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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 configura-
tions, and the crystal-field parameter incorporates both bare-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

analysis of the optical transitions above the interband onset.

I. INTRODUCTON

The optical, magnetic and electronic proper-
ties of 3d transition metal monoxides present a
series of exceptions to many of the rules estab-

conventional band theory,[4-6] as they are usually
predicted to be metals above the Neél 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

and above the Neél temperature. While in such

the one-electron spectra by postulating a

properties at threshold. These transitions occur

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

largely retaining their atomic character with a

ligand-field (cluster) approaches[10] that view the

periodic crystalline environment as a weak pertur-
bation on the free-ion multiplet structures. The
relationship between these approaches and the con-
tent of electronic band structure calculations

such as crystal-field splitting and covalency, that
are extracted from phenomenological multiplet theo-
ries[11] (e.g., the Tanabe-Sugano approach[12]) bear
only a loose relationship to the content of elec-
tronic structure calculations. Self-consistent

structure calculations aim at solving the $\hat{H}_0 + \langle\hat{H}_1\rangle$

$H_1 - \langle H_1\rangle$, separating thereby mean-field ($H_0 + \langle H_1\rangle$)

parametrized directly the $H_0 + H_1$ 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

and C, even small variations in A can significantly

calculations already include some average of

multiplet corrections (since a totally-symmetric

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.

The interelectronic interaction $\hat{H}_1$ 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 energies

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

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

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

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

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

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

$$(4)$$

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

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

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

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

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

that transform in the limit of a separated crystal like the e and t_2 representations, respectively.

that measure the ratio between the interelectronic

$(\lambda_t \lambda_e)1/2$. 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 Wannier local orbitals, respectively, and $\langle dd|dd \rangle$ are atomic interelectronic integrals involving the pure-d

pressed in a standard form[13] in terms of the

ions. Note that the Racah parameter A, which is

pressed therefore solely in terms of λ_e, λ_t, and

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 quan-

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 monoxides[4-6] 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 $d^n \to d^{n*}$ 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	$\{ 0.93(^2E)$ $\{ 1.11(^4T_2)$	-1.67 -0.38	$1.033(^4T_2)$	1.13 1.75	$1.17(^3T_2)$ $1.75(^3T_1)$	-0.42 -0.24	$1.13(^3T_2)$ $1.62(^1E)$
2.026	$2.01(^4A_2)$	-0.52	$1.972(^2T_1)$	2.75	$2.70(^1T_2)$	-1.95	----
2.053	$2.08(^2T_2)$	-2.09	$2.054(^2T_2)$	2.95	$\{ 2.85(^1A_1)$ $\{ 2.96(^3T_1)$	-2.95 -2.08	----
2.137	$2.23(^2A_1)$	-1.49	$2.201(^4A_2)$				----
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

tion spectra of NiO and CoO using the experimental data of Ref. 9 and 8, respectively. We assume ground states of ^3A, ^4T, and ^6A symmetries for

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 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 $^6A_1 \to {}^4T_1$, $^4T_2$, 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]

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

CoO	1.168^d	0.691^e	0.762^c	0.743	0.970	0.837

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

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

the _stable_ aniferromagnetic configuration ("AFII") the e band is actually narrower than the t_2 band due to absence of intra-sublattice $dd\sigma$ coupling in the former case. Spin-unpolarized calculations[6] or cluster calculations[10] omitting metal-metal

2 [$\Delta_{eff}(d^7) \simeq 2\Delta_{eff}(d^8)$, see for example Co(d⁷)→ Co(d⁶) 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 $d^8 \to d^7 s$ indeed occurs

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

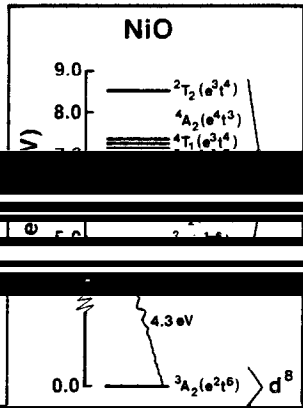Fig. 1 our results for the energy states involved in these $d^7 \to d^{7*}$ transitions. The transition to

NiO

9.0 — $^2T_2(e^3t^4)$
8.0 — $^4A_2(e^4t^3)$
— $^4T_1(e^3t^4)$

4.3 eV

0.0 — $^3A_2(e^2t^6)$ ⟩ d^8

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

excitation energies (i.e., differences between no

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

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 $^4T(e^2t^5) \to {}^4T(e^3t^4)$ involves a change in MC of

the ^2E state at 4.9 eV is the only one involving

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

latter with higher transition probability. Note that the $^4T_2$ state originates from the pure configuration e^3t^4. Hence the ^3A-^4T transition involves the occupation changes $t \to t$ and $e \to e$

or 2p→3d transitions. A detailed analysis of the

closely spaced states: $^2T_{13}$ (mainly e^2t^3),

be discarded. We next examine this possibility in light of our analysis.
1.NiO.
The lines that according to Powell and Spic-

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.
2.MnO.

eV. If we assume that the onset is at 4.3 eV and

3d 4s should start at 2.7 and 4.7 eV, respectively, as determined by electroreflectance tech-

the internal Ni transitions ($d \to d$) would occur at E_i-4.3 = 0.6, 1.8, 2.9 and 4.2 eV, respectively. Using the Ni³⁺ 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: $1.38 < \Delta_{eff} < 1.48$ eV; $\lambda_e = 0.972$, and $\lambda_t = 0.889$ (ranges correspond to experimental uncertainties). Comparing these values with

value of Δ_{eff} is doubled for Co and Mn, (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

(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

by Messick et al.,[21] who suggest that the transition $^6A_1(d^5) \to {}^5E(d^4s^1)$ occurs at 4.6 eV and the transition $^6A_1(d^5) \to {}^5T(d^4)$ occurs at 5.5 eV. From theoretical considerations, it can be shown

difficult to accept the Messick et al.[21] interpre-
tation, in which this difference is 1.0 eV, half
the expected value of Δ_{eff}. In our results the

For CoO we predict that the high intensity
transitions will group in two subsets. The first
involves the $^5T(t^4e^2)$, $^3T(t^5e^1)$, and $^3T(t^5e^1)$
states (2.5, 1.0, and 1.0 units of intensity, re-
spectively) 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,

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

Brandow suggests an energy separation of ~0.2 eV,
considerably closer to the one suggested here.

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