initio calculations unequivocally demonstrate that Cs 2 Au 2 Cl 6 belongs to the class of systems with negative CT gap and with a large contribution of ligand p-holes, see e.g. figure 6. Apparently this large p-hole contribution also plays a crucial role in the spontaneous charge disproportionation of Au 2+ into Au 1+ + Au 3+ : corresponding transfer of the d-electrons between formal configurations of d 7 (Au 2+ ) and (d 10 (Au 1+ ) + d 6 (Au 3+ )); the corresponding energy cost is ΔG ≈ 5−7 eV. But if, as we obtained, the corresponding states are rather Au 2+ = Au 1+ (d 10 ) L 2 and Au 3+ = Au 1+ (d 10 ) L 2 , this process of CD would mainly involve transfer between...
different sites of the ligand p-holes, delocalized over the ligand octahedra (here Cl$_6$) around each Au, which would cost much less Coulomb energy.

Another firm conclusion of our calculations, which is the main topic of this paper, is the at first glance rather surprising result that for the case of negative CT gap the order of (bonding) $d$-levels is inverted with respect to the ‘normal’ one: the $e_g$-levels in an AuCl$_6$ octahedron lie below the $t_{2g}$ ones. This is due to the fact that, at least in this case, the covalency contribution to the CF splitting definitely dominates over the Coulomb contribution, which would have given the ‘normal’ sequence of $d$-levels also in this case.

The question which naturally arises is how general the conclusion reached above is, 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
\[ \Delta_{\text{cov.}}^{\text{CF}} \sim \frac{\Delta_{\text{p-d}}^2}{\Delta_{\text{CT}}}, \] (7)
dominates for systems with small or slightly negative CT gap (apparently Cs$_2$Au$_2$Cl$_6$ belongs to this class). However, in principle it could become small for very large $|\Delta_{\text{CT}}|$. Also the $p$–$d$ hybridization may be expected to be stronger for 5$d$ elements as compared, e.g., with 3$d$ ones. Thus one may expect that the dominance of the covalency over the Coulomb contribution may be more pronounced for the 4$d$ and 5$d$ cases. On the other hand, detailed investigations [6, 17] demonstrate that the covalency contribution is also stronger in 3$d$ compounds with positive CT gap. Thus one may think that the situation in 3$d$ systems with negative CT gap would resemble that in Cs$_2$Au$_2$Cl$_6$, although maybe not to such an extreme.

To check this we carried out model calculations for the hypothetical system CsMeCl$_6$ with perovskite structure, substituting the real Me = Au by the 3$d$ element Cu (real CsCuCl$_6$ does not have a perovskite, but hexagonal structure). The results demonstrate that also in this case the covalency contribution dominates: in this case the $e_g$-levels of Cu also lie below the $t_{2g}$ ones, although their difference (0.11 eV for Cu1 and 0.09 eV for Cu2) is not as large as in the case of Au (0.19 eV for Au1 and 0.12 eV for Au2).

7. Summary

In this paper we analyzed possible features of the crystal field splitting in different situations, and argued that for negative charge-transfer gaps, in contrast to the ‘normal’ situation with $\Delta_{\text{CT}} > 0$, the different contributions to the crystal field splitting, the Coulomb contribution and that of the covalency with the ligands, act in opposite directions: 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 Cs$_2$Au$_2$Cl$_6$ demonstrates that this system indeed has a 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 the $t_{2g}$ ones. Thus in this particular system the $p$–$d$ hybridization dominates and determines the sequence of levels. We discuss 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 one obtained above.

Acknowledgments

We acknowledge fruitful communications with I Mazin and M Haverkort. We are very grateful to D Korotin for the code used for the projection on the Wannier functions, and especially to T Mizokawa for providing us with and allowing to use figure 2.

This work was supported by the German projects SFB 608, DFG GR 1484/2-1 and FOR 1346, by the European project SOPRANO, by the Russian projects RFBR 10-02-00046 and 10-02-96011, by the program of the President of the Russian Federation MK-309.2009.2, the Russian Federal Agency of Science and Innovation N 02.740.11.0217 and the scientific program ‘Development of scientific potential of universities’ N 2.1.1/779.

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