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MANY-ELECTRON MULTIPLET EFFECTS IN THE OPTICAL SPECTRA OF NiO, CoO and MnO

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A new theoretical approach to the multiplet structure of localized states in solids is applied to the Mott insulators NiO, CoO, and MnO. This method circumvents the major approximations underlying the conventional Tanabe-Sugano approach to the multiplet problem in that differential hybridization for e and t_2 states is incorporated directly, the Racah parameter A is allowed to depend on the one-electron configurations, and the crystal-field parameter incorporates both bare-ion effects (as traditionally done) and average multiplet corrections. Analysis of the observed optical spectra of NiO, CoO, and MnO in light of this approach produces (i) an excellent fit to the spectra and new assignments for some of the transitions, (ii) the values of the mean-field parameters for these materials, (iii) a direct measure for the amount by which an ideal, spin-restricted mean-field electronic structure theory would fail to reproduce the excitation energies, and (iv) analysis of the optical transitions above the interband onset.

I. INTRODUCTON

The optical, magnetic and electronic properties of 3d transition metal monoxides present a series of exceptions to many of the rules established by a large body of electronic structure calculations on other binary compounds.[1-3] Among others, they manifest an acute failure of conventional band theory,[4-6] as they are usually predicted to be metals above the Neèl temperature (e.g., CoO), or narrow gap semiconductors (e.g., NiO, MnO) with partially occupied d-bands, whereas in fact, with the exceptions of VO and TiO, they are all wide band gap (Mott) insulators, both below and above the Neèl temperature. While in such calculations it is possible to introduce a gap in the one-electron spectra by postulating a superstructure of spin orientations,[4] such approaches are unable to explain the optical properties at threshold. These transitions occur at subband gap energies (hν = 1-4 eV) and are due to internal d→d* excitations within the d states band theory predicts instead nearly vanishing excitation energies for these transitions. Once it is recognized, however, that the Bloch periodicity of the one-electron orbitals (bands) is not mandated by any fundamental physical principle (as opposed to the Bloch periodicity of the total wavefunction), it is possible to identify a symmetry breaking of the one-electron <u>spatial</u> orbitals, leading to the opening of a gap in the spectrum d→d*. Such is Mott's approach[7] which suggests that strong interelectronic correlations favor a site-localized ground state where the ions largely retaining their atomic character with a small intersite overlap and hence low band conductivity. Such are also the crystal-field[8,9] and ligand-field (cluster) approaches[10] that view the periodic crystalline environment as a weak perturbation on the free-ion multiplet structures. The relationship between these approaches and the content of electronic band structure calculations remains, however, obscured by a number of factors. Perhaps the most significant of these is the fact that the electronic structure parameters, such as crystal-field splitting and covalency, that are extracted from phenomenological multiplet theories[11] (e.g., the Tanabe-Sugano approach[12]) bear only a loose relationship to the content of electronic structure calculations. Self-consistent mean-field (space and spin restricted) electronic structure calculations aim at solving the $\hat{H}_0 + \langle \hat{H}_1 \rangle$ problem, where $\hat{H}_0$ is the bare-ion periodic potential, and $\langle \hat{H}_1 \rangle$ is the totally-symmetric <u>average</u> of the interelectronic interaction $\hat{H}_1$. Rather than focus on the consequences of the <u>correction</u> term $\hat{H}_1 - \langle \hat{H}_1 \rangle$, separating thereby mean-field $\underline{(\hat{H}_0 + \langle \hat{H}_1 \rangle)}$ from many-electron multiplet corrections $(\hat{H}_1 - \langle \hat{H}_1 \rangle)$, standard multiplet approaches[12] have parametrized directly the $\hat{H}_0 + \hat{H}_1$ problem. In so doing, a number of approximations were postulated which are not shared by modern electronic structure calculations, obscuring the comparison between the two. First, the e and t_2 impurity orbitals were often assumed to share a common radial orbital and to have a single $\ell=2$ angular component (neglect of differential hybridization). Second, the Racah parameter A was taken to be independent of the configuration occupation $e^m t^n$ and has been consequently dropped from the calculation, although, being far larger than the other two Racah parameters B and C, even small variations in A can significantly alter the multiplet structure. Finally, whereas crystal-field energies produced in mean-field calculations already include some <u>average</u> of multiplet corrections (since a totally-symmetric projection of the interelectronic interactions is used), the crystal-field energy obtained in the Tanabe-Sugano approach[12] pertains, in principle, to the bare-ion reference system $\hat{H}_0$(multiplet effects can enter indirectly through empirical fitting). A method that circumvents these three difficulties is presented here[13] and used to analyze the intra-d transitions in MnO, CoO, and NiO.

II. METHOD

The interelectronic interaction $\hat{H}_1$ splits the total energy of each single configuration (SC), say, $e^m t^n$, by an amount $E_{SC}(m,n)$. It also introduces a configuration mixing (CM) interaction energy $E_{CM}(m,n;m',n')$ between terms of the same space and spin symmetry. In mean-field electronic structure calculations (which are done for one fixed configuration at a time), there is no place for configuration mixing. However, since the totally-symmetric (a_1) component of the charge density with its attendant interelectronic interaction $\langle \hat{H}_1 \rangle$ is retained, such calculations incorporate the corresponding average of all single configuration energies for the particular configuration for which the calculation is done. This average SC energy $\hat{E}(m,n)$ can be written as a simple weighted sum

$$\hat{E}(m,n) = \sum_i \omega_i E^i_{SC}(m,n) \ , \qquad (1)$$

where the weights

$$\omega_i = (2S + 1)g_\Gamma / \sum\nolimits_{S,\Gamma} (2S + 1)g_\Gamma$$

include both spin (S) and space (Γ) degeneracies. We can now express the SC energy $E^i_{SC}(m,n)$ relative to the mean-field average $\hat{E}(m,n)$, defining thereby the single-configuration energy shift $\Delta E^i_{SC}(m,n)$ which constitutes a correction to MF theory. The diagonal element of the $\hat{H}_0 + \hat{H}_1$ matrix is then

$$^{\Gamma}D_{\alpha\alpha}(m,n) = \hat{E}(m,n) + \Delta E^{\alpha}_{SC}(m,n) + k_{\alpha\alpha}\Delta_{CF} \ , \qquad (2)$$

where Δ_{CF} is the bare-ion crystal-field splitting, and $k_{\alpha\alpha}$ is an integer, as in the Tanabe-Sugano model. If we measure the average energy of the configurations (m,n) relative to a reference configuration $(m^o n^o)$, defining thereby Δ as

$$\hat{E}(m,n) \equiv \hat{E}(m^o,n^o) + \Delta(m,n;m^o n^o) \ , \qquad (3)$$

Eq.(2) can be rewritten as

$$^{\Gamma}D_{\alpha\alpha}(m,n) = \hat{E}(m^o,n^o) + \Delta E^{\alpha}_{SC}(m,n) + [\Delta(m,n;m^o n^o) + k_{\alpha\alpha}\Delta_{CF}] \ . \qquad (4)$$

The term in brackets in Eq.(4) is the effective crystal-field splitting $\Delta_{eff}(m,n)$ and represents the separation between the total energies of the configuration (m,n) and $(m^o n^o)$, including both bare-ion (Δ_{CF}) and average multiplet contributions (Δ). It equals thus the difference in total energies $E_T(m,n) - E_T(m^o,n^o)$ of MF calculations for the two configurations. The diagonal and nondiagonal elements of the interaction matrices are hence given, respectively, as

$$^{\Gamma}D_{\alpha\alpha}(m,n) = \Delta E^{\alpha}_{SC}(m,n) + \Delta_{eff}(m,n;m^o n^o)$$

and

$$^{\Gamma}D_{\alpha\beta}(m,n;m'n') = E^{\alpha\beta}_{CM}(m,n;m'n'). \qquad (5)$$

These elements depend on the 10 independent Coulomb integrals between the 3-fold degenerate t_2 orbitals, (ξ,η,ζ) and the 2-fold degenerate e orbitals (ε,θ). Consider the (unknown) transition-atom-centered impurity Wannier orbitals $|e\rangle$ and $|t_2\rangle$ that transform in the limit of a separated crystal like the e and t_2 representations, respectively. We can define the orbital deformation parameters[14]

$$\lambda_e^4 = \langle ee|ee\rangle_S / \langle dd|dd\rangle_I ; \ \lambda_t^4 = \langle tt|tt\rangle_S / \langle dd|dd\rangle_I , \qquad (6)$$

that measure the ratio between the interelectronic interactions in the solid (S) to those in the free ion (I). For simplicity, assume[14, 15] that $\lambda_{et} = (\lambda_t \lambda_e)1/2$. Here $\langle ee|ee\rangle$ and $\langle tt|tt\rangle$ are interelectronic integrals involving the ε, θ and ξ,η,ζ, partner orbitals of the e and t_2 Wannier local orbitals, respectively, and $\langle dd|dd\rangle$ are atomic interelectronic integrals involving the pure-d states of the free ion. ΔE^{α}_{SC} and $E^{\alpha\beta}_{CM}$ can be expressed in a standard form[13] in terms of the Wannier function deformation parameters λ_e and λ_t and the Racah parameters B_o and C_o of the free ions. Note that the Racah parameter A, which is configuration dependent, does not appear explicitly in Eq.(5), since the dependence of the multiplet splitting on A(m,n) is transformed into $\Delta_{eff}(m,n;m^o n^o)$. There is no need, therefore, to neglect[12] A, or to approximate it by a constant.[15] Given the free-ion values B_o and C_o, the multiplet corrections to the mean-field energies can be expressed therefore solely in terms of λ_e, λ_t, and Δ_{eff}. Notice that for impurities λ_e and λ_t reflect coulomb distortions in both bound and resonant states relative to a free-ion reference system.

In this paper we determine these mean-field parameters from the optical spectra of NiO, CoO, and MnO. This provides the experimentally deduced mean-field quantities to be compared with electronic structure calculations. Given these quantities, we can further calculate the multiplet correction $\Delta E_{MC} = \Delta E_{SC} + \Delta E_{CM}$ to the excitation energies (neglected in MF electronic structure calculations). This provides bounds to the errors expected from mean field band theory; the differences between the observed excitation energies ΔE and these multiplet corrections ΔE_{MC} constitute the excitation energies that ideal MF calculations could legitimately reproduce. This approach has been used successfully for 3d impurities in semiconductors.[13]

III. INTRA-d TRANSITION

The band structure of transition metal monoxides[4-6] shows an occupied oxygen 2p state, a partially occupied metal d band, and empty (at T = 0) 4s and 4p states. Most of the studies of optical properties of transition metal oxides are devoted to the transitions between the oxygen 2p state and the metal 3d, 4s, and 4p states. The optical transitions at subband gap energies are identified[11,16] as intra-d excitations, whereas the transitions above E_g are the inter-band transitions. We will discuss first the $d^n \rightarrow d^{n*}$ transitions below the onset of the interband spectra. Table I shows the results of the fit of the excitation spectra of NiO and CoO using the experimental data of Ref. 9 and 8, respectively. We assume ground states of $^3A_2$, $^4T_1$, and $^6A_1$ symmetries for NiO, CoO, and MnO, respectively. The results of a Tanabe-Sugano fit are given for comparison. The agreement between our results and the experimental spectrum is excellent, except for the line at 2.15 eV in NiO, which, like in previous attempts, is not assigned to any recognizable intrinsic transition (interestingly, this line does not appear in the spectra of $Mg_{1-x}Ni_xO$ of Reinen[17]).

Table-I Excitation energies for CoO and NiO. We show the experimental[8,9] (exptl.) excitation energies ΔE, the fitted results from the present analysis, together with the many-electron component ΔE_{MC}. For comparison, we give the fitted results obtained from a traditional Tanabe-Sugano (TS) analysis.

Cobalt Oxide				Nickel Oxide			
	Present Analysis				Present Analysis		
ΔE (Exptl.)	ΔE (fit)	ΔE_{MC}	TS Analysis (a)	ΔE (Exptl.)	ΔE (fit)	ΔE_{MC}	TS Analysis (b)
0.9, 1.033	$0.93(^2E)$ $1.11(^4T_2)$	-1.67 -0.38	$1.033(^4T_2)$	1.13	$1.17(^3T_2)$	-0.42	$1.13(^3T_2)$
1.610	$1.57(^2T_1)$	-1.57	$1.212(^2E)$	1.75	$1.75(^3T_1)$	-0.24	$1.62(^1E)$
2.026	$2.01(^4A_2)$	-0.52	$1.972(^2T_1)$	1.95	$1.93(^1E)$	-1.92	$1.85(^3T_1)$
2.053	$2.08(^2T_2)$	-2.09	$2.054(^2T_2)$	2.75	$2.70(^1T_2)$	-1.95	---
2.137	$2.23(^2A_1)$	-1.49	$2.201(^4A_2)$	2.95	$2.85(^1A_1)$ $2.96(^3T_1)$	-2.95 -2.08	--- ---
2.26, 2.33	$2.31(^4T_1)$	-1.57	$2.30(^4T_1)$	3.25	$3.24(^1T_1)$	-2.47	---
2.50, 2.56	$2.43(^2T_1)$	-2.44	$2.659(^2T_1)$	3.52	$3.52(^1E)$	-2.01	---
2.605	$2.60(^2T_1)$	-1.86	$2.803(^2A_1)$				

(a) Ref. 8; (b) Ref. 9

Our interpretation of several of the transitions differs from Tanabe-Sugano-type assignments. In NiO we assign $^3T_1$ to the second excited state, whereas Newman and Cherenko[9] deduced an ^1E final state for this line; the line at 2.96 eV according to our results involves two states $^3T_1$ and $^1A_1$. In CoO the ^2E state appears close to the $^4T_2$ state (both states are in the region 0.9-1.033 eV, rather lower than the assignment obtained by Pratt and Coelho[8]). For MnO there are only three observed lines, which we assign to the transition $^6A_1 \rightarrow ^4T_1$, $^4T_2$, and ^4E in agreement with Pratt and Coelho.[8] Note that for MnO, as discussed previously for impurities in semiconductors,[13] the degeneracy of the $^4A_1$ and ^4E states is lifted through the different contributions from e_g and t_{2g} orbitals. This effect does not occur in the Tanabe-Sugano theory, where these states are always degenerate.

The values for the effective crystal-field energies obtained from different theories[6 10 18] are depicted in Table II for the three monoxides studied in this work, together with the values we obtained for the orbital deformation parameters λ_e and λ_t. We note that the effective crystal-field energies deduced from experiment through the Tanabe-Sugano approach are systematically higher than the present results. In the case of MnO, where $\lambda_e \simeq \lambda_t$ and only a small number of transitions exist, the value of Δ_{eff} is very close to the Δ_{CF} from Ref. 8. Although Δ_{eff} corresponds to differences in total energies, we give in Table II, as estimates, the results inferred from the single-particle energies of band and cluster calculations. Clearly, for NiO and CoO the present analysis removes the hitherto unexplained discrepancies between electronic structure calculations and experiment. The orbital deformation parameters for the three oxides are such that $\lambda_e > \lambda_t$, showing that the e states are more localized. This unusual finding agrees with the recent band structure calculations of Terakura et al[19], showing that in

Table-II Values obtained for the crystal-field energies (eV) through different approaches. λ_e and λ_t are the orbital deformation parameters obtained through the present analysis.

Compound	TS Analysis	Cluster (SCF-CI)	Band Theory	Present Analysis Δ_{eff}	λ_e	λ_t
NiO	1.13[a]	0.724[b]	0.762[c]	0.750	0.969	0.883
CoO	1.168[d]	0.691[e]	0.762[c]	0.743	0.970	0.837
MnO	1.214[d]	---	0.776[c]	1.078	0.981	0.973

(a) Ref. 9, (b) Ref. 10, (c) Ref. 6, (d) Ref. 8, (e) Ref. 17

the stable aniferromagnetic configuration ("AFII") the e band is actually narrower than the t_2 band due to absence of intra-sublattice ddσ coupling in the former case. Spin-unpolarized calculations[6] or cluster calculations[10] omitting metal-metal interactions cannot show this effect and lead to the (conventional) opposite ($\lambda_t > \lambda_e$) conclusion.

From λ_e, λ_t and Δ_{eff}, we can now calculate the multiplet correction energies [sum of $\Delta E_{SC} + \Delta E_{CM}$, c.f. Eg. (5)] left out of spin-restricted MF electronic structure calculations (ΔE_{MC} in Table I). Note that all ΔE_{MC} are substantial on the scale of the band gap. For the ground states in NiO ($^3A_2$), CoO($^4T_1$) and MnO ($^6A_1$) we find large many-electron corrections: -1.33, -1.93, and -4.95 eV, respectively. This multiplet energy is a major contributing factor to the binding energy, often outweighing the "crystal field stabilization energy",[13]. In Table I we show the MC for the excitation energies (i.e., differences between MC of the excited and ground states). The characteristic feature is that, in general, in a transition between ground and excited states a substantial change in the MC energies is involved. For MnO, the transition to the first excited state $^4T_1$ (with predominant configuration e^1t^4) involves a change in MC of 3.1 eV. Observe that in this case we have a change in spins, so the important correction comes from exchange energy. But in NiO and CoO we have transitions that conserve spin, but nevertheless they show large changes in multiplet energy. For example, in CoO the transition $^4T_1(e^2t^5) \rightarrow {}^4T_1(e^3t^4)$ involves a change in MC of 1.57 eV. This large piece of the excitation energy is ignored in MF calculations.

IV. ABSORPTION EDGE

In the region from 4 to 8 eV, Powell and Spicer[16] detected in the reflectivity spectra a series of transitions in NiO and CoO which have since been given different interpretations. The main question is whether this band involves 3d→4s or 2p→3d transitions. A detailed analysis of the different interpretations was performed by Brandow[3] who concludes that the second hypothesis can be discarded. We next examine this possibility in light of our analysis.

1.NiO.

The lines that according to Powell and Spicer[16] correspond to excitations $3d^8(Ni^{2+}) \rightarrow 3d^7 4s(Ni^{3+})$, lie at E_i=4.3, 4.9, 6.1, 7.2 and 8.5 eV. If we assume that the onset is at 4.3 eV and corresponds to transition $^3A_2(d^8) \rightarrow {}^4T_1(d^7)$, then the internal Ni^{3+} transitions ($d^7 \rightarrow d^{7*}$) would occur at E_i-4.3 = 0.6, 1.8, 2.9 and 4.2 eV, respectively. Using the Ni^{3+} free-ion values for the Racah parameters B_o and C_o and fitting the spectra, we find the following values of the mean-field parameters: $1.38 < \Delta_{eff} \leq 1.48$ eV; $\lambda_e = 0.972$, and $\lambda_t = 0.889$ (ranges correspond to experimental uncertainties). Comparing these values with those obtained for the $d^8 \rightarrow d^{8*}(Ni^{2+})$ transition (Table II), we see that Δ_{eff} is increased by a factor of about 2, whereas λ_e and λ_t increase only slightly.[7] One expects the average effective crystal-field energy to increase by about a factor 2 [$\Delta_{eff}(d^7) \simeq 2\Delta_{eff}(d^8)$, see for example $Co(d^7) \rightarrow Co(d^6)$ with $6Cl^-$, $6Br^-$ or $6F^-$ ligands in H_2O environment[20]]. In our case we indeed find $\Delta_{eff}(d^7)/\Delta_{eff}(d^8) \simeq 1.95$. We hence conclude that the onset of the transition $d^8 \rightarrow d^7s$ indeed occurs around 4.3 eV, as proposed by Powell and Spicer.[16]

The fitted transitions are also consistent with the observed intensity pattern. We show in Fig. 1 our results for the energy states involved in these $d^7 \rightarrow d^{7*}$ transitions. The transition to the ^2E state at 4.9 eV is the only one involving predominantly a change of the occupation of the e-electrons. In the transition around 6.1 eV the $^4T_2$ state appears close to the $^2T_1$ state, the latter with higher transition probability. Note that the $^4T_2$ state originates from the pure configuration e^3t^4. Hence, the $^3A_2 \rightarrow {}^4T_2$ transition involves the occupation changes $t^6 \rightarrow t^4$ and $e^2 \rightarrow e^3$, and will consequently have a low transition probability. At 7.2 eV we have a set of three closely spaced states: $^2T_1$ (mainly e^2t^5), $^4T_1$ (mainly e^3t^4), and $^4A_2(e^4t^3)$, the last with the smallest transition probability. The state $^4T_1$ has an admixture from the configuration e^2t^5 which increases the transition probability, although by a small amount, since Δ_{eff} is fairly large.

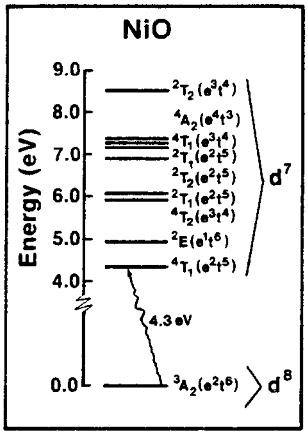

Figure 1.- Calculated multiplet structure for $d^8 - d^7$ transitions in NiO.

2.MnO

For the crystals CoO and MnO the transition 3d→4s should start at 2.7 and 4.7 eV, respectively, as determined by electroreflectance techniques.[16 21] We will assume that, as for NiO, the value of Δ_{eff} is doubled for Co^{3+} and Mn^{3+}, (1.49 and 2.06 eV, respectively). Using the same orbital deformation parameters λ_e, λ_t obtained for the 2+ oxidation state of the ions, we calculate the spectra and analyze it in terms of the available experimental results as well as compare it with the model proposed by Brandow.

In the case of MnO, electroreflectance data and their temperature dependence have been analyzed by Messick et al.,[21] who suggest that the transition $^6A_1(d^5) \rightarrow {}^5E(d^4s^1)$ occurs at 4.6 eV and the transition $^6A_1(d^5) \rightarrow {}^5T_2(d^4)$ occurs at 5.5 eV. From theoretical considerations, it can be shown that the high intensity $d^5 \rightarrow d^4$ transitions are indeed from the $^6A_1$ ground state to the $^5T_2$ and ^5E states (2 and 3 units of intensity, respectively). However, if we consider that the $^5T_2$-^5E energy splitting is approximately equal to Δ_{eff}, it is difficult to accept the Messick et al.[21] interpretation, in which this difference is 1.0 eV, half the expected value of Δ_{eff}. In our results the spacing $^5T_2$-^5E is 2.14 eV, leading us to conclude that, as suggested by Brandow,[3] this transition is related to the electroreflectance peaks at 4.6 and 7.2 eV[21] .

3.CoO.

For CoO we predict that the high intensity transitions will group in two subsets. The first involves the $^5T_2(t^4e^2)$, $^3T_1(t^5e^1)$ and $^3T_2(t^5e^1)$ states (2.5, 1.0, and 1.0 units of intensity, respectively) with the excitation energies centered around 0.58 eV, and the second formed by the $^3T_1$, ^3E, $^3T_2$, $^3A_2$, and $^3T_1$ states originating mainly from the e^2t^4 configuration (1.0, 0.66, 0.5, 0.33, and 0.58 units of intensity, respectively), yielding a centroid around 2.40 eV. The energy difference between the two centroids is ~1.82 eV, in good agreement with the spacing between the two peaks seen in X ray photoelectron spectroscopy (XPS) experiments around 2.0 eV[22] (Brandow,[3] suggested from the same data ~2.2 eV). The energy difference obtained for the states $^5T_2$ and the first $^3T_1$ in the second group (these should be the two most populated states in the transitions) is 2.0 eV. Our conclusion is similar to that Brandow, both formalisms predict a $^1A_1$ ground state (t^6, low-spin), but there is a significant difference in the $^5T_2$ - $^1A_1$ energy separation: our model gives 0.15 eV while Brandow's results in a value of 1.0 eV. The bound polaron hopping data discussed by Brandow suggests an energy separation of ~0.2 eV, considerably closer to the one suggested here.

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