d-d Spectra of Transition Metal Oxides as Calculated in Cluster Approximation with use of Effective Crystal Field Method

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Abstract

The Effective Crystal Field (ECF) method is applied to interpretation of d-d excitations in metal oxides of the first transition series studied by optical absorption (OA) and electron energy loss spectroscopies (EELS). The calculations are performed in the framework of the cluster approximation. The cubic clusters of different size are employed to simulate the transition metal ions in the bulk, on the (100) crystal surfaces and in a vicinity of oxygen vacancies. A fair agreement between the calculation performed without any parameter adjustment and experiment is reached when the effect of the crystalline environment is taken into account by considering clusters of sufficient size.

1 Introduction

Electronic structure of transition metal compounds (TMC) attracts considerable interest in relation to oxide materials like high-T_c superconducting cuprates [1]. However, even the electronic structure of rather simple TMC like their oxides (TMO) with the rock salt crystal structure is not completely understood. Divalent metals in the second half of the series (Mn, Fe, Co, Ni) form the rock salt like oxides which are antiferromagnetic insulators. d-Electrons in these compounds form local momenta corresponding to an integer number of electrons in their d-shells. These momenta interact and form ordered states at low temperature. The spin waves derived from these states are the lowest energy excitations of magnetic 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 $d^n \rightarrow L^{\mp} d^{n\pm1}$ of 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 (or hole) transferred from the band state of the ligands (oxygens) to the d-shell. The materials 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) [2]. 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 respective metal ion but rearrange themselves inside its open d-shell. Classification proposed in Ref. [2] does not override earlier suggestion due to Harrison. In [3] it has been suggested that electronic states of TMO can be described as bands of an ionic insulator (like MgO or CaO) supplied with the local states of d-electrons. These $d^n \rightarrow d^n$ excitations are referred to as the crystal field (CF) excitations. These excitations are important in describing the optical properties of the TMO [3, 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 d-d-excitations of the CF type can be considered in the cluster approximation when single transition metal ion (TMI) and its surrounding is considered explicitly. Within this general setting there are many ways for performing quantum chemical calculations. Largely, they are done by various versions of *ab-initio* techniques which are based on the self consistent field (SCF) approximation. The SCF approximation, however, faces some serious problems when applied to TMC (for more detailed discussion see Ref. [5] and references therein). Those problems suggest that the SCF approach is a poor starting point for studying the electronic structure of TMC. Physically the problem is that the single determinant SCF approximation overestimates the weight of the configurations with electrons transferred from or to the d-shell. The SCF approximation smears the multiplet structure of free TMI which is in fact retained [6] in TMC. The ground state of TMC cannot be presented by a single Slater determinant and some other configurations must be taken into consideration. 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 included. However, the major part of these configurations is necessary to compensate intrinsic errors of the underlying SCF approximation.

The SCF approach completed with some CI expansion in its *ab-initio* version has been tested in [7] using NiO_6^{10-} and CoO_6^{10-} clusters. It turned out that delocalization of d-electrons as obtained from the SCF calculation is indeed artificially strong which 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 (O2p and Ni3d) are included in the CI expansion. This move is equivalent to improving the one-electron basis used for the CI expansion. Further improvement has been proposed in [8], where the ligand-to-metal charge transfer states were taken into consideration in the local basis by means of the first order CI (FOCI) method. The contribution of the charge transfer states to the ground state and the d-d excited states is small, but their effect on their energetics is significant. That made us think that a semiempirical approach recently suggested independently [5] for isolated TMC's might be of use as a simple tool for describing electronic structure of TMO's as well. The effective crystal field (ECF) method [5] starts from the assumption that the d-shell of the central ion contains some number of electrons fixed by the oxidation state of the ion. The rest of electrons residing in the ligands forms the closed shell state which is described in the SCF approximation. The corrections due to electron transfer between the d-shell and the rest are taken into account. However, the fact that the weight of the charge transfer configurations is small led to the idea [5] 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 ECF method which has been implemented semi-empirically. It has been extensively tested and has been proven to be a useful alternative to the SCF based methods in the case of the isolated molecular transition metal complexes [9]. Recently the ECF method has been applied to analysis of the *d*-*d*-spectra of TMO in the cluster approximation [10]. It has been shown that the ECF method is useful for interpreting the data obtained by various methods probing the excitations of the CF type. However, the clusters used in Ref. [10] were very small and some special precautions had to be made to mimic the effect of the Coulomb potential induced by the rest of the crystal (Madelung potential).

For the clusters $MO_n^{2(n-1)-}$ considered in Ref. [10] it has been shown that inclusion of the Madelung field is necessary to obtain reasonable description of the *d*-*d* spectrum. However, in Ref. [10] (like in other works employing clusters of minimal size [7, 8, 11]) the Madelung potential was estimated with use of the formal charges (± 2) ascribed to the ions in the lattice, though the real atomic charges may deviate from the formal values. It seemed to be reasonable both on *ab-initio* and semiempirical levels of description since the charges on oxygen atoms found there [7, 8, 10, 11] were close enough to -2 to support the above estimate for the Madelung potential. In the present study we, however, decided to take into account as many atoms as possible and to calculate all the quantities related to the crystal explicitly. This approach allows us to assess all the effects of the crystal enviroment upon the TMI. First, the MO's of the larger clusters are probably closer to the band states of the crystal. Second, the atomic charges obtained from the explicit calculation are closer to the exact ones present in the real crystal. Also the potentials they induce are closer to the exact Madelung potential provided the cluster size is large enough.

In order to clarify effects of the cluster size upon the *d*-level splitting we calculated electronic structure for a series of cubic MO clusters, chosen to represent the fragments of the oxide crystals: $[M_{13}O_{14}]^{2-}$, $[M_{32}O_{32}]$, and $[M_{63}O_{62}]^{2+}$ ($3\times3\times3$, $4\times4\times4$, and $5\times5\times5$ atoms in the cluster, respectively), where M = Mn, Fe, Co, and Ni, using the ECF method described in the previous section. Also the $[M_{63}O_{61}]^{4+}$ clusters were used to calculate electronic structure of TMI's in a vicinity of an oxygen vacancy. *d*-Level splitting has been calculated for TMI's placed in the center of the clusters (the bulk ion or the ion in the vicinity oxygen vacancy) or in the center of the cluster's face (the ion on the (100) crystal surface). We did not undertake any reparameterization of the ECF method especially for crystals. As in Ref. [10] we used the characteristic parameters of metal-oxygen electron hopping β^{M-O} as they appear in Ref. [9] 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 for the Racah B and C parameters. It has been shown, that the standard oxygen orbital exponents satisfactorily reproduce the experimental dependence of $10Dq$ on Cu–O distance in a series of Ln_2CuO_4 compounds [12]. For this reason we did not change them either.

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 are not precisely equal to those in the bulk. Another problem is posed by the Jahn-Teller ions: The geometries of the latter crystals are distorted and the closest environment of these TMI's is not exactly octahedral. The same applies to the impurity Jahn-Teller ions. Nevertheless, all calculations are performed for the interatomic distances measured by X-ray techniques for the bulk.

2 Account of the method

In the ECF method [5] 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 TMI (d-system). The second part contains $4s$-, $4p$-AOs of the transition metal and the valence orbitals of the ligand atoms (ligand subsystem or l-system). 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-system, H_c and H_r are respectively the Coulomb and the resonance interaction (electron hopping) operators between the two systems.

For most of TMC with closed-shell ligands the excitations in the l-system are very high in energy as compared to the energies of the d-d excitations, and their contribution is negligible. The ground state of the l-system is then 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:

$$\Phi_n = \Phi_d^n \wedge \Phi_l \tag{2}$$

Both the spin multiplicity and the point symmetry of the functions of this type coincide with those of the functions Φ_d^n of the d-system.

The wave functions of the type Eq. (2) correspond to the fixed integer number (n_d) of electrons in the d-shell of the TMI. In order to include the effects of the resonance interaction (*i.e.* the virtual charge transfer) between the subsystems we switch to the *effective* Hamiltonian H^{eff} [5] which operates in the subspace spanned by the functions Eq. (2), but by construction [13] has the eigenvalues equal to those of the original Hamiltonian Eq. (1):

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

(P is the projection operator on the subspace of functions Eq. (2) and $Q = 1 - P$).

The variational problem for the effective Hamiltonian H^{eff} Eq.(3) within the subspace spanned by the wave functions Eq. (2) yields a system of equations for Φ_d^n and Φ_l (see *e.g.* Refs. [5, 13]):

$$\begin{aligned} H_d^{eff}\Phi_d^n &= E_d^n\Phi_d^n \\ H_l^{eff}\Phi_l &= E_l\Phi_l \\ H_d^{eff} &= H_d + \langle\Phi_l\,|H_c + H_{rr}|\,\Phi_l\rangle \\ H_l^{eff} &= H_l + \langle\Phi_d^n\,|H_c + H_{rr}|\,\Phi_d^n\rangle \end{aligned} \tag{4}$$

Since the l-system is described by a single Slater determinant Φ_l the latter must be found from the SCF procedure applied to the Fock operator F_l^{eff} derived from the Hamiltonian H_l^{eff} by the standard method [13, 14]. The solution of the Hartree-Fock problem in the CNDO approximation for the l-system 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 define the electronic structure of the l-system. 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-system. That yields the effective Hamiltonian H_d^{eff} for d-electrons only in the form:

$$H_d^{eff} = \sum_{\mu\nu\sigma} U_{\mu\nu}^{eff} d_{\mu\sigma}^{+} d_{\nu\sigma} + \frac{1}{2} \sum_{\mu\nu\rho\eta} \sum_{\sigma\tau} (\mu\nu \mid \rho\eta) d_{\mu\sigma}^{+} d_{\nu\sigma} d_{\rho\tau}^{+} d_{\eta\tau} \tag{5}$$

where the Coulomb interaction is taken as in the free ion and the effective one-electron parameters $U_{\mu\nu}^{eff}$ contain the corrections both from the Coulomb and the resonance interaction between d- and l-systems:

$$\begin{aligned} U_{\mu\nu}^{eff} &= \delta_{\mu\nu} U_{dd} + W_{\mu\nu}^{\text{ion}} + W_{\mu\nu}^{\text{cov}} \\ W_{\mu\nu}^{\text{ion}} &= \delta_{\mu\nu} \left(\sum_{i \in s,p} g_{\mu i} P_{ii} \right) + \sum_{L} Q_L V_{\mu\nu}^{L} \\ W_{\mu\nu}^{\text{cov}} &= - \sum_{i} \beta_{\mu i} \beta_{\nu i} \left(\frac{1-n_i}{\Delta E_{di}} - \frac{n_i}{\Delta E_{id}} \right) \end{aligned} \tag{6}$$

Here P_{ii} is the diagonal matrix element of the one-electron density matrix of the l-system; Q_L is the atomic charge of the ligand atom L calculated in the CNDO approximation; $V_{\mu\nu}^{L}$ is the matrix element of the potential energy operator describing the interaction between a d-electron and a unit charge placed on the ligand atom L; n_i is the occupation number of the i-th ligand MO ($n_i = 0$ or 1); $\Delta E_{di} (\Delta E_{id})$ is the energy necessary 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 [5].

When 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 d-d excitation energies are then estimated as the differences between the eigenvalues of the corresponding eigenstates of H_d^{eff}.

3 Results and discussion

As we mentioned before, we performed calculations of d-electronic states of TMI embedded in a series of clusters. The results are presented in Tables 1-4.

First we consider the results of our calculations concerning the ligand electronic structure. They are given in Table 1. The charge distribution is extracted from the standard quanum chemical analysis of the CNDO part of the calculation on the l-system. We see that calculated net atomic charges q strongly differ from the formal ones ($0.8 \div 1.05$ rather than 2.0). There is a weak trend towards increase of the absolute values of the charges while the cluster size increases. An apparent source of the difference between the calculated and formal charges is electron delocalization over crystal/cluster bands/orbitals. As it is estimated by Harrison [3] the real charges in KCl are about 50% of the formal ones. Our cluster calculation on crystals formed of divalent cations and anions gives similar result. Nevertheless, the charges calculated for a cluster of finite size differ from those in an infinite crystal (*i.e.* from "real" ones). This is effect of the finite size of the cluster we used to represent the crystal. According to [3] the total energy of the crystal contains only one contribution which favors the separation of charges equal to:

$$-\alpha_M q^2/d$$

where α_M is the Madelung constant and d is the lattice constant. Hence, the difference between the complete crystal calculation (like that of Ref. [15]) and our finite cluster approach can be estimated from the difference between the exact value of the Madelung constant and that obtained for the cluster of the finite size. For the largest clusters we used in our calculations ($5 \times 5 \times 5$) the estimate of the Madelung constant amounts to 1.52 which is pretty close to the exact value characteristic for the rock salt structure 1.75 [3]. Even though our estimate does not suffice for precise calculation of electronic structure, it is difficult to guess that 10% error in the Madelung energy could dramatically change the distribution of charges or other characteristics of the crystal electronic structure we try to represent with use of clusters. The band gap between the O2p-HOMO and M4s-LUMO is, for example, in a fair agreement with the *ab-initio* results [15].

We have to notice also that the atomic charges calculated by quantum chemical programs do not have much sense by themselves and serve largely as a tool for representing calculation results. That particularly applies to the *ab-initio* charges obtained by the Mulliken procedure. On the other hand, some semiempirical parameterizations (in particular the CNDO) provide us with the atomic charges capable to reproduce dipole momenta of small molecules [14] and in this sense the CNDO charges reproduce experimental electron distribution. Next, we have to mention that due to basis set disbalances the *ab-initio* calculations may give rather big charges irrespective to the molecule size. For example, the metal charges in the hexahydrocomplexes of the first row divalent TMI's are all found to be larger than +1.6 [16], which seems to be too large value. On the other hand the calculations on the metal hexahydrates done in the ECF framework all give atomic chagres for divalent metal ions to be about +1.0 [9]. Our conjecture is that the large atomic charges obtained for the metal oxides in Ref. [15] appear due to the same features of the *ab-initio* procedure as do the large charges in the hydrates, rather than represent the exact picture of the electron distribution in oxides.

According to the present calculation the contribution of the atomic charges to the splitting amounts to *ca.* 10% of the total. Those reported in Ref. [10] attribute not more than 20% of the total splitting to the atomic charges. According to Ref. [17] the contribution of the point charges amounts to about 30% of the total splitting. This result, however, must be considered as an exaggeration which can be explained by effectively longer tails of the atomic one-electron d-functions used in Ref. [17] as compared to rather contracted Slater type orbitals with Burns' exponent used in our work and to larger point charges used there. To summarize our discussion of the atomic charges we can say, that their direct contribution to the d-splitting is not that significant so that even considerable error in their determination does not cause big error in the d-d spectrum. On the other hand the positions of the one-electron levels in the l-system must be tightly related to the self consistent atomic charges in the latter. These energies enter the denominators of Eq. (6) so that the reasonable description of the d-d spectra might serve as an indirect proof of the quality of the electronic structure of the l-system.

The characteristic quantity related to the energies of the excited d-states is the $10Dq$ parameter of the CF splitting. Corresponding values are given in Table 2 compared to available experimental data and as dependent on the cluster size. These data also manifest a trend to the bulk values when the cluster size increases. A remarkable coincidence with the experimental data demonstrates general validity of our approach (see below).

The spin and symmetry of ground bulk states in all the cases are found by the ECF method in the exact coincidence with the experimental data [18]. The calculated energies of d^n-multiplet states for clusters are presented in Tables 3-5 together with some related experimental data. Some procedures of comparison of the experimental data and calculated state energies must be discussed here.

The electron energy loss spectra (EELS) is considered as a powerful method probing electronic states of solids. There is, however, an uncertainty in the nature of the states probed by this technique in TMO's. According to [18] one should expect the surface states to be seen in the EELS spectra. However, it is also stated by the same author that in fact the bulk states are seen. This opinion agrees with the fact that the number of the bands observed in the EELS spectra is much smaller than that for the surface TMI with lower symmetry. This is certainly a contradiction since the penetration depth for electrons is relatively small at least for low energy incident beams and for that reason the intensity of the bulk states scattering must be much smaller than that for the surface ones. Accordingly, the EELS spectra generally manifest the band widths of about 0.2 eV which is comparable with the splitting of the states in the clusters where the TMI's are placed on the cluster face which are used to represent the surface TMI's. However, since the surface states appear as a result of the splitting of the bulk states the energy corresponding to the maximum of their convoluting curve may be (but not necessarily are) close to the position of the parent bulk state. All these facts together suggest [10] to consider the intense bands seen in the EELS spectra as convolutions of close surface states whereas weak features in these spectra might be manifestations of the bulk states. With this conjecture an attempt to reinterpret the EELS spectrum of NiO found in Ref. [19] has been undertaken in Ref. [10]. If we accept following [10] (as it was originally proposed in Ref. [19]) that the small bump at 1.8 eV corresponds to a real d-d-transition then the small bumps at about 0.8 eV, at 1.4 eV, and 2.1 eV also do. We interpret them all as the bulk states with low intensity. The intense bands at 1.05, 1.62, and 3.0 eV are then to be treated as the convolutions of transitions to the surface states rather than those to the bulk states. With these assumptions we can fairly correlate the available data with our calculations on the 5×5×5 NiO clusters. Indeed the low energy surface state at 0.6 eV observed in Refs. [20, 22] fairly corresponds to the lowest excited ${}^3E$ state in our calculation on Ni^{2+} surface ion. The small bump at 0.8 eV can be interpreted as the low intensity bulk ${}^3T_{2g}$ transition and/or ${}^3B_2$ surface transition. The wide intense band at 1.05 ÷ 1.10 eV interpreted in Ref. [19] as the bulk ${}^3A_{2g} \to {}^3T_{2g}$ transition is indeed the convolution of two ${}^3B_1 \to {}^3E$ and ${}^3B_1 \to {}^3A_2$ surface transitions. Further analysis allows us to interpret the small peak at 1.4 eV [19] as the ${}^3A_{2g} \to {}^3T_{1g}$ bulk transition. The strong peak at 1.62 eV is then the ${}^3B_1 \to {}^1A_1$ surface transition. It is difficult to decide how the authors [20] distinguish *two* transitions at 1.6 eV and 1.7 eV. We think that this is the 1.62 eV feature from Ref. [18]. At higher energy we can support the interpretation of the data of Ref. [18] in the range of $2.75 \div 3.2$ eV as convolutions of ${}^3B_1 \rightarrow {}^3A_2$, ${}^3B_1 \rightarrow {}^1E$; ${}^3B_1 \rightarrow {}^1B_2$, ${}^3B_1 \rightarrow {}^3E$; and ${}^3B_1 \rightarrow {}^1A_2$, ${}^3B_1 \rightarrow {}^1A_1$ surface transitions. The high energy surface transition ${}^3B_1 \rightarrow {}^1A_1$ almost coincides with the bulk ${}^3A_{2g} \rightarrow {}^1A_{1g}$ visible in the OA spectrum [21] which demonstrates that even precise coincidence of positions of the intensity maxima in the EEL and OA spectra does not mandatory signify that the *states* seen by the two different techniques at this energy are the same.

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 OA measurements [21] on NiO and on Ni^{2+} impurity ions in MgO (for refernece see [4] and discussion below). However, a careful inspection of the data set of Ref. [21] shows that a weak shoulder above 0.8 eV can be seen on the curve presenting the spectrum recorded at the room temperature. Unfortunately, the low temperature spectrum had not been recorded in the energy range $0.5 \div 0.9$ eV and the spectrum in this energy range had been *interpolated* in Ref. [21]. It is not possible to say whether there is any feature in the low temperature spectrum in this energy range. However, if we inspect 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: they become even less pronounced than the shoulder at 0.8 eV in the room temperature spectrum. So we make a conclusion that it is possible that there is a bulk CF state in NiO above 0.8 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 [9].

In order to give an interpretation to the EELS and OA bands in the range $1.0 \div 1.15$ eV we have to consider experimental data in more details. In Ref. [22] it was proposed to expose the (100) surface of NiO to NO in order to study the EELS spectra of the surface covered by the adsorbate. The bands sensitive to the NO adsorption were attributed to the surface states whereas the unsensitive ones to the bulk states. However, even in this case the interpretation of the experimental measurements is not straightforward enough.

First of all it is not that evident that the surface ^3E state at 0.6 eV migrates to 0.9 eV under NO adsorption, as it is suggested in Ref. [22]. 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 Ref. [22] predicts only rather small upward shift for this transition - much smaller than the 0.3 eV shift attributed to it in the same work. At the same time the band at 1.0÷1.15 eV turns out to be sensitive to the NO adsorption though it was assigned previously to the bulk transition on the basis of almost precise coincidence with a band in the OA spectrum [21]. In our work we consider this EELS band as a convolution of the two surface transitions ($^3B_1 \rightarrow {}^3A_2$ and $^3B_1 \rightarrow {}^3E$). The effect of NO adsorption upon such complex bands depends on the nature of the component states. According to our calculation 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 that in an octahedron. 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 $^3A_2$ surface state shifted towards its parent bulk state at about 0.8 eV. On the basis of our calculation we can also assign the band at 1.0÷1.15 eV in the OA spectrum. We already mentioned that attribution of this band in [21] to the bulk $^3A_{2g} \rightarrow {}^3T_{2g}$ transition disagrees with our calculation. Our calculation shows, however, that for a Ni^{2+} ion in the bulk of the lattice, but with an oxygen vacancy next to it, there is an $^3A_2$ excited state having just required energy ($\sim$1.07 eV). We suggest that transition to this state is observed in the OA spectrum [21]. To summarize our discussion of NiO we can say that use of the ECF approach with combination with the cluster approximation allowed us to interpret considerable amount of data. Not all problems have been solved (it is not clear, for example, why the bulk state at 1.4 eV is not seen in the OA spectrum). At the same time we must say that the feature at 2.15 eV which is clearly seen but not interpreted in Ref. [21] simply disappeared from the sets of experimental OA data presented in the works devoted to EELS spectroscopy of NiO and from related calculations. Incidentally, it does not manifest itself in the EELS spectra (though it had to if only the bulk states are really seen by that method). Our calculation suggests an assignment for this feature as to the bulk $^3A_{2g} \rightarrow {}^1E_g$ spin forbidden transition. We are also able to assign the shoulder at 0.8 eV which is ignored by other authors.

Another example well studied experimentally is CoO. In this case as in the case of NiO the number of observed bands in the EELS spectra Ref. [20] is much smaller than the number of calculated states. The data presented in [20] are less detailed than those in [19] and the weak peaks are not seen on the graphs given in the former work. Nevertheless, in the framework of the above approach to assignment of the EELS states we interpret available data and correlate our calculations with the EELS and OA measurements [20, 23] and the high-resolution EELS (HREELS) experiments [24] which give detailed picture of the surface states in the low energy region. All these data are summarized in Table 4. The results of our simple semiempirical calculations when applied to the bulk states are in fair agreement with the OA experimental data [23] and with the results of elaborated numerical studies of Refs. [19, 11]. The bulk states coming from the ^4F state of the free Co^{2+} obtained by the both calculation schemes agree fairly well. Remarkable agreement between our ECF calculation and the HREELS experiment has been reached in the present paper simply by considering the cluster of larger size. According to the calculations and measurements of Refs. [11, 24] the lowest excited ^4E state has the energy of 0.05 eV. This agrees fairly well with our present calculation. In Ref. [10] the position of the ^4E excited state was found to be 0.45 eV with use of the minimal surface cluster CoO_5^{8-}.

Detailed experimental data on surface states of MnO are not available as far as we know. For that reason we compare results of our calculation on MnO clusters with the data on OA cited in Ref. [18] (Table). We can see that a reasonable agreement is reached between the calculated and experimental data. Our result is in agreement with the Low's conjecture concerning the position of the $^4T_{1g}(G)$ state in the spectrum of the Mn^{2+} ion in the octahedral oxygen environment. According to [25] the energy of this state must be higher than 1.7 eV to ensure the interpretation of the EPR data suggsted there. Our calculation supports this. For more detailed discussion of the Low's conjecture see [27]. We have only to add that in the particular case of the Mn^{2+} ions their spectrum is relatively weakly sensitive to the particular value of the $10Dq$ parameter. It largely is determined by the Racah parameters B and C of the intrashell Coulomb interaction between d-electrons.

The electronic states of the Fe^{2+} ion in iron(II) oxide can not be easily assessed due to significant nonstoichiometry of the latter. Wustite (Fe_xO) crystals have strong deficit of the iron ions. The XPS measurements performed in [28] suggest that the value of the $10Dq$ parameter is *ca.* 1.0 eV. Similar result is reported in Ref. [29], where the corresponding value have been estimated to be about 1.25 eV on the basis of analysis of the OA spectrum of the Fe^{2+} impurity in MgO (see, however, discussion below). Our calculation on the 5×5×5 FeO cluster yields the $10Dq$ value of 1.2 eV, which is in a fair agreement with the available experimental data cited above.

According to [18] the parameters of the divalent transition metal impurity ions in MgO must be pretty close to those of the TMI in their oxides. Nevertheless, they have not to coincide with them. The reason can be easily understood from the point of view of the present ECF theory of the d-level splitting. According to [5] the estimates for the energy denominators ΔE_{di} and ΔE_{id} in Eq. (6) have the form:

$$\Delta E_{di} = I_d - A_i - g_{di}$$
$$\Delta E_{id} = I_i - A_d - g_{di}$$

where I_d is the ionization potential of the d-shell, A_i is the electron affinity of the l-system corresponding to an electron placed to the i-th empty l-MO, g_{di} is the Coulomb interaction between electron in the d-shell and in the i-th l-MO, I_i is the ionization potential corresponding to an electron removed from the i-th filled l-MO, A_d is the d-shell electron affinity. It can be checked that the main contribution to the covalent part of the ECF $W^{\mathrm{cov}}_{\mu\nu}$ comes from the charge transfer states with an extra electron in the d-shell which is taken from the filled l-MO's (in our case these are the O2p filled bands/orbitals of the crystal/cluster). Their ionization potential which, as we see, appears in the denominator of Eq. (6) is sensitive to the details of the electronic structure of the rest of the crystal. Clearly, the position of the O2p band depends on whether it is the oxygen band of a TMO or a similar band of MgO. Other terms in the denominator are hardly so much sensitive to the structure of the crystal. Now we can try to assess the effect of different crystal environment on the d-level splitting on the basis of comparison of theoretical reasons and experimental data. It is generally accepted that the energy of the first transition in the octahedrally coordinated Ni^{2+} impurity ion in the MgO lattice equals to $0.99 \div 1.00$ eV (for reference see [4]). The energy of this transition, which can be measured relatively easily for small impurity concentrations, is also equal to $10Dq$. However, our calculations on the NiO clusters together with the OA data of Ref. [21] (see above) show that the $10Dq$ parameter for NiO has somewhat smaller value (about $0.85 \div 0.90$ eV). Possible reason for that may be the difference in the positions of the O$2p$ band in these two crystals. In fact (according to the XES measurements of Ref. [30]) the energy of the O$2p$ band in MgO is by $1.0 \div 1.5$ eV higher than that in NiO. (The energy of the photon emitted in the O$2p \rightarrow$ O$1s$ transition in the Kα XES spectrum of MgO is larger by that value). Respectively, the I_i values and the ΔE_{id} denominators are smaller for the MgO crystal. This factor tends to increase the $10Dq$ parameter in the Ni^{2+} impurity ions in MgO compared to NiO in agreement with our calculation. The same conclusion can be derived in the frame of the impurity model by Gunnarsson and Schönhammer [26], where the energetic characteristics of the bands enter the theory in manner similar to Eq. (6). This effect, clearly, cannot be reprocuced by the calculations performed for minimal clusters, which are used to represent both the impurity ions and those in the TMO. The states localized on the oxygen atoms in such calculations are always the same irrespective to the nature of the crystal the cluster is assumed to represent. We do not discuss here another possible source of difference between the crystal field in different oxide lattices, namely, the difference in the interatomic distances which affect the $\beta_{\mu i}$ parameters. These distances for the bulk ions can be extracted from the X-ray data for the TMO's, but are not exactly known for the impurity and surface ions, particularly when it concerns the Jahn-Teller ions.

With the above analysis of the role the ligand one-electron states play in formation of the crystal field felt by the d-shell we can discuss possible reasons for observed validity of both small cluster calculations on TMI's in various crystal environments reported earlier and that of the present large cluster calculation. One can be surprized by the observation that the ECF calculations like the *ab-initio* ones performed for the minimal TMO clusters give pretty much the same results (except, may be, less important details) concerning the properties of the d-shells as do the large cluster calculations performed in the present study. However, we have to remark that [31] any generally reasonable results can be obtained in the cluster calculations of the d-states only in the case if the energies of the d-levels fall in the energy gap between the ligand HOMO and LUMO (or in the infinite crystal limit into the gap between the valence and conduction bands, like it is stated in the book [3]). In the present calculations using the clusters of larger size this happens quite naturally since the ligand (band) electrons are allowed to move freely so that their energy is rather low and even the ionization potentials calculated for the O2p bands with use of the present clusters are in reasonal agreement with the experimental findings of Ref. [30]. On the other hand in smaller overcharged clusters like $MO_n^{2(n-1)-}$ used in previous ECF calculations [10] and usually employed in the *ab-initio* studies (see [11] for reference) the electrons are confined in the oxygen ions and for that reason have rather high energy (much higher than any reasonable estimate for that of the band states in TMO). This, however, does not give rise to any serious problems since electrons placed in the oxygen ions in order to satisfy the electron count rules induce rather strong electric field which pushes the d-levels higher in energy so that they fall in the energy gap between the oxygen LUMO and HOMO as it must be according to the Harrison's picture of the electronic states of TMO [3]. This somewhat artificial feature of the energetics of smaller clusters ensures the general validity (and similarity) of the ECF and *ab-initio* results almost irrespective to the size of the cluster used in the calculation. Nevertheless, we suppose that using larger clusters must give generaly more accurate results.

Let us conclude our consideration of TMO with a brief discussion of the states of the component ions. Ususally a greate significance is ascribed to the fact that the calculated charges born by the oxygen ions in oxides are close to – 2 (see, for example, [32]). It is considered as a proof of the "O^{2-}" nature of the oxide oxygen. The general reasoning evolves as follows [32]: "the oxygen dianion O^{2-} is unstable in the gas phase – it decays to O^- – and only exists in the solid because of the stabilization by the Madelung field". We have shown above, that the Madelung field (may be reduced by 10%) does not suffice to separate charges to the desired extent. It does not, however, mean that the oxygen ions are not the the O^{2-} ones in the crystal, as one could think; it only means that the Madelung field has nothing to do with this. Indeed, we know that the one-electron states of ions in the crystal are not the same as one-electron states of the free ions [33]. The relevant states are the Wannier states [3] and they by definition are the back Fourier transforms of the band Bloch states. Each band in the crystal generates a Wannier state (in a given unit cell) largely formed by a specific AO of the crystal, but having a contribution from other AO's which reflects the presence of the crystal lattice. The single determinant (SCF) ground state of electrons in the insulating crystal may be equivalently represented either as a product of all filled Bloch states (delocalized) or as a product of all Wannier states (localized) derived from the filled bands. The many electron wave function is the same in these two representations. Due to orthonormalization conditions for the Bloch and Wannier states the latter are always either occupied (when derived from a filled band) or empty (when derived from an empty band). For that reason the overall electron number for all Wannier states centered at a given atom is completely determined by the band filling and thus obeys the formal chemical electron counting rules based on the concept of the oxidation state. That means that the one-electron states pertinent to an oxygen ion in a stoichiometric oxide always bear eight valence electrons which corresponds to the formal charge – 2 of the oxygen ion. The precise form of the oxygen-centered Wannier states depends, of course, on other components of the crystal, on its geometry *etc.* The electronic population on an oxygen centered AO represents only a fraction of the population of the Wannier state defined by the formal rules. It equals to the population of the pure atomic state - without tails. The only meaning of a small charge computed on an oxygen ion by any quantum chemical method is that a corresponding Wannier states (or the oxygen one-electron states in the crystal) are strongly delocalized to the neighbour ions. Extent of this delocalization depends on specific parameters of the component atoms [3]. The above construction, clearly, has no relation to the Madelung potentials. The only mechanism ensuring the "O^{2-}" state of the oxygen ions in the crystals is the resonance interaction with their neighbours, which helps to diminish the energy of a doubly charged oxygen ion, keeping some relation of electrons to the oxygen core. When such delocalization is not possible — in the gas phase — the oxygen dianion simply does not exist. This scheme explains also the validity of the standard quantum chemical orbital exponents in calculations of oxides. Some authors emphasize a need to decrease the standard oxygen orbital exponents ζ in order to reproduce a "weakly bound" electron in the O^{2-} ion [34]. It is clear, that if such a thing as a longer range bound state for electrons in O^{2-} had been possible it should manifest itself also in the gas phase. However, we know that O^{2-} is not stable. In fact, all energy gain necessary to preserve the "O^{2-}"ions in a crystal is provided by standard quantum chemical (mechanical) mechanism – by electron hopping (resonance) interaction between differenr AO's of the crystal.

4 Conclusion

In the present paper we give an account of the effective crystal field (ECF) method and analyze results of its application to the calculation of the d-d spectra in the oxides of divalent manganese, iron, cobalt, and nickel. The method allows to perform systematic calculations of the crystal field for various ligand environments. From the present results we can conclude that the calculations by the ECF method [5] provide important information concerning the experimental probes of the electronic structure of TMO. It is particularly important to take care of proper description of the electronic states and electronic energies of the l-system (oxygen band states for the present particular case of TMO). This is reached by considering TMO clusters of sufficient size (upto 125 atoms in the present work). In this case even very fine features of the surface splitting (like the ^4E state in CoO) can be fairly reproduced.

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Table 1: Calculated atomic charges for metal oxide clusters of different size

Oxide	Atom	Cluster size			Band gap (eV)
		3×3×3	4×4×4	5×5×5	
NiO	Ni	0.82	0.82	0.85	11.82
	O	-0.80	-0.85	-0.84	
CoO	Co	0.86	0.87	0.90	11.25
	O	-0.84	-0.89	-0.89	
FeO	Fe	0.92	0.94	0.96	10.61
	O	-0.89	-0.95	-0.96	
MnO	Mn	0.98	1.01	1.03	9.71
	O	-0.94	-1.01	-1.02	

Table 2: Calculated $10Dq$ (eV) for metal oxide clusters of different size

Oxide	Cluster size				
	3 ×3×3	4×4×4	5×5×5	Exp.	Ref.
NiO	1.02	0.88	0.85	0.85	[21]
CoO	1.03	0.93	0.90	1.00	[23]
FeO	1.16	1.09	1.06	1.20	[18]
MnO	1.61	1.52	1.48	-	[18]

Table 3: Transitions in the NiO 5×5×5 cluster

State	Calcd.	Observed			
		OA	Ref.	EELS	Ref.
$^3A_{2g}$(B),$^3B_1$(S), $^3B_1$(V)	0.00	0.00		0.00	
^3E (S)	0.49			0.60	[20, 22]
^3E (V)	0.51				
$^3B_2$ (S)	0.84			0.80	[19]
$^3T_{2g}$ (B)	0.85	0.85 ?	[21]		
$^3B_2$ (V)	0.97				
$^3A_2$ (S)	1.00			1.05	[19]
$^3A_2$ (V)	1.07	1.13	[21]		
^3E (S)	1.16			1.1	[20, 22]
^3E (V)	1.30				
$^3T_{1g}$ (B)	1.45			1.4	[19]
$^1A_1$ (V)	1.82	1.95	[21]		
$^1A_1$ (S)	1.92			1.62	[22]
$^1B_1$ (S)	2.10			1.87	[22]
$^1B_1$ (V)	2.11				
^1E_g (B)	2.12	2.15	[21]		
^1E (S)	2.51				
$^3A_2$ (S)	2.54			2.75	[20]
^1E (V)	2.55				
$^3A_2$ (V)	2.61				
^3E (S)	2.84				
$^1B_2$ (S)	2.84			2.90	[20]
$^1T_{2g}$ (B)	2.90	2.75	[21]		
$^1A_2$ (V)	2.97				
$^1B_2$ (V)	2.98				
^3E (V)	2.99				
$^3T_{1g}$ (B)	3.01	2.95	[21]		
$^1A_2$ (S)	3.02			3.10	[20]
$^1A_1$ (S)	3.25			3.25	[19]
$^1A_{1g}$ (B)	3.27	3.25	[21]		

Table 4: Transitions in the CoO 5×5×5 cluster

State	Calcd.	Observed			
		OA	Ref.	EELS	Ref.
$^4T_{1g}$(B),$^4A_2$(S), $^4A_2$(V)	0.00		0.00		
^4E (S)	0.03			0.05	[24]
^4E (V)	0.07				
$^4B_2$ (S)	0.38			0.45	[24]
$^4B_2$ (V)	0.44				
^4E (S)	0.68			0.85	[20]
$^4T_{2g}$ (B)	0.77	0.90 ÷ 1.1	[23]		
^4E (V)	0.78				
$^4B_1$ (S)	1.26				
$^4B_1$ (V)	1.44				
$^2A_1$ (V)	1.53				
^2E_g (B)	1.64	1.61	[23]		
$^2A_1$ (S)	1.65				
$^4A_{2g}$ (B)	1.67				
^2E (V)	2.08	2.03	[23]		
$^2B_1$ (S)	2.11			2.05	[20]
^2E (S)	2.14				
$^2B_1$ (V)	2.15	2.05	[23]		
^4E (S)	2.18				
^4E (V)	2.25				
$^2A_2$ (S)	2.26			2.25	[20]
$^2A_2$ (V)	2.26				
$^2T_{1g}$ (B)	2.32	2.26 ÷ 2.33	[23]		
$^2T_{2g}$ (B)	2.35				
^2E (S)	2.40				
$^2B_2$ (S)	2.42				
$^2B_2$ (V)	2.44				
$^4T_{1g}$ (B)	2.45	2.49 ÷ 2.56	[23]		
^2E (V)	2.46				
$^4A_2$ (S)	2.62				
$^2A_1$ (S)	2.70				
^2E (S)	2.75				

Table 4: Continued

State	Calcd.	Observed			
		OA	Ref.	EELS	Ref.
^2E (V)	2.76				
$^2A_1$ (V)	2.79				
$^4A_2$ (V)	2.84				
$^2A_2$ (S)	2.86				
$^2A_2$ (V)	2.88				
$^2T_{1g}$ (B)	2.91	2.61	[23]		
$^2A_{1g}$ (B)	2.93				
$^2A_2$ (S)	3.12				
$^2A_2$ (V)	3.19				
^2E (S)	3.20			3.2	[23]

Table 5: Calculated transitions in the MnO 5×5×5 cluster

State	Calcd.	Observed	
		OA	Ref.
$^6A_{1g}$(B),$^6A_1$(S), $^6A_1$(V)	0.00	0.00	
$^4A_2$ (V)	2.12		
^4E (V)	2.31		
$^4T_{1g}$ (B)	2.33	2.2	[18]
$^4A_2$ (S)	2.39		
^4E (S)	2.62		
$^2T_{2g}$ (B)	2.93	2.9	[18]
$^4T_{2g}$ (B)	2.93	2.9	[18]
^4E (V)	3.11		
$^4B_1$ (V)	3.16		
^4E (S)	3.20		
$^4B_1$ (S)	3.29		
$^4B_2$ (V)	3.39		
$^4B_2$ (S)	3.39		
$^4A_{1g}$ (B)	3.45	3.5	[18]
^4E_g (B)	3.45	3.5	[18]
$^4A_1$ (V)	3.45		
$^4A_1$ (S)	3.45		

Table 6: Transitions in the FeO 5×5×5 cluster

State	Calcd.	Observed			
		OA	Ref.	EELS	Ref.
$^5T_{2g}$(B),^5E(S), ^5E(V)	0.00	0.00		0.00	
$^5B_2$ (S)	0.13				
$^5B_2$ (V)	0.21				
$^5A_1$ (S)	0.48				
$^5A_1$ (V)	0.49				
^5E_g (B)	1.06	1.2	[18]		
$^5B_1$ (S)	1.16				
$^5B_1$ (V)	1.38				
^3E (V)	1.67				
$^3T_{1g}$ (B)	1.71				
^3E (S)	1.79				
$^3B_2$ (V)	1.96				
$^1A_{1g}$ (B)	1.99				
$^3B_2$ (S)	2.10				
$^3T_{2g}$ (B)	2.13				
$^3A_2$ (V)	2.15				
$^3A_2$ (S)	2.22				
$^3A_2$ (V)	2.25				
$^3A_2$ (S)	2.28				
$^1A_1$ (V)	2.40				
^3E (S)	2.44				
^3E (V)	2.46				
$^1A_1$ (S)	2.54				
$^3T_{1g}$ (B)	2.58				
^3E (V)	2.60				
^3E (S)	2.61				
$^3T_{2g}$ (B)	2.79				
^3E (V)	2.82				
^3E (S)	2.83				
$^1T_{1g}$ (B)	2.83				
$^3B_2$ (S)	2.85				
$^3B_1$ (V)	2.85				

Table 5: Continued

State	Calcd.	Observed			
		OA	Ref.	EELS	Ref.
$^3B_1$ (S)	2.86				
^1E (V)	2.86				
$^3A_1$ (S)	2.90				
$^3B_2$ (V)	2.90				
$^3A_2$ (S)	2.92				
^{3} (B)	2.94				
$^3A_1$ (V)	2.95				
^1E (S)	2.97				
$^3A_2$ (V)	2.99				
$^3T_{1g}$ (B)	3.00				
^3E (S)	3.15				
^1E_g (B)	3.18				
^3E (V)	3.21				
^3E (S)	3.26				
^3E (V)	3.30				