Research Letter

Optics of Chromites and Charge-Transfer Transitions

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Specific features of the charge-transfer (CT) states and $O_{2p} \rightarrow Cr_{3d}$ transitions in the octahedral $(CrO_6)^{9-}$ complex are considered in the cluster approach. The reduced matrix elements of the electric-dipole transition operator are calculated on many-electron wave functions of the complex corresponding to the initial and final states of a CT transition. Modeling the optic spectrum of chromites has yielded a complicated CT band. The model spectrum is in satisfactory agreement with experimental data which demonstrates the limited validity of the generally accepted concept of a simple structure of CT spectra.

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1. INTRODUCTION

Since discovering the high- T_c superconductivity in oxides with Cu^{2+} ions and the colossal magnetoresistance in Mn^{3+} systems, a considerable interest has been renewed in transition-metal oxide systems. An important problem of the physics of these strongly correlated systems concerns the nature of their electronic structure and energy spectrum. Optic and magneto-optic techniques are well suitable for studying them. However, the *origin* of low-energy electron-hole excitations in 3d-oxides is still under discussion.

First proposed for iron garnets [1] and developed further for a wider class of ferric oxide compounds [2], the idea that their optic and magneto-optic properties in the near UV range and the fundamental optic absorption edge are determined by the oxygen-to-3d metal ion *charge-transfer* (CT) transitions has become widespread [3, 4]. However, there is no consistent theory of CT states and transitions in 3d oxides. In most studies, the idea of CT transitions has not changed significantly since its appearance. One tries to explain the peculiarities of optic spectra of these compounds by some “2p-3d” CT transitions or, at best, keeping in mind the t_{2g} -, e_g -classification of d-electrons in the crystal field, one reasons in terms of “ $2p \rightarrow 3d t_{2g}$,” “ $2p \rightarrow 3d e_g$ ” CT transitions [5]. But such *one-electron* approach to CT states and transitions is insufficient even for *qualitatively* explaining the observed optic properties of 3d oxides. The one-electron band models, including LDA + U , do not solve the problem, since they fail to reproduce the important intra-

atomic correlation effects which form the term structure of the ground and excited CT states.

We consider here the CT states and transitions in chromites and their optic spectra. The analysis is based on the cluster model of one-center CT transitions which has been successfully used to explain the optics and magneto-optics of orthoferrites, iron garnets, and a number of other 3d oxides [6–12]. The advantages of this model are its physical clarity and the possibility of taking detailed account of the electron-electron correlations and the crystal field effects.

2. CT STATES AND TRANSITIONS IN CHROMITES

Slightly distorted octahedral CrO_6 complexes are the main optic centers of oxide compounds such as perovskite-like $RCrO_3$ (R is a trivalent rare-earth or yttrium cation). The ground state configuration of the $(CrO_6)^{9-}$ complex includes filled molecular orbitals (MOs) O_{1s-2p} predominantly anionic in nature, filled “cationic” MOs Cr_{1s-3p} and 3d-type MOs. The ground state of the complex is the orbital singlet $|\gamma_{2p}^6 t_{2g}^3 {}^4A_{2g}\rangle$. The excited CT configuration of the complex arises at the transition of an electron from the “anionic” γ_{2p} MO ($\gamma = t_{2u}(\pi), t_{1u}(\pi), t_{1u}(\sigma)$) into the 3d-type MO (t_{2g}, e_g) of the central Cr^{3+} ion of the complex. The CT configuration can be written as $\tilde{\gamma}_{2p}^1 3d^4$ where $\tilde{\gamma}_{2p}^1$ denotes the hole in the anion MO core. The transition between

TABLE 1: Many-electron CT transitions generated by one-electron t_{2u} , $t_{1u}(\pi)$, $t_{1u}(\sigma) \rightarrow 3d e_g$ CT transitions.

γ	σ	RME	γ	σ	RME
T_2	2	$\sqrt{5/2} \langle e_g \parallel \hat{\mathbf{d}} \parallel t_{2u} \rangle$	T_1	2	$-\sqrt{5/2} \langle e_g \parallel \hat{\mathbf{d}} \parallel t_{1u} \rangle$
T_2	1	$-\sqrt{3/2} \langle e_g \parallel \hat{\mathbf{d}} \parallel t_{2u} \rangle$	T_1	1	$\sqrt{3/2} \langle e_g \parallel \hat{\mathbf{d}} \parallel t_{1u} \rangle$

the ground and excited configurations is the CT transition $\gamma_{2p} \rightarrow 3d$.

The electric-dipole CT transitions from the ground $^4A_{2g}$ state of the complex are only allowed to the $^4T_{2u}$ terms of $\tilde{\gamma}_{2p}^1 t_{2g}^4$ and $\tilde{\gamma}_{2p}^1 t_{2g}^3 e_g$ configurations (electron transfer to t_{2g} and e_g shell, resp.). Among the highest-energy 2p-type MOs, there are two MOs with the t_{1u} symmetry ($t_{1u}(\sigma)$, $t_{1u}(\pi)$) and one $t_{2u}(\pi)$ -type MO. Thus, there arise six low-energy *one-electron* CT transitions, namely, t_{2u} , $t_{1u}(\pi)$, $t_{1u}(\sigma) \rightarrow t_{2g}$, and t_{2u} , $t_{1u}(\pi)$, $t_{1u}(\sigma) \rightarrow e_g$. These *one-electron* transitions give rise to the following electric-dipole allowed *many-electron* CT transitions of $^4A_{2g} \rightarrow ^4T_{2u}$ type: $\gamma_{2p}^6 ^1A_{1g}$; $t_{2g}^3 ^4A_{2g}$; $^4A_{2g} \rightarrow \gamma_{2p}^5 ^2\gamma_u$; $t_{2g}^4 ^3T_{1g}$; $^4T_{2u}$ (one-electron $\gamma_{2p} \rightarrow t_{2g}$ transition) and $\gamma_{2p}^6 ^1A_{1g}$; $t_{2g}^3 ^4A_{2g}$; $^4A_{2g} \rightarrow \gamma_{2p}^5 ^2\gamma_u$; $t_{2g}^3 ^4A_{2g}$; $e_g^1 ^2E_g$ ($^{2\sigma+1}E_g$); $^4T_{2u}$ (one-electron $\gamma_{2p} \rightarrow e_g$ transition). Here, σ takes the values 1 and 2.

The transition intensity measure is the line strength: the squared modulus of the reduced matrix element (RME) of the operator of a transition between states. The RME of the electric dipole moment on many-electron wave functions of the final and initial configurations corresponding to one-electron $\gamma_{2p} \rightarrow t_{2g}$ CT transition has the form

$$\begin{aligned} & \langle \gamma_{2p}^5 ^2\gamma_u; t_{2g}^3 ^3T_{1g}; ^4T_{2u} \parallel \hat{\mathbf{d}} \parallel \gamma_{2p}^6 ^1A_{1g}; t_{2g}^3 ^4A_{2g}; ^4A_{2g} \rangle \\ &= 3(-1)^{j(\gamma)} \begin{Bmatrix} T_1 & T_2 & \gamma \\ T_1 & T_2 & A_2 \end{Bmatrix} \langle t_{2g} \parallel \hat{\mathbf{d}} \parallel \gamma_u \rangle. \end{aligned} \quad (1)$$

Here, $j(\gamma)$ is the phase factor which is even for representations $\gamma = A_1, E, T_2$ of the cubic group, and odd for $\gamma = A_2, T_1$; $\{ \dots \}$ is the 6F symbol. According to (1), three *one-electron* $\gamma_{2p} \rightarrow t_{2g}$ CT transitions beget three *many-electron* $^4A_{2g} \rightarrow ^4T_{2u}$ CT transitions, the RME on many-electron wave functions being equal to $(-\langle t_{2g} \parallel \hat{\mathbf{d}} \parallel \gamma_u \rangle)$ both for $\gamma = t_1$ and $\gamma = t_2$.

In the case of the one-electron $\gamma_{2p} \rightarrow e_g$ transition, the RME is

$$\begin{aligned} & \langle \gamma_{2p}^5 ^2\gamma_u; t_{2g}^3 ^4A_{2g}; e_g^1 ^2E_g \text{ (} ^{2\sigma+1}E_g \text{)}; ^4T_{2u} \parallel \hat{\mathbf{d}} \parallel \gamma_{2p}^6 ^1A_{1g}; t_{2g}^3 ^4A_{2g}; \\ & e_g^0 ^1A_{1g} \text{ (} ^4A_{2g} \text{)}; ^4A_{2g} \rangle \\ &= (-1)^{j(\gamma)+\sigma+1} \sqrt{3(2\sigma+1)} \begin{Bmatrix} E & E & A_2 \\ T_2 & T_1 & \gamma \end{Bmatrix} \langle e_g \parallel \hat{\mathbf{d}} \parallel \gamma_u \rangle. \end{aligned} \quad (2)$$

Three *one-electron* $\gamma_{2p} \rightarrow e_g$ transitions give rise to six *many-electron* $^4A_{2g} \rightarrow ^4T_{2u}$ CT transitions; the RMEs are gathered in Table 1.

These results can be parameterized in the local approximation [13] consisting in the full neglect of many-center

integrals when calculating the RME of the dipole moment. All such RMEs can be expressed in terms of $\lambda_\sigma, \lambda_\pi$, the effective covalency parameters for σ and π bonds. Since the RME $\langle t_{2u}(\pi) \parallel \hat{\mathbf{d}} \parallel e_g \rangle$, $\langle t_{1u}(\pi) \parallel \hat{\mathbf{d}} \parallel e_g \rangle$, $\langle t_{1u}(\sigma) \parallel \hat{\mathbf{d}} \parallel t_{2g} \rangle$ go to zero in the local approximation, it reveals itself as a *supplementary* selection rule which prohibits the $\sigma \rightarrow \pi$ ($t_{1u}(\sigma) \rightarrow t_{2g}$) and $\pi \rightarrow \sigma$ ($t_{1,2u}(\pi) \rightarrow e_g$) transitions even if they are electric-dipole allowed. Only $\sigma \rightarrow \sigma$ type CT transitions ($t_{1u}(\sigma) \rightarrow e_g$) and $\pi \rightarrow \pi$ type ones ($t_{1,2u}(\pi) \rightarrow t_{2g}$) are allowed in this approximation (“strong” transitions, in contrast with “weak” $\sigma \rightarrow \pi$, $\pi \rightarrow \sigma$ ones).

3. MODELING OF THE CT TRANSITION BAND IN CHROMITES

We apply here the expounded theoretical notions to model the optic properties of chromites like $RCrO_3$. They are usually regarded as Mott-Hubbard insulators, the Coulomb energy being reputedly small in comparison with the CT energy [3], but this attribution seems to be not universally justified [7]. We will treat the chromites from the CT point of view using the following plausible assumptions for modeling the optic spectra.

(1) Since the $3d^4$ configuration of the central atom formally corresponding to Mn^{3+} ion arises at the CT transition, to compute the Tanabe-Sugano diagram (see below) for the *excited* $3d^4$ CT configuration we use the Racah parameters B and C of the Mn^{3+} ion *ground* state [14] in the octahedral oxygen surroundings.

(2) The corrections to the level energies owing to 2p-hole-3d-shell interaction are neglected. Our estimations [12] show that these corrections may take on the value of several tenths of an eV.

(3) The energies of the *nonbonding oxygen* states in the $(CrO_6)^{9-}$ complex are supposed to coincide with those in the $(FeO_6)^{9-}$ complex [15]. This assumption seems justified since the energies of purely oxygen states mainly depend on crystalline environment.

Thus, the energy spectrum of the *one-electron* CT transitions depends on the energies of $3d$ t_{2g} , e_g orbitals and *rigidly* shifts if the latter are changed. It remains true for *many-electron* CT transitions as well. The referencing of the computed theoretical spectrum to the experimental one has been performed according to the fundamental optic absorption edge; thereby the positions of all peaks of the computed spectrum become defined.

To find the energies of many-electron CT transitions and the transition intensities under the mixing of CT states in (1) and (2), we have computed the Tanabe-Sugano diagram for d^4 configuration with parameters $B = 0.12$ eV and $\gamma = C/B = 4.5$ [14]. At the crystal field parameter $Dq = 0.23$ eV [14] we obtain an intensive CT band with the total extent of about 8 eV, from ≈ 2 to ≈ 10 eV: each of the one-electron CT transitions $t_{2u}(\pi)$, $t_{1u}(\pi)$, $t_{1u}(\sigma) \rightarrow t_{2g}$ gives rise to seven many-electron CT transitions, and each of the one-electron CT transitions $t_{2u}(\pi)$, $t_{1u}(\pi)$, $t_{1u}(\sigma) \rightarrow e_g$ generates four many-electron CT transitions, altogether 33 lines!

We have performed a modeling of the band of electric-dipole allowed CT transitions in the optic spectrum of

orthochromite YCrO_3 (note that in our assumptions the specific compound affects the reference energy only). Since in the local approximation the contribution of transitions $t_{1,2u}(\pi) \rightarrow e_g$ and $t_{1u}(\sigma) \rightarrow t_{2g}$ cannot be taken into account, we have introduced “by hand” the corresponding covalency parameter $\lambda_{\pi\sigma} \equiv \lambda_{\sigma\pi}$. Based on reasonable physical notions and the concept of strong and weak transitions, we assumed the following model relationship of covalency parameters: $\lambda_\pi = (1/5)\lambda_\sigma$, $\lambda_{\pi\sigma} = (1/10)\lambda_\sigma$. The line half-width Γ is taken to be equal to 0.4 eV for many-electron CT transitions due to weak transitions, 0.8 eV for those due to strong $t_{1,2u}(\pi) \rightarrow t_{2g}$ transitions, and 1.2 eV for those due to strong $t_{1u}(\sigma) \rightarrow e_g$ transitions. The model Lorentzian line shape used is

$$\frac{4\omega\omega_0\Gamma}{[(\omega^2 - \omega_0^2 - \Gamma^2)^2 + 4\omega^2\Gamma^2]}, \quad (3)$$

ω_0 being the transition frequency.

The computation results are shown in Figure 1. The computed total contribution of all electric-dipole-allowed strong and weak CT transitions to the imaginary part ε_2 of the diagonal permittivity tensor component $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is presented in the main panel. The experimental spectra for $\text{Lu}_{0.85}\text{Y}_{0.15}\text{CrO}_3$ [16], YCrO_3 [17], and LaCrO_3 [17] converted by us from optic conductivity to permittivity are shown in the inset (lines 1, 2, and 3, resp.). The computation results reasonably agree with them. The 3D picture of ε_2 spectra versus the crystal field parameter Dq is shown in Figure 2. Variation of Dq causes not merely the relative change of peaks height, but also the restructuring of the whole spectrum.

4. CONCLUSION

In the cluster approach which combines the crystal field and MO notions, we have considered the peculiarities of CT states and $\text{O}_{2p} \rightarrow \text{Cr}_{3d}$ CT transitions in the octahedral $(\text{CrO}_6)^{9-}$ complex. Using the Racah algebra for the group of rotations and the cubic point group, we have calculated the reduced matrix elements of the electric dipole operator on many-electron wave functions being the initial and final states of a CT transition. Based on the parameterization of the results obtained, we have calculated the relative intensities of the allowed CT transitions. Within the crystal field theory, we have computed the energies of many-electron CT transitions.

Modeling the optic spectrum of chromites yielded an intricate CT transition band consisting of 33 lines, with the main maxima at about 6.8 and 9.1 eV and satellites in the 2–10 eV range. The total extent of the CT band is about 8 eV. The influence of crystal field magnitude on the spectrum structure is examined.

For all the roughness of the model assumptions, the computed spectrum is in satisfactory agreement with the experimental ones. Hence it appears that the rooted opinion of the CT transitions as having a simple, one- or two-peaked structure is groundless. There is a need for refining upon the customary theoretical treatment of peculiarities in the optic spectra of 3d metal-based oxide compounds.

FIGURE 1: Modeling of O_{2p} - Cr_{3d} CT band in chromite. The computed total contribution of electric-dipole allowed CT transitions to $\text{Im } \varepsilon$ and (inset) the experimental spectra of $\text{Im } \varepsilon$ in $\text{Lu}_{0.85}\text{Y}_{0.15}\text{CrO}_3$ [16], YCrO_3 [17], and LaCrO_3 [17] (lines 1, 2, and 3, resp.) are shown.

FIGURE 2: Theoretical modeling of O_{2p} - Cr_{3d} CT band in chromite. The spectral dependence of all electric-dipole allowed CT transitions contribution to $\text{Im } \varepsilon$ versus the crystal field strength.

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