d-d Spectra of Transition Metal Oxides by Effective Crystal Field Method

A.L. Tchougréeff
Karpov Institute of Physical Chemistry,
Vorontsovo pole 10, Moscow 103064 RUSSIA

Abstract

The Effective Crystal Field (ECF) method is applied to d-d excitations in metal oxides of the first transition series as measured by optical and EELS techniques. The computations are performed in the framework of the cluster approximation. The octahedral clusters are employed to simulate the transition metal ions in the bulk, the square pyramidal ones for simulation of the ions on the (100) crystal surfaces. A fair agreement between the calculation performed without additional parameter adjustment and experiment is reached when the effect of the Madelung potential on the electronic structure of the oxygens surrounding the transition metal ion and by this on the effective crystal field induced by them is carefully taken into account.

I. Introduction

Electronic structure of transition metal compounds (TMC) reattracted recently considerable interest in connection with the oxide materials like cuprates or manganites which manifest unusual physical properties being, respectively, high-T_c superconductors or magnetics [1, 2]. Meanwhile, even the electronic structure of relatively simple transition metal compounds like their oxides with the rock salt crystal structure is far from being completely understood. The d-d-spectra of transition metal oxides (TMO) provide important information on their electronic structure. The metals in the second half of the series (Mn, Fe, Co, Ni) form the rock salt oxides which are antiferromagnetic (AF) insulators. d-Electrons in these compounds form local momenta corresponding to an integer number of electrons in their d-shells. These momenta interact by the superexchange mechanism and at low temperatures form ordered (AF) states. The spin waves generated from these states are the lowest energy excitations of the AF TMO. The excited states of higher energy are usually ascribed to one of the two classes: $d^n d^n \rightarrow d^{n+1} d^{n-1}$ excitations of the average energy U and $d^n \rightarrow L^{\mp} d^{n \pm 1}$ with the average energy Δ. The states of the former type are those with an electron transferred from one d-shell to another one; those of the latter type are the states with an electron transferred from (or to) the band state of the ligands (oxygens) to (or from) the d-shell. The oxides where the states of the former type have lower energy ($U \ll \Delta$) are termed as Mott-Hubbard insulators (MHI) whereas those of the latter type ($U \gg \Delta$) are termed as charge transfer insulators (CTI). The classification of the electronic structure of TMO in terms of the excited states of these two types whatever useful it is for understanding of electronic transport in TMO leaves aside other important excitations, namely, those where excited d-electrons do not leave their metal ion but rearrange themselves within its open d-shell. These $d^n \rightarrow d^n$ excitations are frequently referred to as the crystal field (CF) excitations. These excitations are important in describing the optical properties of the TMO [3] and also for analysis of their chemical properties (including catalytic activity) [4]. Some of these excited states have energies lower than those of either Mott-Hubbard or charge-transfer excitations and thus are placed in energy next to the spin-wave excitations. The sequence of the excitations in TMO is thus as follows: spin waves, CF, and then Mott-Hubbard or charge-transfer excitations. This picture of the spectrum combines the ideas of works [5, 6].

The d-d-excitations of the CF type are of the local character and thus can be considered in the cluster approximation when only the TM ion and its closest neighbors are considered explicitly whereas the rest provides the electrostatic potential of the ionic charges only. Within this general setting there are many ways for performing quantum chemical computations. Largely, they are being done by various versions of *ab initio* techniques and are largely based on the self consistent field (SCF) approximation. The SCF approximation faces the

following main problems when applied to TMC (for more detailed discussion see Ref. [7] and references therein):
(i) the Koopmans' theorem is not valid for the states with large contributions from the atomic d-states;
(ii) the *Aufbauprinzip* is frequently broken for the orbitals with significant contributions from the atomic d-states;
(iii) the iteration procedures implied by the SCF approximation converge very slowly or oscillate.

These problems indicate that the SCF approach is a poor starting point for description of the electronic structure of TMC. Physically the problem with the single determinant SCF approximation is that the latter overestimates the weight of the configurations with electrons transferred from or to the d-shell. This effect was termed by Malrieu [8] as strong fluctuations of charge in the SCF ground state. This property of the SCF approximation lead to smearing of the multiplet structure of free transition metal ion. Such a smearing is acceptable for carbon atoms in organic molecules but is unacceptable for the TMC where the multiplet structure of the free transition metal ion is in fact retained [9]. Their ground state cannot be presented by a single Slater determinant with sufficient accuracy and some other configurations must be added. The problem which arises in this concern is that the CI series taking the SCF orbitals as a one-electron basis set converge rather slowly and thus a large number of configurations must be taken. Meanwhile, the major part of these configurations is necessary to compensate the intrinsic error of the underlying SCF approximation *i.e.* the strong fluctuations of charge in the d-shell [9]. This approach has been tested in [10] using NiO and CoO clusters as examples. It turned out that delocalization of d-electrons as obtained from the SCF calculation is indeed an artifact of this method and is cured alternatively either by a CI treatment including the delocalized states or by pairwise rotations involving the same occupied delocalized states. A more or less satisfactory result may be obtained only in the case when all the orbitals of the t_{2g} symmetry (O$2p$ and Ni$3d$) are included in the CI expansion. This move effectively improves the one-electron d-basis for the CI expansion. However, the magnitude of $10Dq$ obtained in [10] is too small. Further improvement has been proposed in [11], where the ligand to metal charge transfer states were taken into consideration in the local basis by means of so called first order CI (FOCI) method. It turned out that the contribution of the charge transfer states to the ground state and the d-d excited states was small, but their effect on their energies was significant. That made us think than an alternative approach recently suggested independently [7] for isolated transition metal complexes might be of use as a simple tool for describing electronic structure of TMO's as well. The effective crystal field (ECF) method [7] starts from the assumption that the d-shell of the central ion contains some number of electrons which is fixed by the oxidation state of the ion. The rest of electrons forms the closed shell state and is described in the SCF approximation. This setting from very beginning excludes the possibility of excessive charge fluctuations. The corrections due to electron transfer between the d-shell and the rest are taken into account (like in [11]). However, the fact that the weight of the charge transfer configurations is small led to the idea [7] to restrict the configuration space to that of the CFT by replacing the total Hamiltonian of the system by an effective one (see below). This approach led to the effective crystal field (ECF) method which has been implemented semi-empirically [7]. It was extensively tested and has been proven to be a useful alternative to the SCF based methods [12] in the case of the isolated molecular transition metal complexes. In this paper we apply the ECF method to analysis of the d-d-spectra of TMO and show that the method is useful for interpreting the data obtained by various methods probing the excitations of the CF type.

II. Account of the method

The formal derivation of the effective crystal field (ECF) method proceeds as follows [7]. The whole set of the valence atomic orbitals (AO) of the TMC (it includes the $4s$-, $4p$- and $3d$-AOs of the metal and the valence AOs of the ligand atoms) is divided in two parts. The first part contains only $3d$-orbitals of the transition metal atom (d-subsystem). The second part contains $4s$-, $4p$-AOs of the transition metal and the valence orbitals of the ligand atoms (ligand subsystem or l-subsystem). Then the total Hamiltonian for a TMC can be written as follows:

$$H = H_d + H_l + H_c + H_r \tag{1}$$

where H_d is the Hamiltonian for the d-electrons in the field of the atomic cores of TMC, H_l is the Hamiltonian for the electrons of the l-subsystem, H_c and H_r are respectively the Coulomb and the resonance interaction (electron hopping) operators between the two subsystems.

For most of TMC with closed-shell ligands the excitations in the l-subsystem are very high in energy as compared to the energies of the $d-d$ excitations, and thus their contribution is negligible. The ground state of the l-subsystem can be described by a fully symmetric closed shell Slater determinant Φ_l with zero total spin. The wave function Φ_n for the n-th electronic state of a TMC then takes the form:

$$\Phi_n = (\sum_k C_k^n \mid n_d k >) \wedge \Phi_l = \Phi_d^n \wedge \Phi_l \tag{2}$$

where $\mid n_d k >$ are the spin and symmetry adapted n_d-electron wave functions constructed on the metal d-orbitals; C_k^n are variation parameters. Both the spin multiplicity and the point symmetry of the functions of this type coincide with the multiplicity and the symmetry of the functions Φ_d^n of the d-subsystem.

The wave functions of the type Eq. (2) correspond to the fixed integer number (n_d) of electrons in the d-shell of the metal ion. All matrix elements of the resonance operator H_r calculated with the functions of that type are vanishing. In order to include the effects of the resonance interaction (*i.e.* the virtual charge transfer) between the subsystems we pass to the *effective* Hamiltonian H^{eff} [7] which operates in the subspace spanned by the functions Eq. (2), but by construction [13] has the eigenvalues coinciding with those of the original Hamiltonian Eq. (1):

$$\begin{aligned} H^{eff} &= PH_oP + H_{rr} \\ H_o &= H_d + H_l + H_c \\ H_{rr} &= PH_rQ(EQ - QH_oQ)^{-1}QH_rP \end{aligned} \tag{3}$$

Here P is the projection operator on the subspace of functions with the fixed number of d-electrons and $Q = 1 - P$.

The variational problem for the effective Hamiltonian H^{eff} within the subspace spanned by the wave functions of the type Eq. (2) splits into a pair of interconnected equations for Φ_d^n and Φ_l(see *e.g.* Refs. [7, 13]):

$$\begin{aligned} H_d^{eff}\Phi_d^n &= E_d^n\Phi_d^n \\ H_l^{eff}\Phi_l &= E_l\Phi_l \end{aligned} \tag{4}$$

with the effective Hamiltonians for the subsystems defined by:

$$\begin{aligned} H_d^{eff} &= H_d + \langle\Phi_l\,|H_c + H_{rr}|\,\Phi_l\rangle \\ H_l^{eff} &= H_l + \langle\Phi_d^n\,|H_c + H_{rr}|\,\Phi_d^n\rangle \end{aligned} \tag{5}$$

Since the l-subsystem is described by a single Slater determinant Φ_l the latter must be found from the self-consistent field procedure applied to the Fock operator F_l^{eff} derived from the Hamiltonian H_l^{eff} by the standard method [13, 14]. Proceeding semiempirically we apply the standard CNDO parameterization [14] for all ligand orbitals. The solution of the Hartree-Fock problem for the l-subsystem gives one electron density matrix P_{kl}, energies of the molecular orbitals (MO) ϵ_i, and MO LCAO coefficients c_{ik} [14]. These quantities completely describe the electronic structure (including atomic charges) of the l-subsystem within the accepted approximation. They are used to construct the effective Hamiltonian H_d^{eff} Eq. (5) by averaging the operators H_c and H_{rr} over the ground state Φ_l of the l-subsystem. That leads to the effective Hamiltonian H_d^{eff} for d-electrons only:

$$H_d^{eff} = \sum_{\mu\nu\sigma} U_{\mu\nu}^{eff} d_{\mu\sigma}^{+} d_{\nu\sigma} + \frac{1}{2} \sum_{\mu\nu\rho\eta} \sum_{\sigma\tau} (\mu\nu \mid \rho\eta) d_{\mu\sigma}^{+} d_{\nu\sigma} d_{\rho\tau}^{+} d_{\eta\tau} \tag{6}$$

where the Coulomb interaction is taken as in the free ion and the effective core attraction parameters $U_{\mu\nu}^{eff}$ contain the corrections originating both from the Coulomb and the resonance interaction of d- and l-subsystems:

$$U_{\mu\nu}^{eff} = \delta_{\mu\nu} U_{dd} + W_{\mu\nu}^{\mathrm{ion}} + W_{\mu\nu}^{\mathrm{cov}} \tag{7}$$

where

$$W_{\mu\nu}^{\mathrm{ion}} = \delta_{\mu\nu} (\sum_{i \in s,p} g_{\mu i} P_{ii}) + \sum_{L} (P_{LL} - Z_L) V_{\mu\nu}^{L} \tag{8}$$

is an ionic term having the standard CFT form and

$$W_{\mu\nu}^{\mathrm{cov}} = - \sum_{i} \beta_{\mu i} \beta_{\nu i} (\frac{(1 - n_i/2)}{\Delta E_{di}} - \frac{(n_i/2)}{\Delta E_{id}}) \tag{9}$$

comes from the resonance. Here P_{ii} is the diagonal matrix element of the one-electron density matrix of the l-subsystem; $P_{LL} = \sum_{l \in L} P_{ll}$ is the electronic population on the ligand atom L; Z_L is the core charge of the ligand atom L; $V_{\mu\nu}^{L}$ is the matrix element of the potential energy operator describing the interaction between a d-electron and an electron placed on the ligand atom L; n_i is the occupation number of the i-th ligand MO ($n_i = 0$ or 2); $\Delta E_{di} (\Delta E_{id})$ is the energy which is required to transfer an electron from the d-shell (from the i-th MO) to the i-th MO (to the d-shell); $\beta_{\mu i}$ is the resonance integral between the μ-th d-orbital and the i-th ligand MO [7].

After the effective Hamiltonian for d-electrons is constructed the states of n_d electrons in the d-shell are calculated by diagonalizing the matrix associated with H_d^{eff} in the n_d electron wave function basis set. The ground state of the whole complex is then obtained by taking the external product of the ligand Slater determinant and that n_d-electron wave function obtained by the diagonalization of H_d^{eff} which has the lowest eigenvalue. The d-d excited states (they are the low lying excitations of the whole) are then obtained by multiplying other n_d-electron functions by the same Slater determinant. The $d - d$ excitation energies can be then estimated as the differences between the eigenvalues of the corresponding eigenstates of the effective Hamiltonian H_d^{eff}.

III. Calculation details

We used the ECF method described in the previous section to calculate electronic structure of a series of the $MO_n^{2(n-1)-}$ clusters, where M=Mn, Fe, Co, Ni, chosen to represent the fragments of the oxide crystals. Only one metal ion with surrounding oxygen ions were taken into account. Octahedral clusters MO_6^{10-} were used to represent the TMI's in the bulk of the respective oxides. We did not undertake any reparameterization of the ECF method. We used the parameters β^{M-O} as they were obtained in [12] in order to describe the d-d spectra of the $[M(H_2O)_6]^{2+}$ ions and the Burns' exponents for the metal d-orbitals. We also employed the free ion values of the Racah B and C parameters. Of course, one could expect that the orbital exponents for oxygen ions must be different from those accepted in the standard quantum chemical approaches to take into account very different ionic state of the "O^{2-}" in oxides oxygen from the oxygen atom in water molecule. It turned out however, that the standard oxygen exponents satisfactorily reproduce the experimental dependence of $10Dq$ on Cu-O distance in a series of Ln_2CuO_4 cuprates [18]. Hence, we decided it to be worthwhile to check the apllicability of the ECF approach *as is* - without additional reparameterizations. We also consider our calculation present in this paper as a test for general validity of our methodology developed in Ref. [7] for molecular complexes of transition metals in the case of TMO's.

Several aspects may be important in this concern. First, in the case of the extended TMO crystal the ligand states are the 4s-, 4p-M-2p-O bands which split the d-states of each TMI by the mechanism described above. In the cluster approach these bands are mimicked by the MO's of the ligand system of the cluster. It is, however, known that the properties of the band states are fairly well reproduced by the delocalized MO-LCAO of the cluster. Second, the electric field felt by the electrons in the singled out cluster differs from that in the three-dimensional crystal due to the Madelung field. The influence of the charges outside the cluster is threefold. First, the charges outside the cluster induce additional splitting of the d-levels. It is, however, known [15] that the splitting due to the charges outside the cluster is negligible. Second effect which might be operative is the variance of the net atomic charges of the opposite signs from those in the crystal due to the Madelung terms in the total energy. The Madelung term in the energy tends to separate charges and thus those obtained in the cluster calculation must be smaller by the absolute value than those in the actual crystal. This effect is known to be not very strong. Moreover, in the case of the isolated complexes the calculated atomic charges on the ligand atoms contribute at best 10% of the total splitting. We think thus that small corrections to the splitting due to minor variations of the atomic charges may be neglected. The last effect of the Madelung forces is the most important of all listed. According to [5, 16, 17] the difference of one electron potentials in the unit cell can be expressed in terms of the Madelung potentials. This potential applies to all electrons on any site of the unit cell. The corresponding change must be taken into account when the energy denominators in Eq. (9) are calculated. This effect is relatively strong due to the fact that a major fraction of the splitting is controlled by the covalent terms. However, one must note that the values of ΔV_M given in Ref. [16] cannot be directly inserted in denominators of Eq. (9). The reason is that the charges in the cluster itself also contribute their Coulomb field to the energies of the charge transfer states in the energy denominators. We must thus replace the energy difference due to the charges in the cluster itself by the energy difference found for the entire crystal [18].

Some remarks concern the procedure of correlation the calculated energies of the surface states and those measured by different experimental techniques. The most important uncertainty here comes from the fact that even for the surfaces which do not reconstruct in a sense which is accepted in surface science, the interatomic distances definitely are not equal to those in the bulk. Nevertheless, all calculations are performed for the interatomic distances measured by X-ray techniques for the bulk, and ultimately must not coincide with experimental data.

IV. Results and discussion

We undertook the study of the TMO's of the second half of the first transition row. The detailed results of our calculations concern NiO and CoO clusters.

When considering the results on charge distribution in the clusters extracted from the analysis of the CNDO part of our calculation on the ligand subsystem one can see that they fairly correspond to the intuitive picture of the charges in the TMO's with the rock salt structure. The net charges on the oxygen ions are about $1.80 \div 1.85$ for all four considered oxides. The only counterintuitive feature is the total charge on the TMI's which amounts about $+1e$ rather than about $+2e$ which one could expect for the bulk of the crystal. This is one of the consequences of cutting the cluster from the crystal. These charges are not consistent with the crystal structure and they are also smaller by the absolute values than the correct ones. The counterintuitively low charge on the metal atom can be nevertheless easily understood if the balance of the total charge in the cluster is taken into account. The atomic charges obtained within the ECF approach do not have much sense by themselves and give only a general picture of electron distribution in the complex (cluster).

The energies of the excited d-states are very important since they can be related with the observable properties. The characteristic quantity in this respect is the $10Dq$ parameter which is 0.81 eV for NiO, 0.88 eV for CoO, 1.01 eV for FeO, and 0.94 eV for MnO. For these highly ionic clusters our calculations ascribe 20% of the total splitting to the contribution of the atomic charges. This result will not change significantly if the net charges on the oxygen ions are increased by further account of the Madelung corrections. That means that perhaps the result of [19] where the contribution of the point charges amounts to about 30% of the total splitting can be attributed to effectively longer tails of the atomic one-electron d-functions used in [19] as compared to rather contracted Slater type orbitals with Burns' exponent used in our work.

The ground bulk states in all the cases are defined within our method in the exact coincidence with the experimental data [20]. The calculated excited states ^5E_g at 1.0 eV for FeO and $^4T_{1g}$ at 2.83 eV, $^4T_{2g}$ at 3.25 eV, and degenerate ^4E_g and $^4A_{1g}$ states for MnO are in acceptable agreement with the experimental data for these oxides [20].

The calculated energies of d^n-multiplet states for clusters cut from CoO and NiO are presented in Tables 1, 2 together with some comparable experimental data [20-27]. Another remark concerns the procedures of comparison of the experimental data and calculated state energies. The electron energy loss spectra (EELS) is concerned as a powerful method probing electronic states of solids. There is, however, a considerable uncertainty concerning the nature of the states probed by this technique. According to [20] one should expect the surface states to be seen in the EELS spectra. However, it is also stated by the same author that in effect the bulk states are seen. This opinion is ultimately based on the fact that the number of the bands observed in the EELS spectra is much smaller than the number of the states found in the CF calculation for the surface cluster with the lower symmetry C_{4v}. This is certainly a contradiction since the penetration depth of the incident electrons is relatively small at least for low energy of the incident beam and for that reason the intensity of the bulk states scattering must be much smaller than for the surface ones. Accordingly, the EELS spectra generally manifest the width of the bands of about 0.2 eV which is comparable with the splitting of the states in the C_{4v} clusters MO_5^{8-} used to represent the surface TMI's. All these facts together suggest an idea that the intense bands seen in the EELS spectra might be in effect convolutions of close surface states whereas weak features in these spectra are due to the bulk states. With this idea in mind we can try to reinterpret the EELS spectrum of NiO found in Ref. [21]. If we accept as it is proposed in [21] that the small bump at 1.8 eV is a real band then the small bumps at about 0.8 eV, at 1.4 eV, and 2.1 eV also are. We interpret them as the bulk states with low intensity. The intense bands at 1.05, 1.65, 1.8, and 3.0 eV are then the convolutions of the surface states rather than the bulk transitions. With this assumption we can fairly correlate the available data with our calculations on the NiO_6^{10-} and NiO_5^{8-} clusters. Indeed the low energy surface state at 0.6 eV observed in Ref. [22] fairly corresponds to the lowest excited ^3E state in our calculation on NiO_5^{8-}, the small bump at 0.8 eV can be interpreted as the low intensity bulk $^3T_{2g}$ state. The wide intense band at $1.05 \div 1.10$ eV interpreted in [21] as the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition is indeed the convolution of two $^3B_1 \rightarrow {}^3B_2$ and $^3B_1 \rightarrow {}^3A_2$ surface transitions. Further analysis allows us to interpret the small peak at 1.4 eV [21] as the $^3A_{2g} \rightarrow {}^3T_{1g}$ bulk transition, strong peak at 1.66 eV is then the $^3B_1 \rightarrow {}^1A_1$ surface transition and the small feature at 1.8 eV on the slope of the latter as the $^3B_1 \rightarrow {}^1E$ surface transition. It is difficult to decide how the authors [22] distinguish *two* transitions at 1.6 eV and 1.7 eV. We think that this is the 1.66 eV feature from [21]. However, at higher energy we can support the interpretation of the data of Ref. [21] in the range of $2.75 \div 3.10$ eV as ${}^3B_1 \rightarrow {}^3A_2$, ${}^3B_1 \rightarrow {}^1A_2$, ${}^3B_1 \rightarrow {}^1B_2$, and ${}^3B_1 \rightarrow {}^1E$ surface transitions. The high energy surface transition ${}^3B_1 \rightarrow {}^1A_1$ is for an unknown reason visible also in the optical absorption spectra. Some of our assignments are in certain disagreement with those present in the literature. However, the latter are not always unequivocal. It is generally accepted that in the NiO crystal the first bulk CF transition (${}^3A_{2g} \rightarrow {}^3T_{2g}$) is about $1.1 \div 1.15$ eV in energy which is supported by the optical absorption measurements [23]. However, a careful inspection of the data set of [23] shows that, first, the intensity of this presumably spin allowed transition is very low. It is in effect less intense than any other transition observed in the optical experiments [23] including the spin forbidden ones. On the other hand if we accept that some very weak transitions are possible we can see a weak shoulder at about 0.75 eV on the curve presenting the spectrum recorded at the room temperature [23]. Unfortunately, the low temperature spectrum had not been recorded in the energy range $0.5 \div 0.9$ eV and this part of the spectrum had been *interpolated* in [23]. It is not possible to say whether there is any feature on the low temperature spectrum in this energy range. However, if we look at the higher energy features at 1.95, 2.15 and 2.75 eV visible in the low temperature spectrum we can see that these features almost completely disappear in the room temperature spectrum. At best they become even less pronounced than the shoulder at 0.75 eV. So we make a conclusion that it is possible that there is a bulk CF state in NiO at about 0.75 eV which we interpret as the ${}^3T_{2g}$ state. This is in agreement with our calculation made with the parameters extracted from analysis of the hexahydrate complexes of transition metals [12]. At the same time we must say that the feature at 2.15 eV which was clearly seen but not interpreted in [23] simply disappeared from the sets of the experimental optical data presented in the works devoted to EELS spectroscopy of NiO and related calculations. Our approach gives a suggestion allowing to assign this feature to the bulk ${}^3A_{2g} \rightarrow {}^1E$ spin forbidden transition. Of course, we can not give any other interpretation to the bands in the range $1.0 \div 1.15$ eV rather to consider them as convolutions of the surface states. In [24] it is proposed to expose the (100) surface of NiO to NO in order to study the EELS spectra of the surface covered by adsorbate. The bands sensitive to the NO adsorption were attributed to the surface states whereas the insensitive ones to the bulk states. However, also in this case the interpretation of the experimental measurements is not that straightforward either. First of all it is not that evident that the surface ${}^3E$ state at 0.57 eV migrates to 0.9 eV under NO adsorption. It may well happen that the 670 meV=0.67 eV feature with somewhat lower intensity is the ${}^3B_1 \rightarrow {}^3E$ surface transition slightly shifted under NO coordination. Incidentally the calculation of [24] predicts only rather small upward shift for this transition - much smaller than the 0.3 eV shift attributed to it in that work. At the same time the band at $1.0 \div 1.15$ eV turns out to be sensitive to the NO adsorption though it was assigned previously to the bulk transition. In our work we consider it as a convolution of the two surface transitions ($^3B_1 \rightarrow {}^3B_2$ and $^3B_1 \rightarrow {}^3A_2$). The effect of NO adsorption towards such complex bands depends on the nature of the component states. According to our calculation (which is also in agreement in this respect with [24]) the surface states $^3B_2$ and $^3A_2$ appear due to the splitting on the surface of two different triply degenerate bulk manifolds: $^3T_{2g}$ and $^3T_{1g}$, respectively. Adsorption of NO molecule on a surface Ni^{2+} ion makes its environment more symmetric and closer to the octahedral one. For that reason the splitting of these two triply degenerate manifolds must be smaller and their components must become closer to the respective bulk states. That is exactly what happens to the band at 1.0÷1.15 eV in the experiment: a new feature appears at 0.9 eV which corresponds to the $^3B_2$ surface state shifted down towards its parent bulk manyfold at about 0.75÷0.8 eV. We consider all these observations as an indication of certain problems existing in simultaneous interpretation of the optical and EELS spectra of NiO. We can not assign reliably the band at 1.0÷1.15 eV in the absorption spectrum. However, the shoulders at 0.75 and 2.15 eV are not assigned by other authors.

Another available set of experimental data is that on the states of CoO. Here as in the case of NiO the number of observed bands in the EELS spectra [22] is much smaller than the number of calculated states. The data presented in [22] are less detailed than those in [21] and the weak peaks are not seen on the graphs given in the former work. Nevertheless, in the framework of the above hypothesis concerning the assignments of the EELS states we try to interpret available data and correlate our results with the optical absorption measurements [25]. This is done in Table 2. Of certain interest is the correspondence of results of our simple semi-empirical calculations with the elaborated ones of Refs. [19, 26]. We can say that the bulk states coming from the ^3F atomic state obtained in the both calculations fairly coincide. However, in the calculations Ref. [19, 26] the lowest energy excited ^4E state lays much lower than in our calculation. However, one more possibility must be taken into account in the course of the interperetation of the HREELS data [27]. This is the Jahn-Teller distortion of the ground $^4T_{1g}$ state of the Co^{2+} ion. Indeed, the CoO crystal is tetragonally distorted (see [19,25] and reference therein) such that one pair of oxygen ions is closer to the Co atom by 0.025 Å then the other four ions. In agreement with [19] this results in a weak Jahn-Teller distortion which is all the same too small (0.014 eV) to explain the observed HREELS peak at $\sim$ 0.05 eV [27]. However, with this geometry of distortion (compressed octahedron), the ground state of the Co^{2+} ion remains spatially degenerate (^4E rather than $^4A_{2g}$) and thus further distortion is possible. The situation is pretty close to that in the *trans*-[$Co(H_2O)_4Cl_2$] complex which is also distorted from the C_{4v} symmetry due to the fact that the ground state of the symmetric complex is spatialy degenerate [28] and some very low-energy excited states appear due to the Jahn-Teller splitting of the latter. In our calculation we assumed that further distortion is an elongation of a pair of the equatorial Co-O distances upto 2.17 Å. This yielded the splitting of ~ 0.03 eV. By the order of magnitude this is in agreement with that observed in the HREELS experiment [27], however, this is certainly beyond the accuracy of our approach, since at that scale the corrections necessary because of the cluster approximation itself (in first place due to the charge distribution inconsistency) are larger than this tiny value. Nevertheless, we would like to draw attention to the possibility that the low-energy (0.05 eV) feature in the HREELS spectrum [27] appears due to the Jahn-Teller distortion of the ^4E ground state of the tetrahedrally distorted CoO_6^{10-} cluster.

V. Conclusion

In the present paper we give an account of the effective crystal field (ECF) method and analyze the preliminary results of its application to the calculation of the d-level splitting and $d-d$ spectra in the oxides of divalent manganese, iron, cobalt, and nickel. This method allows one to perform systematic calculations of the ligand field for various ligand environments. From the present results we can conclude that the calculations by the ECF method [7] provide important supplementary information to the experimental probes of the electronic structure of TMO. There is certain discrepancy when the ECF method parameterized for the transition metal hexahydrates is extended to the transition metal oxides. Two options to escape these contradictions can be foreseen: (i) some more detailed measurements on the optical absorption spectra might be useful to decide definitively whether the low-energy bulk electronic transition is present in the spectrum of NiO; (ii) perhaps, in order to reproduce experimental values of $10Dq$ the ECF method when applied to the TMO's requires more elaborated reparameterization to take into account distinctions in the atomic basis of oxygen atoms in different environments: H_2O in an isolated complex and O^{2-} in the crystal.

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References

1. J.G. Bednorz, K.A. Müller. Z. Phys. B 64, 189 (1986).

2. S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, L.H. Chen. Science 264, 413 (1994).

3. C.A. Morrison. *Crystal Fields for Transition-Metal Ions in Laser-Host Materials.* (Springer-Verlag, Berlin, 1992).

4. A.L. Tchougréeff. Int. J. Quant. Chem. 58, 67 (1996).

5. W.A. Harrison. *Electronic structure and the properties of solids* (Freeman, San Francisco, 1990).

6. J. Zaanen, G.A. Sawatzky, J. Allen. Phys. Rev. Lett. 55, 418 (1985).

7. A.V. Soudackov, A.L. Tchougréeff, I.A. Misurkin. in Electron-Electron Correlation Effects in *Low-Dimensional Conductors and Superconductors.* A.A. Ovchinnikov and I.I. Ukrainskii (Eds.)(Springer-Verlag, Berlin, 1991); A.V. Soudackov. PhD Thesis. Karpov Institute of Physical Chemistry, Moscow (1991) [in Russian]; A.V. Soudackov, A.L. Tchougréeff, I.A. Misurkin. Theor. Chim. Acta. 83, 389 (1992).

8. J.-P. Malrieu. in Z.B. Maksić (Ed.) *Theoretical Models of Chemical Bonding.* Part. 2 (Springer-Verlag, Berlin, 1991)

9. A.V. Soudackov, A.L. Tchougréeff, I.A. Misurkin. Int. J. Quant. Chem. 58, 161 (1996).

10. P.S. Bagus, U. Wahlgren. Mol. Phys. 33, 641 (1977); H. Johansen, U. Wahlgren. Mol. Phys. 33, 651 (1977).

11. G.J.M. Janssen, W.C. Nieuwpoort. Int. J. Quant. Chem. Quant. Chem. Symp. 22, 679 (1988); G.J.M. Janssen, W.C. Nieuwpoort. Phys. Rev. B 38, 3449 (1988).

12. A.V. Soudackov, A.L. Tchougréeff, I.A. Misurkin. Zh. Fiz. Khim. 68, 1257 (1994) [in Russian]; Russ. J. Phys. Chem. 68, 1135 (1994) [in English]; A.V. Soudackov, A.L. Tchougréeff, I.A. Misurkin. Zh. Fiz. Khim. 68, 1265 (1994) [in Russian]; Russ. J. Phys. Chem. 68, 1142 (1994) [in English]; A.L. Tchougréeff, A.V. Soudackov, I.A. Misurkin, H. Bolvin, O. Kahn. Chem. Phys. 193, 19 (1995).

13. R. McWeeny, B.T. Sutcliffe. *Methods of molecular quantum mechanics.* (AP, London, 1969).

14. J.A. Pople, D.L. Beveridge. *Approximate molecular orbital theory.* (McGraw-Hill, NY, 1970).

15. S.Y. Shashkin, W.A. Goddard III, Phys. Rev. B, 33, 153 (1986)

16. J. Li, H.-L. Liu, J. Ladik. Chem. Phys. Lett. 230, 414 (1994).

17. J.B. Torrance, R.M. Metzger. Phys. Rev. Lett. 63, 1515, (1989); J.B. Torrance, P. Lacorro, C. Asavaroengchai, R.M. Metzger. J. Sol. State Chem. 90, 168 (1991).

18. A.L. Tchougréeff, I.A. Misurkin. Zh. Fiz. Khim. Submitted.

19. S. Shi, V. Staemmler. Phys. Rev. B, 52, 12345 (1995).
20. P.A. Cox. *Transition Metal Oxides.* (Clarendon Press,. Oxford, 1992).
21. P.A. Cox, A.A. Williams. Surf. Sci. 152, 791 (1985).
22. A. Gorschlüter, H. Merz. Phys. Rev. B 49, 17293 (1994).
23. R. Newman, R.M. Chrenko. Phys. Rev. 114, 1507 (1959).
24. A. Freitag, V. Staemmler, D. Cappus, C.A. Ventrice, K. Al Shamery, H. Kuhlenbeck, H.-J. Freund. Chem. Phys. Lett. 210, 10 (1993).
25. G.W. Pratt, R. Coelho. Phys. Rev. 116, 281 (1959).
26. V. Staemmler. Ab Initio Calculations of Electronic Surface States of Transition Metal Oxides and of the Superexchange Coupling in Oxo-Bridged Transition Metal Complexes, in: Nino Russo and Dennis R. Salahub, eds., *Proceedings of the NATO Advanced Study Institute on Metal-Ligand Interactions: Structure and reactivity, Cetraro, Italy, September 4-16, 1994* (Kluwer Academic Publishers, Dordrecht/Boston/London, 1996) 473-492.
27. M. Haßel, H. Kuhlenbeck, H.-J. Freund, S. Shi, A. Freitag, V. Staemmler, S. Lütkehoff, M. Neumann. Chem. Phys. Lett. 240, 205 (1995).
28. A.V. Soudackov, A.L. Tchougréeff, I.A. Misurkin. Int. J. Quant. Chem. 57, 663 (1996).

Table 1: Calculated transitions in the $[NiO_n]^{10-}$ clusters

State	Calcd.	Obsd.			
		OA	Ref.	EELS	Ref.
$^3A_{2g}(B),^3B_1(S)$	0.00	0.00		0.00	
^3E (S)	0.57			0.60	[22,24]
$^3T_{2g}$ (B)	0.81	0.75?	[23]	0.80	[20]
$^3B_2$ (S)	0.90			1.05 $\div$	[21,
$^3A_2$ (S)	1.05	1.13	[23]	1.1	22,24]
^3E (S)	1.33				
$^3T_{1g}$ (B)	1.39			1.4	[21]
$^1A_1$ (S)	1.76			1.62	[24]
^1E_g (B)	1.98	1.95	[23]		
$^1B_1$ (S)	2.12			1.87	[24]
^1E (B)	2.59	2.15	[23]		
$^3A_2$ (S)	2.66				
$^1T_{2g}$ (B)	2.72	2.75	[23]		
$^1A_2$ (S)	2.80			2.75	[22]
$^1B_2$ (S)	2.95			2.90	[22]
$^3T_{1g}$ (B)	3.00	2.95	[23]		
^3E (S)	3.09			3.10	[22]
$^1A_{1g}$ (B)	3.11	3.25	[23]		
$^1A_1$ (S)	3.23			3.25	[21]

Table 2: Calculated transitions in the [CoO_n] clusters

State	Calcd.	Obsd.			
		OA	Ref.	EELS	Ref.
$^4T_{1g}$ (B),$^4A_2$ (S)	0.00		0.00		
^4E (S)	0.22			0.05	[27]
$^4B_2$ (S)	0.66			0.45	[27]
$^4T_{2g}$ (B)	0.76	$0.90 \div 1.1$	[25]		
^4E (S)	0.89			0.85	[22]
$^2A_1$ (S)	1.56				
^2E_g (B)	1.66	1.61	[25]		
$^4A_{2g}$ (B)	1.64				
$^4B_1$ (S)	1.63				
^2E (S)	2.17			2.05	[22]
$^2A_2$ (S)	2.25			2.25	[22]
$^2B_1$ (S)	2.29				
$^2T_{1g}$ (B)	2.32	2.03	[25]		
$^2T_{2g}$ (B)	2.35	2.05	[25]		
^4E (S)	2.34				
$^2B_2$ (S)	2.52				
$^4T_{1g}$ (B)	2.44	$2.26 \div 2.33$	[25]		
^2E (S)	2.63				
^2E (S)	2.84				
$^2T_{1g}$ (B)	2.91	$2.49 \div 2.56$	[25]		
$^2A_2$ (S)	2.92				
$^2A_{1g}$ (B)	2.91	2.61	[25]		
$^2A_1$ (S)	2.98				
$^2T_{2g}$ (B)	3.29				
$^4A_2$ (S)	3.19			3.2	[22]
^2E (S)	3.37				

Table 3: Atomic charges in octahedral $[MO_6]^{10-}$ clusters

NiO	Ni	s	0.21	
		p_z	0.24	1.06
	O	s	1.89	
		p_x	1.97	
		p_y	1.99	
		p_z	1.99	-1.84
CoO	Co	s	0.22	
		p_z	0.25	1.02
	O	s	1.89	
		p_x	1.98	
		p_y	1.99	
		p_z	1.99	-1.84
FeO	Fe	s	0.23	
		p_z	0.26	0.98
	O	s	1.87	
		p_x	1.98	
		p_y	1.99	
		p_z	1.99	-1.83
MnO	Mn	s	0.24	
		p_z	0.28	0.93
	O	s	1.87	
		p_x	1.98	
		p_y	1.99	
		p_z	1.99	-1.82