Improving Levine model for dielectric constants of transition metal compounds

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Improving Levine model for dielectric constants of transition metal compounds

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The density of states and optical properties of several transition metal compounds have been simulated using local density approximations+U. Results show that s electrons of nontransition elements in the compounds cannot be considered to have the same contribution on the number of valence electrons. In light of this observation, the parameter Γ in the Levine model is improved, which leads to better prediction for dielectric constants of transition metal compounds. © *2009 American Institute of Physics.*
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I. INTRODUCTION

Dielectric constants of semiconductors and insulators that have remarkable optical and electronic properties have received considerable attention for optoelectronic applications, such as microwave filters, resonators, and high density memory cell capacitors.[1–3] Several techniques including synchrotron radiation,[4] *in situ* x-ray and ultraviolet valence band spectroscopy measurements,[5] and first principles calculations[6] have been used to the dielectric constants of materials. Theoretically, Penn[7] used an isotropic version of the nearly free electron model to calculate the static, real part of the electronic dielectric constant $\varepsilon = (4\pi)^{-1}A(\hbar\omega_p/\bar{E}_g)^2 + 1$, which is evaluated by the average energy gap $\bar{E}_g$ for compounds with A-group elements,[7–9] where $A = 1 - (\bar{E}_g/4E_F) + (\bar{E}_g/4E_F)^{2/3}$ is the correction factor with the Fermi energy E_F, the plasma energy $\hbar\omega_p = (4\pi N_e e^2/M)^{1/2}$ where N_e is the number of valence electrons per unit volume, and e and M show the electronic charge and mass respectively. For transition metallic (TM) compounds, however, Penn's model leads to errors due to the existence of *unfilled* d shells or *unfilled* valence bands where an excited electron, in the sense of transition selection rules, can be transferred into the valence band, besides the transitions from the valence band to the conduction band.[10,11]

Levine[10] found that the number of the d electrons in valence band, or the number of d holes (n), is proportional to ε since valence electrons transit to the empty d levels where n may be a part of the loosely bound valence d electrons. Thus, ε function can be modified as[10]

$$\varepsilon = (4\pi)^{-1}A(1+\Gamma)(\hbar\omega_p/\bar{E}_g) + 1, \tag{1}$$

where Γ describes the fractional increase in oscillator strength relating to $\hbar\omega_p$, which is defined by Levine as[10]

$$\Gamma = n/m, \tag{2}$$

where m is the total number of valence electrons. Equation (2) implies that all valence electrons can transit to the empty d levels. However, the obtained $\bar{E}_g$ values from Eq. (1) show negative discrepancy from experimental results.[12,13]

In this contribution, first principles simulation is carried out for electronic structures of several TM compounds. It is found that the number of s electron levels of nonmetals in the compounds, s^n, cannot fully contribute m value and Eq. (2) should be improved.

II. EXPERIMENTATIONS

The partial density of states (PDOS) and optical absorption properties of five TM compounds with the rocksalt ($Fm3m$ space group) structure are carried out by using the first principles calculations. The calculations are based on the density functional theory with Perdew–Burke–Ernzerhof functional of generalized gradient approximation and with norm-conserving pseudopotentialsc,[14] as implemented in CASTEP code.[15] Geometry optimizations of all compounds are made on conventional unit cells using ultrafine cutoff energies for the plane-wave expansion. The k-point sampling set is $10 \times 10 \times 10$ division of the reciprocal unit cell based on the Monkhorst–Pack scheme.[16] The convergence tolerance of energy of 1.0×10^{-5} eV/at., maximum force of 0.03 eV/Å, and maximum displacement of 0.001 Å were used. Spin polarized and local density approximations (LDA)+U (Refs. 17–19) have been used because LDA+U is now a well-established model to deal with electron correlation in TM and rare earth compounds, which guarantee that electronic structures of these materials will be consistent with that of experiment.[20] In this LDA+U method, the strong correlation between localized d electrons is explicitly taken into account through the screened effective electron-electron interaction parameter U, which are cited from literatures with 2.5 eV for Sc, 3.6 eV for Mn, 4.6 eV for Fe, 5.0 eV for Co, and 5.1 eV for Ni, respectively.[21] When analyzing all PDOS and absorption diagrams, the scissors values have been considered as 0.7 eV for ScN, 0.4 eV for MnS, 1.2 eV for FeO,
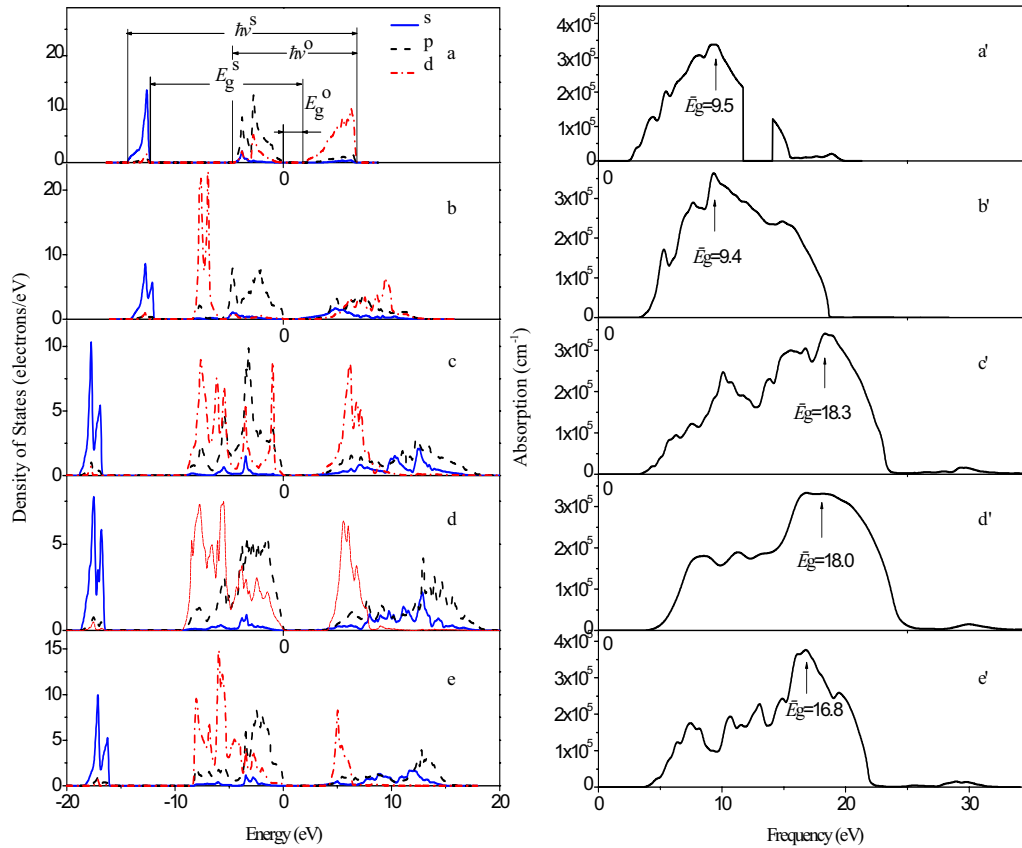
FIG. 1. (Color online) PDOS of ScN (a), MnS (b), FeO (c), CoO (d), and NiO (e), and absorption diagrams of ScN (a'), MnS (b'), FeO (c'), CoO (d'), and NiO (e').

1.9 eV for CoO, and 1.0 eV for NiO, respectively, which are obtained by comparing our simulated electron structures or absorption diagrams with experimental results.[5,13,22,23] This technique commendably drops the differences of $\bar{E}_g$ values between simulation and experimental results.[24]

III. RESULTS AND DISCUSSIONS

PDOS and absorption diagrams of TM compounds are shown in Fig. 1 where the Fermi level is defined as zero in abscissa. A few of valence electrons are far away from the Fermi level, which lie from -12.3 to -14.4 eV for ScN, -11.8 to -14.1 eV for MnS, -16.7 to -18.8 eV for FeO, -16.5 to -18.7 eV for CoO, and -16.4 to -18.5 eV for NiO, respectively. These electrons should be $2s$ electrons of nonmetal elements in the compounds, which will be confirmed in Fig. 2. When the photon energy $\hbar\nu$ is larger than the energy bond width E_g, which denotes the difference between the top of each valence band and the bottom of empty d levels, which is almost the same as that between the top of each valence band and the bottom of conduction bands, the valence electrons can be activated and transited to the empty d levels or conduction bands. Generally speaking, the absorption coefficient of direct transition α is two orders larger than that of indirect transition, which denotes the transition between the valence electrons to the empty d levels and reflects electronic transition probability; we thus only consider the former as[25]

$$\alpha = B(\hbar\nu - E_g)^{3/2}, \tag{3}$$

where B is a material constant. Thus, the average value of α with photon energy from x to y ($\acute{\alpha}$) is taken as

$$\acute{\alpha} = \left[B \int_x^y (\hbar\nu - E_g)^{3/2} \right] / (y - x). \tag{4}$$

Let superscripts s and o denote $2s$ electrons of nonmetal elements and other valence electrons, respectively, $E_g^{\ s}$ and $E_g^{\ o}$ are the corresponding bandgap, which are the smallest photon energies absorbed for electrons transiting to the empty d levels, respectively. $E_g^{\ s}$ is much larger than $E_g^{\ o}$ as seen in Fig. 1 and Table I, or $2s$ electrons transit to the empty
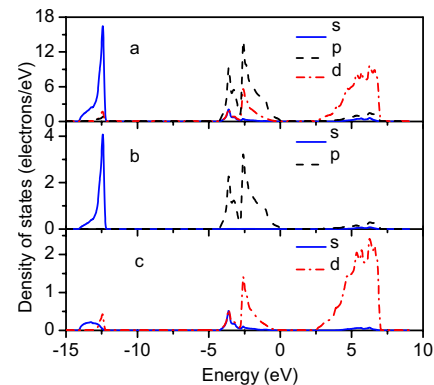

FIG. 2. (Color online) PDOS of ScN (a), Sc in ScN (b), and N in ScN (c).

TABLE I. Related parameters used in Eqs. (1)–(6). E_g^{o}, E_g^{s}, and $\bar{E}_g$ values are simulation results. I is determined by Eq. (5). Γ^{Le} and Γ' are determined by Eqs. (2) and (6). ε^{Le} and ε' are calculated in light of Eq. (1) with Γ^{Le} and Γ' values, respectively. $\bar{E}_g''$ and ε'' denote experimental values.

	E_g^{o}	E_g^{s}	$\hbar\nu^{o}$	$\hbar\nu^{s}$	I	$\bar{E}_g$	$\bar{E}_g''$	n	m	Γ^{Le}	Γ'	ε^{Le}	ε'	ε''
ScN	1.9	14.2	11.5	21.2	0.62	9.5		9	8	1.125	1.286	11.4	12.2	12.2[a]
MnS	3.4	15.4	21.2	27.0	0.53	9.4		5	13	0.385	0.417	6.5	6.7	6.8[b]
FeO	3.5	20.3	20.2	30.0	0.45	18.3		4	14	0.286	0.308	4.2	4.3	4.9[c]
CoO	4.1	20.6	20.3	29.7	0.42	18.0	18.4[d]	3	15	0.200	0.214	4.4	4.5	4.8[d]
NiO	3.9	20.0	18.1	27.4	0.38	16.8	17.6[d]	2	16	0.125	0.133	5.3	5.4	5.4[d]

[a]Reference 26.
[b]Reference 21.
[c]Reference 27.
[d]Reference 13.

d levels with much lower transition probability than other valence electrons. Let $I=\acute\alpha^{s}/\acute\alpha^{o}$; in light of Eqs. (3) and (4), there is

$$I = [(\hbar\nu^{s} - E_g^{s})/(\hbar\nu^{o} - E_g^{o})]^{3/2}. \tag{5}$$

In terms of Eq. (5), I values are determined and are listed in Table I, It is found that $I\approx 0.5$. Thus, $2s$ electrons should have only a half possibility to transit to the empty d levels.

PDOSs of ScN, Sc, and N in ScN are plotted in Fig. 2 as an example to identify $2s$, $3d$, and $N\ 2p$ orbitals. The valence electrons between -12.2 and -14.4 eV are $N\ 2s$ electrons, while valence electrons between -4.6 and 0 eV are Sc $2s$ and $3d$ and $N\ 2p$ electrons, which have hybridized and are close to the Fermi level. E_g^{s} value is indeed large. Because $I\approx 0.5$, their contribution on the m value should be halved and Eq. (2) should be improved,

$$\Gamma' = n/(m-1). \tag{6}$$

Table I shows the ε values calculated in terms of Eq. (1) while the Γ values in Eq. (1) are determined separately using Eqs. (2) and (6). The $\bar{E}_g$ values are determined by the peak position of the absorption diagrams in Fig. 1.[12] These values are in accordance with the experimental values $\bar{E}_g''$ for NiO and CoO, which confirms the rationality and correctness of the considered scissors values in our simulation. It is obvious that $\varepsilon^{Le}<\varepsilon'$ and Eq. (6) gives better approximation than Eq. (2) when the experimental values ε'' are compared. Thus, Levine's model overestimates the effects of s electron levels of nonmetals on m values.

IV. CONCLUSION

In summary, the electronic structures of several transition metal compounds are carried out by using LDA+U technique. The results show that s electron levels of nonmetals can only contribute a half of the levels on m. Thus, Levine model should be improved, which leads to a more accurate prediction on the dielectric constants and average optical energy gap of TM compounds.

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