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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 conven-

Racah parameter A is allowed to depend on the one-electron configurations and the crystalfield parameter, incorporating both band-ion

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 crystal field splitting parameter, and (iv) a direct measure for the Racah parameter A. This theory would allow to reproduce the excitation energies, and the analysis of the optical transitions above the interband onset.

I. INTRODUCTION

The optical, magnetic and electronic properties of 3d transition metal monoxides present a series of exceptions to many of the rules established by a long body of electronic structure

conventional band theory,⁴⁻⁶ as they are usually predicted to be metals above the Neel 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 Neel temperature. While in such

the one-electron spectra by postulating a

properties at threshold. These transitions occur at subband gap energies ($h\nu = 1-4$ eV) and are due to internal $d \rightarrow d^*$ 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 spatial orbitals, leading to the opening of a gap in the spectrum. Such a Mott-like approach⁷ which

largely retaining their atomic character with a well defined crystal field and hence low band covalency, such are also the crystal field and ligand-field (cluster) approaches¹⁰ 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

such as crystal-field splitting and covalency, that are extracted from phenomenological multiplet theories¹¹ (e.g., the Tanabe-Sugano approach¹²) 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 $\hat{H}_0 + \langle \hat{H}_1 \rangle$

trial, and $\langle \hat{H}_1 \rangle$ is the totally-symmetric average of

$\hat{H}_1 = \langle \hat{H}_1 \rangle$, separating thereby mean-field ($\hat{H}_0 + \langle \hat{H}_1 \rangle$) from many-electron multiplet corrections ($\hat{H}_1 - \langle \hat{H}_1 \rangle$), standard multiplet approaches¹² 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 $l=2$ angular component (neglect of differential hybridization). Second, the Racah parameter A was taken to be independent of the configuration occupancies of d and has been consequently

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 average of

multiplet corrections (since a totally-symmetric component of the crystal field energy obtained in the Tanabe-Sugano approach¹² 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 here¹³ and used to analyze the intra-d transitions in MnO, CoO, and NiO.

The interelectronic interaction H_1 splits the

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 energy calculation is done. This average SC energy $E(m,n)$

$$E(m,n) = \sum_{\lambda} \omega_{\lambda} E_{SC}^{\lambda}(m,n), \quad (1)$$

the single-configuration energy shift $\Delta E_{SC}^{\lambda}(m,n)$

$$\Gamma_{D_{\alpha\alpha}}(m,n) = \hat{E}(m,n) + \Delta E_{SC}^{\alpha}(m,n) + k_{\alpha\alpha} \Delta_{CF}, \quad (2)$$

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^0, n^0) , then

$$\hat{E}(m,n) \equiv \hat{E}(m^0, n^0) + \Delta(m,n; m^0, n^0), \quad (3)$$

$$[\Delta(m,n; m^0, n^0) + k_{\alpha\alpha} \Delta_{CF}]. \quad (4)$$

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^0, n^0) , including both

gies $E_T(m,n) - E_T(m^0, n^0)$ of MF calculations for the two configurations. The diagonal and nondiagonal elements of the interaction matrices are hence given, respectively, as

$$\Gamma_{D_{\alpha\beta}}(m,n; m', n') = E_{CM}^{\alpha\beta}(m,n; m', n').$$

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-charge transformation in the limit of a separated crystal like the e and t_2 representations, respectively.

that measure the ratio between the interelectronic

$(\lambda_e \lambda_e)^{1/2}$. Here $\langle ee|ee \rangle$ and $\langle tt|tt \rangle$ are interelectronic integrals involving the ϵ, θ and ξ, η, ζ , Wannier local orbitals, respectively, and $\langle dd|dd \rangle$ are atomic interelectronic integrals involving the pure-d pressed in a standard form¹³ in terms of the

ions. Note that the Racah parameter A , which is in Eq.(5), since the dependence of the multiplet splitting on $A(m,n)$ is transformed into neglect A or to approximate it by a constant.

pressed therefore solely in terms of λ_e, λ_t , and A . Notice that for transitions λ_e and λ_t reflect

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 $\Delta E_{MP} = \Delta E_{SC} + \Delta E_{MP}$ to the excitation energies (compare with the corresponding mean-field calculations). This provides bounds to the errors expected from mean field band theory; the differences between the observed excitation energies ΔE

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 monoxides⁴⁻⁶ shows an occupied oxygen 2p state, a par-

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 identi-

fied^{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.

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

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

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

tion spectra of NiO and CoO using the experimental data of Ref. 9 and 8, respectively. We assume ground states of ³A₁, ⁴T₁, and ⁶A₁ symmetric for

Table-II Values obtained for the crystal-field energies (eV) through different approaches. λ_e and

agreement between our results and the experimental spectrum is excellent except for the line at 2.15 assigned to any recognizable intrinsic transition

Our interpretation of several of the transitions differs from Tanabe-Sugano-type assignments.

whereas Newman and Cherenko⁹ deduced an ¹E final state for this line; the line at 2.96 eV according to our results involves two states ³T₁ and ¹A₁. In CoO the ²E state appears close to the ⁴T₂ state (both states are in the region 0.9-1.033 eV, rather lower than the assignment obtained by Pratt and Coelho⁸). For MnO there are only three observed lines, which we assign to the transition ⁶A₁ → ⁴T₁, ⁴T₂, 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 ⁴A₁ 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}

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CoO	1.168 ^d	0.691 ^e	0.762 ^c	0.743	0.970	0.837
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(a) Ref. 9, (b) Ref. 10, (c) Ref. 6, (d) Ref. 8, (e) Ref. 17

where $\lambda_e = \lambda_t$ 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

the stable antiferromagnetic configuration ("AFII") the e band is actually narrower than the t₂ band due to absence of intra-sublattice d-d coupling in the former case. Spin-unpolarized calculations⁸ or cluster calculations¹⁰ omitting metal-metal interactions cannot show this effect and lead to

$2 [\Delta_{\text{eff}}(d^7) \approx 2\Delta_{\text{eff}}(d^8)$, see for example $\text{Co}(d^7) \rightarrow \text{Co}(d^6)$ with 6Cl^- , 6Br^- or 6F^- ligands in H_2O environment²⁰). In our case we indeed find $\Delta_{\text{eff}}(d^7)/\Delta_{\text{eff}}(d^8) \approx 1.95$. We hence conclude that the onset of the transition $d^8 \rightarrow d^7$ s indeed occurs

multiplet correction energies [sum of $\Delta E_{\text{SC}} + \Delta E_{\text{CM}}$, 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

Fig. 1 our results for the energy states involved in these $d^7 \rightarrow d^8$ transitions. The transition to

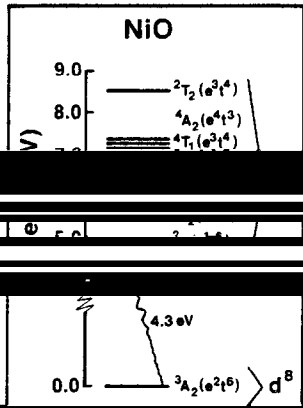


Figure 1.- Calculated multiplet structure for $d^8 - d^7$ transitions in NiO.

excitation energies (i.e., differences between no 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

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 $^4T_1(e^2t^5) \rightarrow ^4T_1(e^1t^4)$ involves a change in MC of

the $2T_2$ state at 4.0 eV is the only one calculated

IV. ABSORPTION EDGE

In the region from 4 to 8 eV, Powell and Spicer¹⁶ detected in the reflectivity spectra a series of transitions in NiO and CoO which have

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 $t^2 \rightarrow t^1$ and $e^2 \rightarrow e^3$.

or $2p \rightarrow 3d$ transitions. A detailed analysis of the

closely spaced states: 2T_1 (mainly e^2t^5), 4T_1 , 4A_1 , 4E_g

be discarded. We next examine this possibility in light of our analysis.

1. NiO.

The lines that according to Powell and Spicer¹⁶ are at $E_1 = 4.3, 4.5, 4.7, 4.8$ and 4.9 eV. If we assume that the onset is at 4.3 eV and

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.

the internal $d-d$ 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_0 and C_0 and fitting the spectra, we find the following values of the mean-field parameters: $1.38 < \Delta_{\text{eff}} < 1.48$ eV; $\lambda_e = 0.972$, and $\lambda_t = 0.889$ (ranges correspond to experimental uncertainties). Comparing these values with

should start at 2.7 and 4.7 eV, respectively, as determined by electroreflectance tech-

(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

value of Δ_{eff} is doubled for Co²⁺ and Mn²⁺, (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 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 $^6A_1(d^5) \rightarrow ^5T(d^4)$ occurs at 5.5 eV. From theoretical considerations, it can be shown

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

(XPS) experiments around 2.0 eV²² (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

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 ${}^3T_1(t^5e^1)$ 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^t configuration (1.0, 0.66, 0.5, 0.33,

the 3T_1 energy separation. Our model gives 0.15 eV. Brandow's results are 0.15 eV. Brandow suggests an energy separation of ~0.2 eV, considerably closer to the one suggested here.

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