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Influence of d orbitals on the nonlinear optical response of transparent transition-metal oxides

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The bond-orbital theory of linear and nonlinear electronic response in optically transparent materials, developed earlier for pretransition-metal halides and chalcogenides, is expanded to embrace the transition-metal (TM) oxides. The extension requires an explicit recognition of the influence of cationic empty d orbitals on electronic polarizability. Two competing mechanisms, involving, respectively, virtual electronic excitations to the d orbitals and to the conduction-band "sp orbitals," are shown to be essentially additive for linear polarizability $\chi^{(1)}$ and lowest-order nonlinear polarizability $\chi^{(2)}$, but not for $\chi^{(3)}$. The d-orbital contributions to linear and nonlinear response are found to be negligible for bond lengths $d \gtrsim 2.3$ Å, but to increase rapidly as a function of decreasing bond length within each TM series to become dominant when $d \lesssim 2.0$ Å. Numerical evaluations of non linear refractive index n_2 are presented for each series of TM oxides.

I. INTRODUCTION

In two earlier publications[1,2] a bond-orbital theory of optical response was set out for binary pretransition-metal halides and chalcogenides. This theory, inspired by the earlier work of Harrison and co-workers for the tetrahedral semiconductors,[3] describes long-wavelength electronic response as a perturbation of local bonding orbitals by an applied electric field. Each such orbital is formed along a representative bond axis as a linear combination of two unspecified atomic orbitals $|h_M\rangle$ and $|h_X\rangle$ centered, respectively, on the cation (M) and anion (X) sites. Although these bond orbitals are not independent in the high-coordination context of ionic materials, they do contribute to electronic response in an essentially independent fashion, a property which enables us to cast the latter completely in terms of the parameters which define the individual bond orbitals.

Since the bond-orbital theory is parametrized in terms of matrix elements within and between $|h_M\rangle$ and $|h_X\rangle$ (which are then, in turn, empirically related to valencies, bond lengths, ionic radii, and the like), the detailed nature of the parent wave functions is never *explicitly* involved. There is merely an implicit assumption that the virtual electronic excitations which dominate this electronic response take place between a single filled valence band and a single empty conduction band which can, within the model, be derived from bonding and antibonding combinations of a uniquely defined pair of atomic wave functions, whatever their character. The theory is most quantitative in materials for which the relevant band widths are smaller than their associated mean band gaps. In the opposite limit (e.g., narrow band-gap sp^3 semiconductors) its predictions for high-order response can sometimes fail even as to sign.[3]

Since the theory works well for all the ionic pretransition-metal compounds discussed in Refs. 1 and 2, the effective "two-level" scheme appears to be quite adequate in that context. In addition, comparing the measured Sellmeier gaps[1] E_S with the known band structures for many of these materials makes it clear that $|h_X\rangle$ must be associated almost exclusively with valence p electrons on the anion, since a relatively narrow p band is the only band in the energy regime $\approx E_S$ below the conduction band edge. The conduction band, on the other hand, is quite broad and contains admixtures of cationic s, p, and for heavier cations, d-electron contributions. Since energy levels $\approx E_S$ above the narrow valence p band correspond to the lower energy region of the conduction band, it is probable that $|h_M\rangle$ is largely of s character (s electrons tending to dominate the band structure near the bottom of the band and also the strongest exciton resonances below it[4,5]) although the possibility of a significant p-electron contribution cannot be excluded. However, in spite of the fact that relatively narrow cationic d bands completely overlap and admix with the lower energy portion of the s/p conduction band in the heavier cation pretransition metal halides and chalcogenides,[5] the evidence of this paper will be that they do not measurably contribute to $|h_M\rangle$. The reason is that their radial extent is not sufficient to produce significant overlap and electronic interaction with the anionic valence p orbitals at the equilibrium bond lengths possessed by the pretransition metal series.

In this paper we analyze the variation of long-wavelength linear optical response $\epsilon = n_0^2$ (where n_0 is linear refractive index) upon progression along each of the respective cationic rows 4 to 6 of the Periodic Table, i.e., from the pretransition metal insulators into the corresponding transition metal series. We restrict ourselves to optically transparent (i.e., empty d-band) compounds and, since most experimental evidence presently available is for oxides, our interest centers upon the trends along the respective $3d$, $4d$, and $5d$ oxide series: viz.,

$$K_2O,\ CaO,\ Sc_2O_3,\ TiO_2,\ V_2O_5, \ldots,$$

$$Rb_2O,\ SrO,\ Y_2O_3,\ ZrO_2,\ Nb_2O_5,\ MoO_3, \ldots,$$

$$Cs_2O,\ BaO,\ La_2O_3,\ CeO_2,\ HfO_2,\ Ta_2O_5,\ WO_3, \ldots .$$

Upon progression into the transition metal (TM) series along each row, the equilibrium bond length decreases and the empty d levels fall progressively below the conduction sp band. Both of these trends lead to a progressive increase in dielectric response via virtual transitions to the d levels. This "d-orbital" contribution to ϵ is found to rise from negligible values for bond lengths $d \gtrsim 2.3$ Å to values exceeding the "sp-orbital" contribution for $d \lesssim 2.0$ Å.

In Sec. II the d-orbital "correction" to two-level bond orbital theory is first isolated empirically by comparing experimental values of TM oxide (linear) dielectric response with the "sp-orbital" expectations of the pretransition metal theory. Section III formally extends bond orbital theory to include a second cationic orbital $|h'_M\rangle$, to be associated with d orbitals, and theoretically justifies the additivity of "sp-orbital" and "d-orbital" contributions to linear response which is implicitly assumed in Sec. II. However, within the theory, such a linear decomposition does not extend to third-order response (in particular, as measured by the nonlinear refractive index n_2). Section IV demonstrates the manner in which n_2 can be uniquely related to the separate contributions to linear response. Using this formalism, Sec. V then reports a numerical evaluation of n_2 for the three separate TM series of oxides, and carries out a comparison with experiment which enables a determination of local field factors to be made. The paper then concludes in Sec. VI with a summary of the findings.

II. COMPARISON OF TWO-LEVEL THEORY WITH EXPERIMENTAL TM DATA

The theory of Ref. 1 leads to an expression for the long-wavelength electronic response ϵ of binary pretransition-metal compounds MX_n (where M is a metallic cation and X an anion) of the form[6]

$$\epsilon - 1 = 4\pi\chi_{sp} = (|Z_X|^{1.5} n d^{4.4}/4V_M)(1+g\Delta/d)^2 , \qquad (2.1)$$

where χ denotes macroscopic polarizability. In this equation Z_X is formal anion valence, d is the MX bond length (in Å), V_M is molar volume (in cm^3), $g=1$ for halides and ≈ 0.65 for chalcogenides, and

$$\Delta/d = (d/2R_M)^{1/2} - 1 , \qquad (2.2)$$

where R_M is the ionic radius of the cation. This formula has an rms accuracy of 3.4% over the 44 crystals detailed in Ref. 1, for which the measured dielectric response ϵ varies between a low of 1.74 (for NaF) and a high of 5.28 (for MgSe).

Although derived ideally for materials in which the degree of anionic symmetry is sufficient to retain the degeneracy of the three anionic p orbitals, Eq. (2.1) also retains its essential accuracy for other wide band-gap pretransition-metal compounds such as the alkaline earth chlorides, bromides, and iodides,[2] some of which possess a very low symmetry anionic coordination. Necessary (though not sufficient) conditions for the essential validity of Eq. (2.1) seem to be a high coordination number (≥ 6) for either the cation or anion (or both) and a Sellmeier energy gap E_S large compared to the width of the anion p band (say $\gtrsim 3$ eV). The former condition excludes crystals possessing significant intraionic (e.g., sp^2 or sp^3) hybrid bonds, while the latter condition is necessary to justify a representation which neglects the details of band structure.

An additional condition, predicated by the two-level nature of the model, is the assumption of negligible explicit response contributions involving d-electron levels. Since the series of TM oxides listed in the Introduction all possess high cationic coordinations and Sellmeier gaps $\gtrsim 4$ eV, they should provide an excellent monitor of the influence (if any) of empty cationic d orbitals on dielectric response as a function of decreasing bond length and increasing $\langle d|p\rangle$ overlap. We quantitatively measure this influence by recording the deviation of measured response ϵ from the two-level prediction of Eq. (2.1) as we progress along the respective ($3d$ to $5d$) TM rows of the Periodic Table. Accordingly we define a d-electron polarizability χ_d via the equation

$$\epsilon(\text{expt}) - 1 = 4\pi(\chi_{sp} + \chi_d) , \qquad (2.3)$$

where $\epsilon(\text{expt})$ is the extrapolated long-wavelength linear electronic response from direct measurements, and $4\pi\chi_{sp}$ is the valence to sp-conduction band response defined by the theoretical form of Eq. (2.1).

Experimental measurements of ϵ are available in the literature[7-16] for almost all of the compounds listed in the Introduction except the alkali metal oxides. We list them, together with $4\pi\chi_{sp}$, $4\pi\chi_d$, and the parameters d, V_M (Refs. 17–25), and R_M (Ref. 26) necessary for the evaluation of $4\pi\chi_{sp}$ via Eqs. (2.1) and (2.2), in Table I.[27] A few of the experimental ϵ values (particularly for the $5d$ transition-metal series) are available at present only for thin-film specimens.[13] Since thin-film values are notoriously sample dependent, a few words concerning these are in order. We have noted that the particular thin films of Ref. 13, from which the relevant data are taken, also include several compositions for which single-crystal equivalent values of ϵ are known. For the latter the single-crystal values are consistently about 15% larger than their thin-film counterparts. We have assumed that the same remains true for those compositions for which the single-crystal data are not yet available. Values so deduced have been included in Table I in parentheses.

From the raw data of Table I it is already clear that the Eq. (2.1), which neglects explicit d-orbital response, is quite accurate for bond-lengths d greater than about 2.3 Å. For shorter d, significantly nonzero positive values of χ_d develop and, for $d \lesssim 2.0$ Å, χ_d generally exceeds χ_{sp}. We shall assume that the "excess" response $4\pi\chi_d$ arises, as implied by its symbolic designation, from virtual electronic excitations to d levels. However, in order to confirm the implied additivity of the sp and d contributions to ϵ, and to establish a theoretical form for χ_d, it is necessary to develop a bond-orbital theory which goes beyond the two-level scheme leading to Eq. (2.1). This extension is developed in the following section.

At this juncture we can only surmise that any one-electron matrix elements between anionic p orbitals and cationic d orbitals must be relatively small for $d \gtrsim 2.3$ Å, but increase rapidly with decreasing d at the shorter bond lengths. We note, in particular, that the additional contribution χ_d is absent for short-bond-length *pre*transition metal compounds from rows 2 and 3 of the Periodic Table (e.g., LiF, MgF_2, MgO, Al_2O_3, and Li_2O).[1] Since all these compounds have $d \lesssim 2.1$ Å we confirm that the response labeled $4\pi\chi_d$ is indeed attributable in some manner to the presence of additional excitations and is not some universal breakdown of bond-orbital theory for short bonds.

III. THE EXTENSION OF THEORY TO INCLUDE *d* LEVELS

In the basic two-level bond orbital theory[1,2] a representative bonding orbital

$$|b_0\rangle = u_X|h_X\rangle + u_M|h_M\rangle \tag{3.1}$$

is written as a linear combination of a single normalized anionic orbital $|h_X\rangle$ and a single cationic equivalent $|h_M\rangle$. The extension to incorporate TM cations is accomplished by defining a second normalized cationic orbital $|h'_M\rangle$ and including it in the bonding orbital by recasting Eq. (3.1) in the form

$$|b_0\rangle = u_X|h_X\rangle + u_M|h_M\rangle + u'_M|h'_M\rangle \ . \tag{3.2}$$

Like $|h_X\rangle$ and $|h_M\rangle$, the orbital $|h'_M\rangle$ remains unspecified as to its detailed form; it is, however, assumed to be dominantly of d character.

Paralleling the procedure for two-level theory, the coefficients u and bond-orbital energy E are determined by minimizing the one-electron energy $\langle b_0|H_0|b_0\rangle / \langle b_0|b_0\rangle$ with respect to the three u coefficients. This leads to the stationary conditions

$$\begin{bmatrix} E+E_0 & ES+M & ES'+M' \\ ES+M & E-E_0 & 0 \\ ES'+M' & 0 & E+E_0-2E'_0 \end{bmatrix} \begin{bmatrix} u_X \\ u_M \\ u'_M \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} , \tag{3.3}$$

in which the primed symbols are the "d-orbital"

TABLE I. Bond-length d, molar volume V_M, cationic radius R_M, "sp-orbital" contribution to dielectric response $4\pi\chi_{sp}$ [from Eqs. (2.1) and (2.2)], experimental dielectric constant ϵ, and $4\pi\chi_d$ (defined as $\epsilon - 1 - 4\pi\chi_{sp}$) for the $3d$, $4d$, and $5d$ series of empty d-band transition metal oxides. Experimental values ϵ are for single crystals except for those in parentheses, which have been obtained by adjustment (see text) from thin-film data.

Material units	d Å	$V_M^{a,g}$ cm^3	R_M^b Å	ϵ	$4\pi\chi_{sp}$	$4\pi\chi_d$
CaO	2.41[a]	16.8	1.00	3.3[c]	2.3	0.0
$ScO_{1.5}$	2.11[d]	17.8	0.81	3.7[e,f]	1.9	0.8
TiO_2 (rutile)	1.96[a]	18.8	0.61	6.3[c]	2.0	3.3
TiO_2 (anatase)	1.93[a]	20.5	0.61	5.6[c]	1.7	2.9
$VO_{2.5}$	1.83[g]	27.0	0.50	5.3[h]	1.4	2.9
SrO	2.58[a]	20.7	1.18	3.4[c]	2.4	0.0
$YO_{1.5}$	2.28[i]	22.4	0.96	3.6[j]	2.0	0.6
ZrO_2	2.16[k]	21.1	0.78	4.2[l]	2.4	0.8
$NbO_{2.5}$	2.00[n]	27.3	0.64	5.3[o]	1.8	2.5
MoO_3	1.96[g]	30.1	0.59	?	1.9	?
BaO	2.76[a]	25.4	1.35	3.7	2.5	0.2
$LaO_{1.5}$	2.54[p]	24.8	1.10	(3.9)[m]	2.9	(0.0)
HfO_2	2.15[a]	20.8	0.76	(4.3)[m]	2.5	(0.8)
CeO_2	2.34[a]	23.9	0.97	(4.0)[m]	2.8	(0.2)
$TaO_{2.5}$	2.04[q]	26.6	0.69	5.0[o]	2.0	2.0
WO_3	1.87[r]	32.4	0.60	4.9[s,t]	1.4	2.5

[a] Reference 17.
[b] Reference 26.
[c] Reference 7.
[d] Reference 18.
[e] Reference 8.
[f] Reference 9.
[g] Reference 19.
[h] Reference 10.
[i] Reference 20.
[j] Reference 11.
[k] Reference 21.
[l] Reference 12.
[m] Reference 13.
[n] Reference 22.
[o] Reference 14.
[p] Reference 23.
[q] Reference 24.
[r] Reference 25.
[s] Reference 15.
[t] Reference 16.

equivalents of their unprimed "*sp*-orbital" counterparts according to the definitions

$$\langle h_M|H_0|h_M\rangle - \langle h_X|H_0|h_X\rangle = 2E_0 \ , \tag{3.4}$$

$$\langle h'_M|H_0|h'_M\rangle - \langle h_X|H_0|h_X\rangle = 2E'_0 \ , \tag{3.5}$$

$$\langle h_M|H_0|h_X\rangle = -M, \ \ \langle h'_M|H_0|h_X\rangle = -M' \ , \tag{3.6}$$

$$\langle h_M|h_X\rangle = S, \ \ \langle h'_M|h_X\rangle = S' \ . \tag{3.7}$$

The zero of energy has been chosen (arbitrarily) using the condition

$$\langle h_M|H_0|h_M\rangle + \langle h_X|H_0|h_X\rangle = 0 \ , \tag{3.8}$$

and the cationic orbitals are assumed to be eigenstates of the cation in the absence of bonding such that $\langle h_M|H_0|h'_M\rangle$ and $\langle h_M|h'_M\rangle$ are both equal to zero.

In the ionic limit (as defined in Ref. 1) the bonding orbital contains no cationic contributions, i.e., $|b_0\rangle = |h_X\rangle$, $E = -E_0$. It results from the stationary conditions when

$$M = E_0 S, \ \ M' = E_0 S' \ , \tag{3.9}$$

criteria which diagonalize the matrix in Eq. (3.3). It follows that in this ionic limit (and only for this case) the lowest order perturbational response to an applied field along the bond axis must be expressible as the sum of terms corresponding to virtual excitations from $|h_X\rangle$ to the appropriate antibonding levels associated predominantly with the respective cationic *sp* and *d* levels. In fact, if we work with a normalized orthogonal set of basis wave functions (in place of $|h_X\rangle$, $|h_M\rangle$, and $|h'_M\rangle$) it becomes analytically tractable in this limit to set up a conventional time-independent nondegenerate perturbation theory of dielectric response to any order in applied field and to examine in detail the additivity (or lack of additivity) of this response in each order as regards *sp*- and *d*-orbital contributions.

Consider the set of orbitals

$$\begin{aligned} &\phi_1 = |h_X\rangle \ , \\ &\phi_2 = N(|h_M\rangle - S|h_X\rangle) \ , \\ &\phi_3 = N'(|h'_M\rangle - S'|h_X\rangle) \ , \end{aligned} \tag{3.10}$$

in which the normalizing factors are

$$N = 1/(1-S^2)^{1/2} \ , \ \ N' = 1/(1-S'^2)^{1/2} \ . \tag{3.11}$$

We note that, while both excited states ϕ_2 and ϕ_3 are properly orthogonal to the ground state, they are not rigorously orthogonal to each other. In particular,

$$\langle \phi_2|\phi_3\rangle = -NN'SS' \ . \tag{3.12}$$

Although it is quite possible to find a true orthogonal set which also diagonalizes H_0 (for example, by defining $\Psi_2 \propto \phi_2 + a\phi_3$ and $\Psi_3 \propto \phi_2 + b\phi_3$ and determining coefficients a and b by requiring $\langle \Psi_2|\Psi_3\rangle$ and $\langle \Psi_2|H_0|\Psi_3\rangle$ to be zero) the algebraic complexity of this scheme leads us to prefer working with the set ϕ_i, thereby neglecting terms of order SS'.

Using the basis set ϕ_i, and the ionic limiting conditions of Eq. (3.9), the matrix of H_0 reduces to the form $-E_0\mathbb{1} + \underline{H}_0$ (where $\mathbb{1}$ is the unit matrix) in which

$$\underline{H}_0 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 2N^2E_0 & NN'SS'E_0 \\ 0 & NN'SS'E_0 & 2N'^2E'_0 \end{bmatrix} . \tag{3.13}$$

Since this is diagonal (if terms in SS' are neglected) with eigenstates ϕ_i, we can now proceed to consider perturbation by an applied field E_x directed along the bond axis x. The required perturbation operator is

$$V = -efxE_x \ , \tag{3.14}$$

where e is electronic charge and f is a local field factor.[1] Measuring x along the bond from the anion nucleus at $x=0$ toward the cation nucleus at $x=d$ we readily deduce the matrix representation of V in basis ϕ_i $(i=1,2,3)$ as

$$\begin{aligned} &V_{11} = 0 \ , \\ &V_{12} = V_{21} = -NSLefE_x \ , \\ &V_{13} = V_{31} = -N'S'L'efE_x \ , \\ &V_{23} = V_{32} = -NN'\langle h_M|x|h'_M\rangle efE_x \ , \\ &V_{22} = -N^2(d-2S^2L)efE_x \ , \\ &V_{33} = -N'^2(d-2S'^2L')efE_x \ , \end{aligned} \tag{3.15}$$

where

$$L = \langle h_M|x|h_X\rangle / \langle h_M|h_X\rangle \ , \tag{3.16}$$

$$L' = \langle h'_M|x|h_X\rangle / \langle h'_M|h_X\rangle \ , \tag{3.17}$$

and terms in SS' have been neglected. Since $\langle h_M|x|h'_M\rangle$ is an intraionic term it is likely to have a value which is small compared to d. Moreover it is consistent with the spirit of the bond-orbital approach (in which interionic terms are assumed to be dominant throughout) to set it equal to zero within the model, making $V_{23} = V_{32} = 0$.

The matrix equation for the perturbation of the zeroth order ground state $\phi_1 = |h_X|\rangle$ by V now takes the form

$$\begin{bmatrix} -E & V_{12} & V_{13} \\ V_{12} & E_2 - E + V_{22} & 0 \\ V_{13} & 0 & E_3 - E + V_{33} \end{bmatrix} \begin{bmatrix} 1+a_1 \\ a_2 \\ a_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} , \tag{3.18}$$

in which

$$E_2 = 2N^2E_0, \ \ E_3 = 2N'^2E'_0 \ , \tag{3.19}$$

and eigenvalue E and eigenfunction coefficients a_i are small quantities which may be determined to any order in V by standard time-independent nondegenerate perturbation theory. To third order we find values

$$E = -\left[\frac{V_{12}^2}{E_2} + \frac{V_{13}^2}{E_3} \right] + \left[\frac{V_{12}^2V_{22}}{E_2^2} + \frac{V_{13}^2V_{33}}{E_3^2} \right] , \tag{3.20}$$

$$a_1=-\frac{1}{2}\left[\frac{V_{12}^2}{E_2^2}+\frac{V_{13}^2}{E_3^2}\right]+\left[\frac{V_{12}^2V_{22}}{E_2^3}+\frac{V_{13}^2V_{33}}{E_3^3}\right], \tag{3.21}$$

$$a_2=-\frac{V_{12}}{E_2}+\frac{V_{12}V_{22}}{E_2^2}+\frac{1}{2}\left[\frac{3V_{12}^3-2V_{12}V_{22}^2}{E_2^3}+\frac{V_{12}V_{13}^2}{E_2E_3}\left[\frac{2}{E_2}+\frac{1}{E_3}\right]\right], \tag{3.22}$$

$$a_3=-\frac{V_{13}}{E_3}+\frac{V_{13}V_{33}}{E_3^2}+\frac{1}{2}\left[\frac{3V_{13}^3-2V_{13}V_{33}^2}{E_3^3}+\frac{V_{13}V_{12}^2}{E_2E_3}\left[\frac{2}{E_3}+\frac{1}{E_2}\right]\right]. \tag{3.23}$$

The perturbed normalized bond orbital $|b\rangle$ now takes the form

$$|b\rangle=(1+a_1)\phi_1+a_2\phi_2+a_3\phi_3 , \tag{3.24}$$

in terms of which linear and nonlinear bond susceptibilities $\chi_b^{(n)}$ can be defined according to

$$\langle b|ex|b\rangle=\text{const}+\sum_{n=1}^{\infty}\chi_b^{(n)}E_x^n . \tag{3.25}$$

Using Eqs. (3.21)–(3.25) the bond susceptibilities follow in the form

$$fE_x^2\chi_b^{(1)}=2\left[\frac{V_{12}^2}{E_2}+\frac{V_{13}^2}{E_3}\right], \tag{3.26}$$

$$fE_x^3\chi_b^{(2)}=-3\left[\frac{V_{12}^2V_{22}}{E_2^2}+\frac{V_{13}^2V_{33}}{E_3^2}\right], \tag{3.27}$$

$$fE_x^4\chi_b^{(3)}=4\left[\frac{V_{12}^2V_{22}^2-V_{12}^4}{E_2^3}+\frac{V_{13}^2V_{33}^2-V_{13}^4}{E_3^3}-\frac{V_{12}^2V_{13}^2}{E_2E_3}\left[\frac{1}{E_2}+\frac{1}{E_3}\right]\right]. \tag{3.28}$$

Clearly the responses $\chi_b^{(1)}$ and $\chi_b^{(2)}$ are additive with respect to the *sp*- and *d*-orbital contributions, and may therefore be expressed as

$$\chi_b^{(1)}=\chi_{b,sp}^{(1)}+\chi_{b,d}^{(1)} , \tag{3.29}$$

$$\chi_b^{(2)}=\chi_{b,sp}^{(2)}+\chi_{b,d}^{(2)} , \tag{3.30}$$

in an obvious notation. Third-order response $\chi_b^{(3)}$, on the other hand, is not additive, but contains a cross term as

$$\chi_b^{(3)}=\chi_{b,sp}^{(3)}+\chi_{b,d}^{(3)}-f\chi_{b,sp}^{(1)}\chi_{b,d}^{(1)}(E_2^{-1}+E_3^{-1}) . \tag{3.31}$$

Using Eqs. (3.15) and relating L to the parameter Δ of Eq. (2.2) via the equation[28]

$$L=(1/2)(d+\Delta) , \tag{3.32}$$

we confirm the representation

$$\chi_{b,sp}^{(1)}=\frac{e^2fS^2(d+\Delta)^2}{2E_Sa^2} , \tag{3.33}$$

$$\chi_{b,sp}^{(2)}=\frac{3e^3f^2S^2(d+\Delta)^2(d-S^2\Delta/a^2)}{4E_S^2a^2} , \tag{3.34}$$

$$\chi_{b,sp}^{(3)}=\frac{e^4f^3S^2d^2(d+\Delta)^2D}{4E_S^3a^4} , \tag{3.35}$$

in which $a^2=(1-S^2)$, E_S is the *sp*-Sellmeier gap [equal to E_2 of Eq. (3.19)] and

$$D=4-5S^2-10S^2(\Delta/d)+(S/a)^2(5S^2-1)(\Delta/d)^2 , \tag{3.36}$$

which agrees exactly[28] with the 2-level bond-orbital findings in Eqs. (2.2)–(2.6) of Ref. 29 when the latter are taken to the ionic limit (viz., $\alpha=S$, $g=1$, $V_2=E_0S/a^2=SE_s/2$ in the representation of that paper). The analogous formulations for "*d*-orbital" response $\chi_{b,d}^{(n)}$ follow from Eqs. (3.32)–(3.36) by the substitutions $S\to S'$, $E_s\to E_s'=E_3$, and $L\to L'=(1/2)(d+\Delta')$.

IV. NONLINEAR RESPONSE IN THE TM OXIDES

Although the response decompositions represented by Eqs. (3.29)–(3.31) become less valid as we deviate from the ionic limit, they are expected to be entirely adequate for the high coordination TM oxides of this paper since, for their pretransition metal counterparts discussed in Refs. 1 and 2, the anionic component of the bonding orbital $|b_0\rangle$ of Eq. (3.1) is never found to be smaller than $u_X\approx 0.96$. In discussing first- and third-order responses for the TM oxides (second-order response is at most small and extremely sensitive to structural details for these materials) we therefore assume the validity of Eqs. (3.29) and (3.31) but in terms of the generalized (i.e., $\alpha\geq S$) response functions of Eqs. (2.2) and (2.4) of Ref. 29 which are applicable for both halides and chalcogenides. Specifically these are

$$\chi_{b,sp}^{(1)}=\frac{e^2\alpha^2f}{2(1-S^2)E_S}(d+g\Delta)^2 , \tag{4.1}$$

$$\chi_{b,sp}^{(3)}=\frac{e^4\alpha^2f^3d^2D}{4(1-S^2)^2E_S^3}(d+g\Delta)^2 , \tag{4.2}$$

in which

$$D\approx 4-5\alpha^2-10g\alpha^2(\Delta/d) , \tag{4.3}$$

$$g=\frac{S}{\alpha}\left[\frac{1-\alpha^2}{1-S^2}\right]^{1/2} , \tag{4.4}$$

and α is a measure of covalency (which can, in general, range between an ionic limit of $\alpha=S$ and a covalent limit $\alpha=1$) in the form

$$\alpha=V_2/(V_2^2+V_3^2)^{1/2} , \tag{4.5}$$

where

$$V_2=M/(1-S^2),\quad V_3=E_0/(1-S^2)^{1/2} \tag{4.6}$$

and

$$E_s = 2V_2/\alpha \ . \tag{4.7}$$

Analogous relationships are valid for $\chi^{(1)}_{b,d}$ and $\chi^{(3)}_{b,d}$ if α, Δ, S, g, V_2, V_3, M, and E_0 are all replaced by their primed counterparts.

Summing over all one-electron bonds for a crystal with formula unit MX_n now provides an expression for linear response of form[1,2]

$$\epsilon - 1 = \frac{Gn\gamma^3(d+g\Delta)^2}{V_M V_2} + \frac{G'n\gamma'^3(d+g'\Delta')^2}{V_M V_2'} \ , \tag{4.8}$$

where

$$\gamma = \alpha/S, \quad \gamma' = \alpha'/S' \ , \tag{4.9}$$

and

$$G = \frac{18.2zfS^3}{(1-S^2)}, \quad G' = \frac{18.2zfS'^3}{(1-S'^2)} \ , \tag{4.10}$$

with z equal to the number of *nn* cations per anion and d being measured in Å, V_2 in eV, and molar volume V_M in cm^3. We note, in particular, that since only one of the five d orbitals per cation strongly σ bonds to an anion p orbital along a bond axis, there is no added degeneracy factor to be included in the (d orbital) primed term of Eq. (4.8).

The utility of the formalism for *sp* orbitals is manifested empirically by the observation that close agreement with experiment is obtained for all binary pretransition metal halides and chalcogenides[1,2] if

$$\gamma = |Z_X|^{1/2} \ , \tag{4.11}$$

$$G/V_2 = d^{2.4}/4 \ , \tag{4.12}$$

and

$$\Delta = d[(d/2R_M)^{1/2} - 1] \ , \tag{4.13}$$

where Z_X is formal anion valence and R_M is cationic radius. These empiric observations, when inserted into the unprimed component on the right-hand side of Eq. (4.8), then lead directly to Eqs. (2.1) and (2.2). Unfortunately, analogous relationships cannot automatically be assumed to hold for the d-orbital contributions. We shall probe their d-orbital counterparts (to the degree possible with the limited TM experimental information presently available) in the following section. Nevertheless, somewhat surprisingly, we do already possess essentially all the information necessary to obtain reliable numerical estimates of third-order nonlinear response throughout the three separate TM series of oxides.

This we can do because, by use of Eqs. (4.1) and (4.2), we can directly relate $\chi^{(3)}_{b,sp}$ and $\chi^{(3)}_{s,d}$ to their linear counterparts as

$$\chi^{(3)}_{b,sp} = \left[\frac{efd}{aE_S}\right]^2 (D/2)\chi^{(1)}_{b,sp} \ , \tag{4.14}$$

$$\chi^{(3)}_{b,d} = \left[\frac{efd}{a'E_S'}\right]^2 (D'/2)\chi^{(1)}_{b,d} \ , \tag{4.15}$$

where $a^2 = (1-S^2)$ and $a'^2 = (1-S'^2)$. It follows that $\chi^{(3)}_b$, via Eq. (3.31), can be wholly related to linear response in the form

$$\chi^{(3)}_b = \left[\frac{efd}{aE_S}\right]^2 (D/2)\chi^{(1)}_{b,sp} + \left[\frac{efd}{a'E_S'}\right]^2 (D'/2)\chi^{(1)}_{b,d} - f(E_S^{-1} + E'^{-1}_S)\chi^{(1)}_{b,sp}\chi^{(1)}_{b,d} \ . \tag{4.16}$$

Transforming to the macroscopic polarizabilities χ_{sp} and χ_d of Eq. (2.3) by summing over one-electron bonds in the fashion

$$\chi_{sp} = (2z/3)(nN_0/V_M)\chi^{(1)}_{b,sp} \ , \tag{4.17}$$

$$\chi_d = (2z/3)(nN_0/V_M)\chi^{(1)}_{b,d} \ , \tag{4.18}$$

where N_0 is Avogadro's number and the factor $\frac{1}{3}$ arises from an angular average, the entire pretransition metal theoretical development of Ref. 29 for the nonlinear optical coefficient n_2 in compound MX_n remains valid if only the term $(fd/aE_s)^2 D\chi_{sp}$ is replaced in it by its expanded equivalent, from Eq. (4.16), viz.,

$$J = \left[\frac{fd}{aE_S}\right]^2 D\chi_{sp} + \left[\frac{fd}{a'E_S'}\right]^2 D'\chi_d - \left[\frac{3V_M f}{nN_0 ze^2}\right](E_S^{-1} + E'^{-1}_S)\chi_{sp}\chi_d \ , \tag{4.19}$$

or

$$J = \left[\frac{fd}{aE_S}\right]^2 D\chi_{sp} + \left[\frac{fd}{a'E_S'}\right]^2 D'\chi_d - 0.346\left[\frac{V_M f}{nz}\right](E_S^{-1} + E'^{-1}_S)\chi_{sp}\chi_d \ , \tag{4.20}$$

if d is expressed in Å, E_S and E_S' in eV, and V_M in cm^3. Accordingly, the extension of Eq. (3.14) of Ref. 29 for use with TM oxides is (in cm^3/erg)

$$n_2 = \frac{4\pi 10^{-11} fJ\langle\beta_b^4\rangle}{n_0} \ , \tag{4.21}$$

which is relevant for linearly polarized light propagating with the electric field at an angle of direction cosine β_b with respect to bond b. For the TM oxides it is most convenient for comparative purposes to express n_2 as an angular average (i.e., $\langle\beta_b^4\rangle = \frac{1}{5}$) in the form

$$n_2(av) = T_{sp} + T_d - T_{sp,d} \ , \tag{4.22}$$

where

$$T_{sp} = f^3(20/n_0)(d/E_s)^2(D/a^2)(4\pi\chi_{sp}) \ , \tag{4.23}$$

$$T_d = f^3(20/n_0)(d/E_s')^2(D'/a'^2)4\pi\chi_d) \ , \tag{4.24}$$

$$T_{sp,d} = f^2(0.55V_M/nn_0 z)(E_S^{-1} + E_S'^{-1}) \times (4\pi\chi_{sp})(4\pi\chi_d) \ , \tag{4.25}$$

in units of 10^{-13} cm^3/erg, where n_0 is linear refractive index.

V. NUMERICAL

In order to predict the numerical nonlinear properties of the TM oxides via Eqs. (4.22)–(4.25), it is necessary to deduce from the linear response measurements the separate values of the bond-orbital parameters E_S, D, and S and their primed equivalents. The Sellmeier gaps E_S and E_S' are related to the frequency dependence of linear electronic response $\epsilon(\omega)$ on approach to the long-wavelength limit according to the relationship

$$\epsilon(\omega)-1=\frac{4\pi\chi_{sp}E_S^2}{E_S^2-\hbar^2\omega^2}+\frac{4\pi\chi_d E_S'^2}{E_S'^2-\hbar^2\omega^2} . \tag{5.1}$$

Unfortunately the published data on $\epsilon(\omega)$ for the TM oxides is usually analyzed (if at all) in terms of a single effective Sellmeier gap E_s (eff), i.e., by writing

$$\epsilon(\omega)-1=\frac{(\epsilon-1)E_S^2(\text{eff})}{E_S^2(\text{eff})-\hbar^2\omega^2} . \tag{5.2}$$

The effective gap is therefore related to the real gaps via the equation

$$\frac{\epsilon-1}{E_S^2(\text{eff})}=\frac{4\pi\chi_{sp}}{E_S^2}+\frac{4\pi\chi_d}{E_S'^2} . \tag{5.3}$$

Thus, the E_S(eff) values for the oxides at the beginning of the TM series (e.g., CaO, SrO, BaO), for which $\chi_d \ll \chi_{sp}$, are essentially equal to E_S. On the other hand, for those oxides further into the series [like TiO_2 and V_2O_5, with $E_S(\text{eff})=5.5$ and 4.4 eV, respectively][7,10] the E_S(eff) values are closer to E_S' since, for them, $\chi_d > \chi_{sp}$.

Since the energy gap between the valence p bands and conduction sp bands is known to vary little right across the respective TM series, it is sufficient for our purpose to take the E_S values for CaO, SrO, and BaO as representative for the respective series, i.e.,[1]

$$\begin{aligned} &E_S(3d\ \text{series})\approx 10\ \text{eV} ,\\ &E_S(4d\ \text{series})\approx 8.5\ \text{eV} ,\\ &E_S(5d\ \text{series})\approx 7\ \text{eV} .\end{aligned} \tag{5.4}$$

From Eqs. (5.3), (5.4), and Table I it follows that $E_S'\approx 4.6$ eV for TiO_2 and ≈ 3.7 eV for V_2O_5. The effective Sellmeier gaps E_S(eff) presently known for single-crystal (TM) oxides are (in units of eV)

5.5 (TiO_2,rutile)(Ref. 7), 5.5 (TiO_2 anatase)(Ref. 7), 4.4 (V_2O_5)(Ref. 10) ,

8.9 (Y_2O_3)(Ref. 11), 6.8 (Nb_2O_5)(Ref. 14), 7.5 (Ta_2O_5)(Ref. 14), 4.5 (WO_3) (Ref. 16) .

For the subset of these with $\chi_d > \chi_{sp}$ (see Table I) the above method enables reasonably quantitative estimates of the d-orbital Sellmeier gap E_S' to be obtained. These have been calculated and are plotted as a function of bond-length d in Fig. 1. For the oxides with larger d values, E_S' cannot reliably be obtained in this manner. However, it is known from band-structure computations[30] that the center of the relatively narrow d band in CaO lies about (12 ± 1) eV above the valence p band, suggesting a value $E_S'\approx 12$ eV when $d\approx 2.4$ Å. Including this information in Fig. 1 now suggests an approximately linear dependence of E_S' on bond length of the form (in eV)

$$E_S'=15(d-1.6) \tag{5.5}$$

with d in Å. We note, in particular (Fig. 1), that this expression also accounts closely for the peak to peak valence to d-band gaps in the density of states curves for $SrTiO_3$ and $KTaO_3$.[31]

For the unprimed bond-orbital parameters, a combination of Eqs. (4.7)–(4.12) now leads to the relationship (with E_S in eV and d in Å)

$$E_S=\frac{145zfS^2}{(1-S^2)|Z_X|^{1/2}d^{2.4}} \tag{5.6}$$

which, once the Lorentz factor f is known, determines S for the TM oxides ($|Z_X|=2$) directly from a knowledge of d and E_S (both of which we now possess). Values of $\alpha=\sqrt{2}S$ and of D [of Eq. (4.3)] then follow immediately. We give them numerically, for the case of $f=1$,[32] in Table II. Other unprimed bond-orbital parameters like g (which never deviates from the range 0.65 ± 0.01), V_2, V_3, M, and E_0 follow directly from Eqs. (4.4)–(4.7).

To complete an enumeration of n_2 from Eq. (4.22) also requires at least a limited knowledge [specifically $D'/(1-S'^2)$] of the values of the primed bond-orbital parameters. Unfortunately, since there is at present almost no experimental information on linear response for TM halides or chalcogenides other than oxides, our knowledge of "d-orbital" response parameters will remain less than complete. However, a number of interesting deductions can be made from the existing data, from which $D'/(1-S'^2)$ can be evaluated with adequate precision to enable numerical estimates for $n_2(av)$ to be completed.

Firstly, by combining Eqs. (2.3) and (4.8)–(4.10), we can write

$$4\pi\chi_d=\frac{18.2zfn\alpha'^3(d+g'\Delta')^2}{(1-S'^2)V_M V_2'} . \tag{5.7}$$

Defining from this equation a parameter U' according to

$$4\pi\chi_d=U'nd^2/V_M , \tag{5.8}$$

we may immediately evaluate it for the TM oxides by utilizing the χ_d values of Table I. As a function of bond-length d, we observe (Fig. 2) that it decreases monotonically from values ≈ 9 at $d=1.8$ Å to values essentially equal to zero for $d\gtrsim 2.5$ Å. Using the relationship

TABLE II. Values of the valence to *sp*-conduction band Sellmeier gap E_S (in eV), the mean number z of cation *nn* of an oxygen anion, overlap S, "covalency" α, and parameters Δ/d of Eq. (2.2), D of Eq. (4.3), and D/a^2 for the 3*d*, 4*d*, and 5*d* series of TM oxides, where $a^2=1-S^2$.

Material	E_S	z	S^a	α^a	Δ/d	D	D/a^2
CaO	10	6	0.34	0.49	0.10	2.7	3.0
$ScO_{1.5}$	10	4	0.36	0.51	0.14	2.5	2.8
TiO_2 (rutile)	10	3	0.37	0.53	0.27	2.2	2.5
TiO_2 (anatase)	10	3	0.37	0.53	0.26	2.2	2.5
$VO_{2.5}$	10	2.4	0.38	0.54	0.35	1.9	2.2
SrO	8.5	6	0.34	0.49	0.05	2.8	3.1
$YO_{1.5}$	8.5	4	0.36	0.51	0.09	2.6	2.9
ZrO_2	8.5	3.5	0.36	0.51	0.18	2.4	2.8
$NbO_{2.5}$	8.5	2.4	0.39	0.55	0.25	2.0	2.4
BaO	7	6	0.34	0.48	0.01	2.8	3.2
$LaO_{1.5}$	7	4.7	0.35	0.49	0.07	2.7	3.0
HfO_2	7	3.5	0.33	0.47	0.19	2.6	2.9
CeO_2	7	4	0.34	0.48	0.10	2.7	3.0
$TaO_{2.5}$	7	2.6	0.36	0.50	0.22	2.3	2.7
WO_3	7	2.0	0.36	0.52	0.25	2.3	2.6

[a] These values are calculated assuming no local field enhancement (i.e., $f=1$). For $f\neq1$, they scale approximately as $1/f^{1/2}$ from which D and D/a^2 can be recalculated via Eq. (4.3).

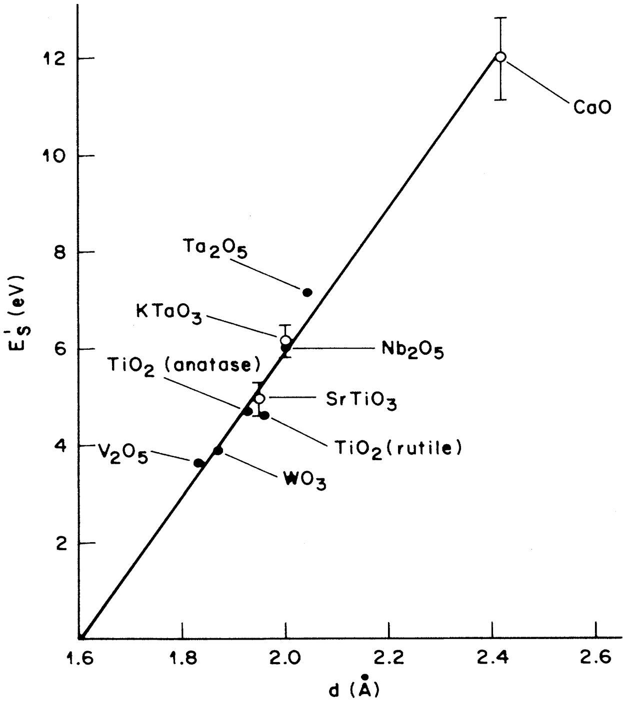

FIG. 1. The known *d*-orbital Sellmeier gaps E'_S as a function of mean bond-length d (solid circles) for the TM oxides. Also shown (open circles) are the best theoretical estimates from band theory (Refs. 30 and 31) for $SrTiO_3$, $KTaO_3$, and CaO (see text). The solid curve gives the best linear fit to the combined data.

$$E'_S=2(V_2'^2+V_3'^2)^{1/2}=2V'_2/\alpha' \tag{5.9}$$

in Eq. (5.7) we obtain, via Eq. (5.8), the form

$$U'=\frac{36.4zf\alpha'^2F}{E'_S}\ , \tag{5.10}$$

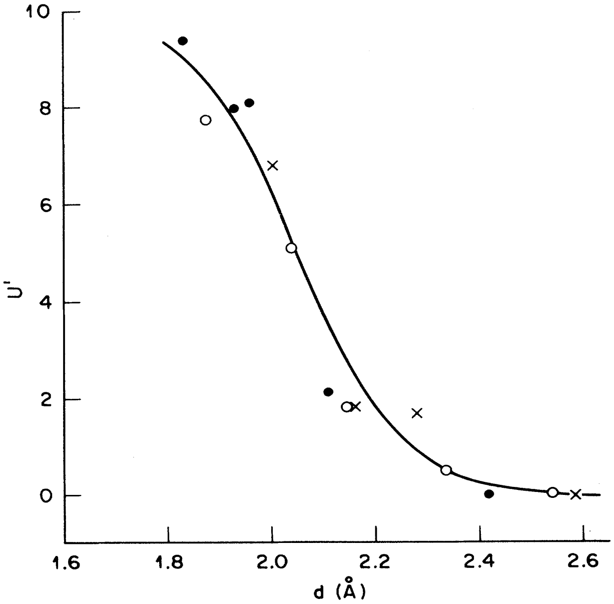

FIG. 2. The parameter U' of Eq. (5.8) as evaluated for the 3*d* (solid circles), 4*d* (crosses), and 5*d* (open circles) TM oxides. The solid line is a guide to the eye and suggests a functional variation of U' with bond-length d which is essentially independent of the *d*-electron principal quantum number.

in which

$$F=\frac{(1+g'\Delta'/d)^2}{(1-S'^2)}\ . \tag{5.11}$$

Since U', z, and E_s' are now all known as functions of d, only this factor F now stands between us and an evaluation (at least for $f=1$) of the "d-orbital" covalency parameter α' as a function of bond length. Let us first consider the tentative assumption

$$F=\frac{(1+g'\Delta'/d)^2}{(1-S'^2)}\approx\frac{(1+g\Delta/d)^2}{(1-S^2)}\ , \tag{5.12}$$

for which F varies within the range 1.1 to 1.7. It assumes a not grossly different radial extent for wave functions $|h_M\rangle$ and $|h_M'\rangle$ with the same principal quantum number, and leads to values for α' as a function of d as shown in Fig. 3. It is apparent from the figure that α', at least within the context of oxides, is a similar function of bond length for each of the TM series. In particular, for $d\lesssim 2.0$ Å this measure of "d-orbital" covalency reaches values ≈ 0.5 comparable with the unprimed α values of Table II. It therefore seems likely that the approximation of Eq. (5.12) is adequate in this region. Clearly, however, as d increases to values in excess of 2.4 Å, the covalency measure α' becomes progressively smaller than its unprimed equivalent, implying that here the radial extent of $|h_M'\rangle$ becomes progressively less than that of $|h_M\rangle$ and that the assumption of Eq. (5.12) is likely to be much poorer. However, since d-electron contributions to both ϵ and n_2 become negligibly small at larger d values, and $\alpha'\rightarrow 0$, errors accruing from the assumption Equation (5.12) are relatively inconsequential in estimates of electronic response in this limit. For present purposes, therefore, Eq. (5.12) is adequate.

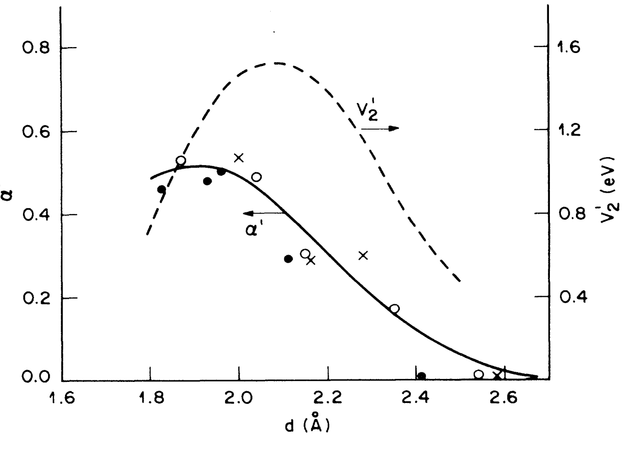

FIG. 3. The d-orbital covalency parameter α' as a function of bond-length d for the $3d$ (solid circles), $4d$ (crosses), and $5d$ (open circles) TM oxides calculated for $f=1$. The solid line is merely a guide to the eye. The dashed line exhibits the d-dependence of the anion p-orbital to cation d-orbital matrix element V_2' as deduced from the solid line via Eq. (5.13). For $f\neq 1$, both α' and V_2' scale approximately as $1/f^{1/2}$.

We note that the one-electron matrix element V_2' follows from α' via (in eV)

$$V_2'=E_S'\alpha'/2=7.5\ (d-1.6)\alpha'\ , \tag{5.13}$$

and can therefore be deduced directly from Fig. 3. We sketch it as a function of d in that same figure. It reaches peak values[33] of about 1.5 eV that are only slightly smaller than their unprimed counterparts ($V_2=E_S\alpha/2$) which, in turn, range between ≈ 1.7 eV for the $5d$ TM series to ≈ 2.6 eV for the $3d$ series. However, to this point, all these values α, V_2, α', V_2' in absolute terms still rest on an assumed absence of local field corrections. For $f\neq 1$ they would scale approximately as $f^{-1/2}$.

The d-orbital function required for the evaluation of n_2, namely,

$$\frac{D'}{1-S'^2}=\frac{4-5\alpha'^2-10g'\alpha'^2(\Delta'/d)}{1-S'^2}\ , \tag{5.14}$$

clearly approaches, independently of f, a value of four at large bond lengths, for which α' (and therefore S' also) goes to zero. Our absence of knowledge of the magnitude of Δ' in this regime is therefore of no consequence. At shorter bond lengths for which $\alpha'\approx\alpha$, it is safe to assume that Δ' and α'/S' approach values not greatly different from their unprimed counterparts. We therefore approximate $g'\Delta'$ by $g\Delta$, and α'/S' by $\alpha/S=|Z_X|^{1/2}$, in terms of which Eq. (5.14) can be recast as

$$\frac{D'}{1-S'^2}=\frac{4-5\alpha'^2-10g\alpha'^2(\Delta/d)}{1-(\alpha'^2/2)}\ . \tag{5.15}$$

Taking α' values from Fig. 3, Δ/d values from Table II and setting $g=0.65$, now enables us to obtain numerical values for $D'/(1-S'^2)$. They are given, together with α' and E_S', for each of the individual TM oxides in Table III.

We now possess all the numerical data necessary for an evaluation of $n_2(av)$, via Eqs. (4.22)–(4.25), excepting only the local field factor f. We shall calculate first assuming $f=1$, which was the value found to be valid for the pretransition metal halides.[29] Numerical values for $n_2(av)$, together with the individual component values for T_{sp}, T_d, and $T_{sp,d}$ are all given in Table III. We note that as we progress along each TM series toward higher cation valence, the term T_{sp} (which arises from virtual excitations to cationic sp levels) progressively decreases, and the term T_d (due to virtual excitations to d levels) increases. The "cross-term" $T_{sp,d}$ is never more than about 15% of $T_{sp}+T_d$ and is usually much less. Since T_{sp} and T_d are explicitly proportional to f^3 [see Eqs. (4.23) and (4.24)] the $n_2(av)$ values so calculated are essentially in units of $10^{-13} f^3\,\text{cm}^3/\text{erg}$.[34]

The values of f can, in principle, be obtained by direct comparison with experiment. In practice the procedure is hampered by a paucity of experimental data for TM oxides, coupled with uncertainties concerning the variation of n_2 with optical polarization and propagation direction (which is often undocumented in the literature) and the lack of a universally acknowledged reference standard[29] among experimentalists. The best data avail-

TABLE III. Values of the valence to *d*-band Sellmeier gap E_S' (in eV), *d*-band covalency parameter α', ratio $D'/(1-S'^2)$ of Eq. (5.15) and, in units of 10^{-13} cm^3/erg, the three terms T_{sp}, T_d, and $T_{sp,d}$ of Eqs. (4.23) to (4.25) which, in combination $T_{sp}+T_d-T_{sp,d}$, combine to form the nonlinear refractive index $n_2(av)$.

Material	E_S'	α'	$D'/(1-S'^2)$	T_{sp}	T_d	$T_{sp,d}$	$n_2(av)$[a]
CaO	≈12	≈0	4	4.4	≈0	≈0	4.4
$ScO_{1.5}$	7.6	0.29	3.6	2.5	2.3	0.3	4.5
TiO_2 (rutile)	4.6	0.50	2.6	1.5	12.4	1.4	12.5
TiO_2 (anatase)	4.7	0.48	2.8	1.3	11.6	1.2	11.7
$VO_{2.5}$	3.6	0.46	2.8	0.9	18.2	1.7	17.4
SrO	≈15	≈0	4	7.4	≈0	≈0	7.4
$YO_{1.5}$	10	0.30	3.7	4.4	1.2	0.3	5.3
ZrO_2	8.4	0.29	3.6	4.2	1.9	0.4	5.7
$NbO_{2.5}$	6.0	0.54	2.4	2.1	5.8	1.4	6.5
BaO	≈17	≈0	4	12.9	≈0	≈0	12.9
$LaO_{1.5}$	≈14	≈0	4	11.6	≈0	≈0	11.6
HfO_2	8.2	0.30	3.6	6.6	1.9	0.4	8.1
CeO_2	≈11	0.17	3.8	9.4	0.3	0.1	9.6
$TaO_{2.5}$	6.6	0.49	2.9	4.1	5.0	1.2	7.9
WO_3	3.9	0.53	2.6	2.4	12.5	1.8	13.1

[a] All these values except E_S' are obtained by assuming the absence of any local field enhancement (i.e., with $f=1$). For $f\neq 1$, α' and S' scale approximately as $1/f^{1/2}$; T_{sp}, T_d, and $n_2(av)$ approximately as f^3 and $T_{sp,d}$ approximately as f^2. The parameter $D'/(1-S'^2)$ is relatively insensitive to f.

able at present for our purposes are those of Adair *et al.*[35] Our prior analysis of these data for the pretransition metal halides has been reported in Ref. 29.

In order to remove any uncertainties concerning absolute values,[36] we scale both the theoretical findings (Table III) and Adair's measurements (Table IV of Ref. 35) to that of a representative halide for which we have evidence[29] that $f=1$ is a good representation. Choosing this halide to be NaCl (any other would have sufficed without significantly affecting the results to follow) we adopt as our "unit" reference point that experimental value $n_2=1.59\times 10^{-13}$ cm^3/erg from Adair *et al.*[35] and the theoretical value $n_2(av)=(3/5)n_{2,1}=4.4\times 10^{-13}$ cm^3/erg from Table I of Ref. 29. A direct comparison of relative n_2 values (experiment versus $f=1$ theory) are shown in columns 1 and 2 of Table IV for a selection of halides and for CaO, SrO, $YO_{1.5}$, ZrO_2, and TiO_2. Also included in the tabulation are the pretransition metal oxides MgO and $AlO_{1.5}$ and indirect experimental estimates for $NbO_{2.5}$ and $TaO_{2.5}$. The $NbO_{2.5}$ estimate is obtained by extrapolation from measurements on Nb-doped silicate glass[37] while that for $TaO_{2.5}$ follows from data on $KTaO_3$ (Ref. 36) assuming n_2 in this compound to be dominated by its $TaO_{2.5}$ component. Note that a similar estimate for WO_3 cannot be made from n_2 data on $CaWO_4$ (Ref. 35) since W in $CaWO_4$ is tetrahedrally bonded with an effective Sellmeier gap ≈9 eV,[38] close to double that of octahedrally bonded WO_3.

Since the experimental values[35] are obtained at a wavelength of 1 μm, the theoretical values should be adjusted for frequency dependence to this same value (or, equivalently, to $\hbar\omega=1.24$ eV). At frequencies for which $\omega^2 \ll E_S^2/\hbar^2$ and $\omega^2 \ll E_S'^2/\hbar^2$, a nonlinear response $n_2(\omega)$ which is dominated by T_{sp} varies with frequency approximately as[39] $[E_S^2/(E_S^2-\hbar^2\omega^2)]^4$, while one dominated by T_d varies correspondingly as $[E_S'^2/(E_S'^2-\hbar^2\omega^2)]^4$. The required frequency shift for the materials of Table IV is negligibly small except for TiO_2, $NbO_{2.5}$, and $TaO_{2.5}$ where it has been included in the pertinent values of that Table.

We see clearly from Table IV that while the $f=1$ theoretical values are close to experiment for the halides, they are significantly smaller than experiment for the oxides (both in the case of pretransition metal and TM cations). Recomputing $n_2(av)$ for each oxide as a function of f now enables us to calculate those values of the local field enhancement factor f which would bring the theory and experiment back into agreement. These values are shown in column 3 of Table IV. A pattern emerges as follows: $f\approx 1.0$ for the pretransition metal halides, $f=1.3\pm 0.1$ for the pretransition metal oxides and those TM oxides for which T_{sp} dominates the nonlinear response, and finally $f\approx 1.9\pm 0.1$ for the TM oxides dominated by "*d*-band" response.

Without claiming anything more profound than coincidence, these values can all be cast in the form $(0.75\pm 0.1)f_L$, where $f_L=(\epsilon+2)/3$ is the Lorentz local field factor. This empiric observation, coupled with the fact that $n_2(av)$ is almost always dominated separately by T_{sp} or T_d of Eqs. (4.23) and (4.24), now enables us to offer a very simple expression for $n_2(av)$ which appears to have at least semiquantitative validity for all the pretransition metal and TM halides and chalcogenides discussed to this point. It is, in cm^3/erg,

$$n_2(av)=\frac{25 f_L^3 d^2 (n_0^2-1)}{n_0 E_S^2(\text{eff})}10^{-13}\;, \tag{5.16}$$

TABLE IV. Nonlinear refractive index n_2 (at 1 μm) scaled down to n_2 (NaCl)$=1$, from experiment (Ref. 35) and from the $f=1$ theory of this paper. Also shown are the values of the local field enhancement factor f which are required to produce agreement between theory and experiment, and the Lorentz values f_L of this same parameter.

Material	n_2 (expt)	$n_2^{(f=1)}$ (theor)	f	f_L
NaCl	1	1	1	1.44
LiF	0.16	0.16	1.0	1.31
NaF	0.21	0.22	1.0	1.25
KF	0.47	0.35	1.1	1.28
KCl	1.26	1.17	1.0	1.39
NaBr	2.05	1.69	1.1	1.53
KBr	1.84	1.85	1.0	1.45
MgO	1.0	0.5	1.2	1.65
CaO	3.3	1.0	1.4	1.76
SrO	3.2	1.7	1.2	1.78
$AlO_{1.5}$	0.8	0.25	1.4	1.69
$YO_{1.5}$	3.4	1.2	1.3	1.87
ZrO_2	3.6	1.3	1.3	2.07
TiO_2	35.0	3.6	2.0	2.77
$NbO_{2.5}$	12.0[a]	1.6	1.8	2.43
$TaO_{2.5}$	$\gtrsim$ 18.0[a]	2.0	$\gtrsim$ 1.9	2.33

[a] See text.

where E_S(eff) in eV is the common "one-parameter" Sellmeier gap as defined in Eq. (5.2) and bond-length d is in Å. For the materials of Table IV, the representation of Eq. (5.16) has an rms accuracy (for relative values) of ±25%, with a maximum error of 50%, over values which span a range of more than a factor of 200 in magnitude.

Since it is quite possible that the local field parameter f could adopt different numerical values for the $\langle p|d\rangle$ and $\langle p|s\rangle$ based interactions which, respectively, dominate the primed and unprimed contributions to electronic response we have not recast Tables II and III to incorporate the estimate $f \approx 3f_L/4$ explicitly. We shall, however, give a final tabulation of $n_2(av)$, via Eq. (5.16) and its frequency-dependent analog (in cm³/erg)

$$n_2(av) = \frac{25 f_L^3 d^2 (n_0^2 - 1) E_S^6(\text{eff})}{n_0 [E_S^2(\text{eff}) - \hbar^2\omega^2]^4} 10^{-13} \tag{5.17}$$

for the complete series of 3d, 4d, and 5d TM oxides. It is shown in Table V, and values are quoted both for the long-wavelength electronic limit and for the vacuum wavelength $\lambda = 1$ μm. For each case, numerical values are quoted both in esu (cm³/erg) and mks (m²/W), the conversion factor being[40]

$$1\ \text{m}^2/\text{W} \equiv (3n_0 10^8/40\pi)\text{cm}^3/\text{erg}\ , \tag{5.18}$$

in which n_0 is the long-wavelength limiting value of refractive index.

VI. SUMMARY

This paper extends the two-level bond-orbital theory of electronic response in pretransition metal halides and chalcogenides to the three levels required for a discussion of the optically transparent transition metal (TM) oxides. The extension recognizes the increasing importance of virtual transitions from the filled valence band to the empty cationic d band on progression along each of the 3d, 4d, and 5d TM series (e.g., from CaO to Sc_2O_3, TiO_2, and V_2O_5 in the 3d series). The "d-orbital" contributions

TABLE V. Final numerical estimates for the angularly averaged nonlinear refractive index $n_2(av)$, from Eq. (5.18). They are given for the complete list of TM oxides at the long-wavelength limit $\lambda \rightarrow \infty$ (electronic contribution only) and at $\lambda = 1$ μm, and are expressed in both esu (cm³/erg) and mks (m²/W).

Material	$n_2(av)(\lambda \rightarrow \infty)$		$n_2(av)[\lambda = 1\ \mu\text{m}]$	
units	10^{-12} cm³/erg	10^{-19} m²/W	10^{-12} cm³/erg	10^{-19} m²/W
CaO	1.0	2.3	1.1	2.5
$ScO_{1.5}$	1.3	2.8	1.4	3.0
TiO_2 (rutile)	14	24	17	29
TiO_2 (anatase)	10	17	12	21
$VO_{2.5}$	12	22	17	31
SrO	1.8	4.0	1.9	4.3
$YO_{1.5}$	1.5	3.3	1.6	3.6
ZrO_2	2.2	4.5	2.4	5.0
$NbO_{2.5}$	6	11	7	12
BaO	3.7	8	4.2	9
$LaO_{1.5}$	3.7	8	4.2	9
HfO_2	3.3	7	3.7	8
CeO_2	3.3	7	3.7	8
$TaO_{2.5}$	5	10	6	11
WO_3	9	17	13	24

to linear response $\epsilon = n_0^2$ (where n_0 is linear refractive index) are found to be negligible for bond lengths $d \gtrsim 2.3$ Å, but to increase rapidly with decreasing bond length to exceed the "*sp*-orbital" conduction band contribution when $d \lesssim 2.0$ Å. The effect is due primarily to the rapid increase in overlap of the valence anionic *p* orbitals and lowest energy cationic *d* orbitals at the shorter equilibrium bond lengths. The lowering of the *d* band relative to the conduction *sp* band on progression along a TM series also plays a significant role, but only at the shortest bond lengths.

The two competing mechanisms, viz., virtual excitations to "*d*-orbitals" and to conduction band "*sp*-orbitals," are found to be essentially additive for linear polarizability $\chi^{(1)}$ and for the lowest order nonlinear polarizability $\chi^{(2)}$, but not for $\chi^{(3)}$ where a small, but not negligible, cross term is present. By relating the three $\chi^{(3)}$ terms to the components of linear response, we are able to numerically evaluate the third-order electronic response (in the form of the nonlinear refractive index n_2) for each series of TM oxides. The only remaining "unknown," namely, the local field enhancement factor f, is then determined by direct comparison of theory with experiment for n_2 in cases where the latter is known. The implied values, namely, $f \approx 1.3 \pm 0.1$ for the "*sp*-orbitally dominated" oxides, and $f \approx 1.9 \pm 0.1$ for the "*d*-orbitally dominated" oxides compare with the $f \approx 1.0$ found in an earlier discussion of pretransition metal halides. Since all these values fall into a general range $f \approx 3f_L/4$, where $f_L = (n_0^2 + 2)/3$ is the Lorentz value, it proves possible to set out a common theoretical form for n_2 which covers all the above series of compounds. This very simple representation [Eq. (5.16)] appears to be rms accurate to about ±25% over n_2 values which span a range of more than a factor of 200 in relative magnitude. Finally (Table V) we predict n_2 values for each series of optically transparent TM oxides both in the long-wavelength electronic limit and at wavelength $\lambda = 1 \mu$m.

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[34] This statement is not quite true since, for values $f \neq 1$, values of S, α, S', α', etc., also depend on f via Eqs. (5.6) and (5.10). A self-consistent calculation shows that $n_2(av)$ varies with f more closely as $f^{3.4 \pm 0.1}$.

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