On the Volume-Dependence of the Index of Refraction from the Viewpoint of the Complex Dielectric Function and the Kramers−Kronig Relation

Xavier Rocquefelte,[†] Stéphane Jobic,*,[†] and Myung-Hwan Whangbo*,[‡]

Institut des Matériaux Jean Rouxel, Laboratoire de Chimie des Solides, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 03, France and Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

How indices of refraction $n(\omega)$ of insulating solids are affected by the volume dilution of an optical entity and the mixing of different, noninteracting simple solid components was examined on the basis of the dielectric function $\epsilon_1(\omega) + i\epsilon_2(\omega)$. For closely related insulating solids with an identical composition and the formula unit volume V, the relation $[\epsilon_1(\omega) - 1]V = \text{constant}$ was found by combining the relation $\epsilon_2(\omega)V = \text{constant}$ with the Kramers−Kronig relation. This relation becomes $[n^2(\omega) - 1]V = \text{constant}$ for the index of refraction $n(\omega)$ determined for the incident light with energy less than the band gap (i.e., $\hbar\omega < E_g$). For a narrow range of change in the formula unit volume, the latter relation is well approximated by a linear relation between n and $1/V$.

1. Introduction

In 1863, Gladstone and Dale[1] observed a simple correlation between the index of refraction n and the mass density ρ_m of a liquid mixture, which can be written as

$$(n - 1)/\rho_m = \sum_i g_i f_i \tag{1}$$

where g_i and f_i are respectively the "specific refractivity" (often called the refractive coefficient) and the weight fraction of a component i making up the solution. The refractive coefficient is given by $g_i = (n_i - 1)/\rho_{m,i}$, where n_i and $\rho_{m,i}$ are the index of refraction and the mass density of a pure component i, respectively. Sixty years later, Larsen found[2] that such a relation, i.e., $(n - 1)/\rho_m = \text{constant}$, can also be used to describe indices of refraction of vitreous and crystalline substances, and calculated the "specific refractivity" g_i, often referred to as the refractive coefficient or the Gladstone−Dale (GD) constant, for simple oxide components of numerous minerals. A revised set of g_i values was obtained for an increasing number of minerals by Jaffe[3] and by Mandarino.[4] Jaffe investigated 121 minerals to find that the GD relation holds surprisingly well for most minerals. In addition, Mandarino proposed to define a "compatibility index" to estimate the internal consistency of an index of refraction data. These investigations elaborated the empirical GD relation without probing its theoretical foundation.[5] A theoretical justification for the GD relation was attempted by Eggleton,[6] who derived the GD relation from the Anderson's general refractivity equation for specific cases of $1.4 < n < 1.8$. However, the GD relation is applicable to many other systems for which $n > 1.8$.

In the present work, we investigate the theoretical origin of the GD relation by studying the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, where ϵ_1 and ϵ_2 are the real and the imaginary

parts of the dielectric function, respectively. The dielectric function describes the linear response of the electronic structure of an insulating material to the electrical field of the incident radiation with energy $\hbar\omega$. Recently, we investigated the indices of refraction of seven TiO_2 allotropes, $TiOF_2$, and TiF_4 on the basis of first-principles density functional theory (DFT) electronic band structure calculations.[7,8] These studies showed that the trends in the experimentally determined indices of refraction n (determined by employing the sodium D line, i.e., $\lambda = 589$ nm or $\hbar\omega = 2.1$ eV) of these compounds are not explained by their optical band gaps, but by the total absorption power per unit volume $I(\epsilon_2)$, i.e.,

$$n \propto I(\epsilon_2) \tag{2}$$

where

$$I(\epsilon_2) = \int_0^{+\infty} \epsilon_2(\omega) \, d\omega \tag{3}$$

For the seven TiO_2 allotropes, the total absorption power per formula unit is nearly constant,[7] i.e.,

$$I(\epsilon_2)V = \text{constant} \tag{4}$$

where V is the formula unit volume. Consequently, $n \propto 1/V \propto \rho_m$, which provides a theoretical support for the GD relation and implies that as long as the optical entity is the same (i.e., the atoms involved in the optical transitions are the same with similar chemical coordination and identical oxidation state), the index of refraction does not depend sensitively on how the electron density is distributed. This observation led us to introduce the concept of "optical channels",[8] which are defined as chemical bonds associated with a light absorbing entity. This local view of light absorption enables one to consider two factors affecting optical properties, i.e., the effect of the optical entity and that of the formula unit volume.

Equations 2 and 4 provide a theoretical support of the GD relation, but they are empirical observations from DFT electronic

* To whom correspondence should be addressed. E-mail: Mike_Whangbo@ncsu.edu, jobic@cnrs-imn.fr.
† Institut des Matériaux Jean Rouxel.
‡ North Carolina State University.
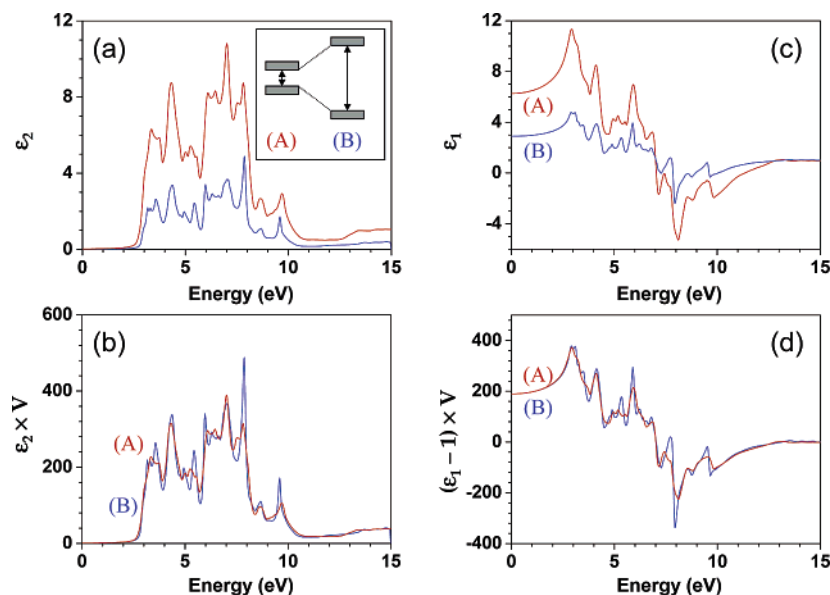
Figure 1. Optical properties obtained from DFT electronic band structure calculations (ref 7) for two hypothetical CdI$_2$ structures A and B of TiO$_2$ as a function of the formula unit volume V: (a) $\epsilon_2(\omega)$, (b) $\epsilon_2(\omega)V$, (c) $\epsilon_1(\omega)$, and (d) $[\epsilon_1(\omega) - 1]V$. For A and B, $V = 36$ and 100 Å^3, respectively.

structure calculations. To provide a more rigorous theoretical justification for the GD relation, we examine in the present work a new relation between the index of refraction and the formula unit volume on the basis of the Kramers−Kronig relation, show how this leads to the GD relation and propose a simple rule by which to estimate the index of refraction of a mixture of different optical entities.

2. Quadratic Relation Between Index of Refraction and Formula Unit Volume

An implicit assumption of the GD relations describing minerals is that there is no interaction between different, simple components in a mineral (e.g., BaO, TiO$_2$, and SiO$_2$ in BaTiSi$_3$O$_9$). To probe the implications of this assumption, it is convenient to consider an ideal set of systems. For this purpose, our previous study[7] employed the hypothetical CdI$_2$-type structure of TiO$_2$, which consists of TiO$_2$ layers made up of edge-sharing TiO$_6$ octahedra. Thus, the formula unit volume of the CdI$_2$-type structure can be changed gradually by simply varying the interlayer separation without changing the individual TiO$_2$ layer structures. In this case, the optical channel (i.e., the Ti−O bonds) remains the same during the change in the formula unit volume. This set of model structures will be used in the present discussion. An identical reasoning can be applied to the seven polymorphs of TiO$_2$ (i.e, the columbite, rutile, brookite, anatase, ramsdellite, bronze, and hollandite structure types), although they span a narrow range of volume variation.[7]

For a given structure of the CdI$_2$-type TiO$_2$, we denote the index of refraction and the formula unit volume by n and V, respectively. In terms of the formula unit volume, the GD relation $(n - 1)/\rho_m = $ constant can be rewritten as,

$$(n-1)V = K_{GD} \qquad (5)$$

where K_{GD} is a constant that depends on the chemical composition (e.g., TiO$_2$) and the light absorbing entities (e.g., TiO$_6$ octahedra) and is directly related to the GD constant g and the formula weight for TiO$_2$. This expression means that $(n - 1)V$ = constant. As already mentioned, our DFT calculations of the indices of refraction for different structures of the CdI$_2$-type TiO$_2$ showed the empirical observations, $n \propto I(\epsilon_2)$, $I(\epsilon_2)V =$

constant, and $n \propto 1/V$. We now consider how to derive more rigorously the relation between the index of refraction and the formula unit volume. For this purpose, we compare the $\epsilon_2(\omega)$ spectra calculated for different structures of the CdI$_2$-type TiO$_2$. As shown in Figure 1a, the two $\epsilon_2(\omega)$ spectra have a similar shape. Therefore, this similarity and eq 4 indicate for any structure of the series that, to a first approximation, the absorption power at an incident light energy $\hbar\omega$ might satisfy the expression,

$$\epsilon_2(\omega)V = \text{constant} \qquad (6)$$

As compared in Figure 1b for the two different structures of the CdI$_2$-type TiO$_2$, this relation is surprisingly good. For two different structures A and B, eq 6 means that

$$\epsilon_2(\omega)_A V_A = \epsilon_2(\omega)_B V_B \qquad (7)$$

Equation 6 is a more stringent approximation than is eq 4. In what follows, we examine the implications of eq 6.

According to the Kramers−Kronig relation, $\epsilon_1(\omega)_A$ and $\epsilon_2(\omega)_A$ of a given structure A, which are related to the electronic polarizability and the electronic absorption, respectively, obey the relation

$$\epsilon_1(\omega)_A - 1 = \frac{2}{\pi}P\int_0^{+\infty}\frac{\omega'\epsilon_2(\omega')_A}{\omega'^2 - \omega^2}\,\mathrm{d}\omega' \qquad (8)$$

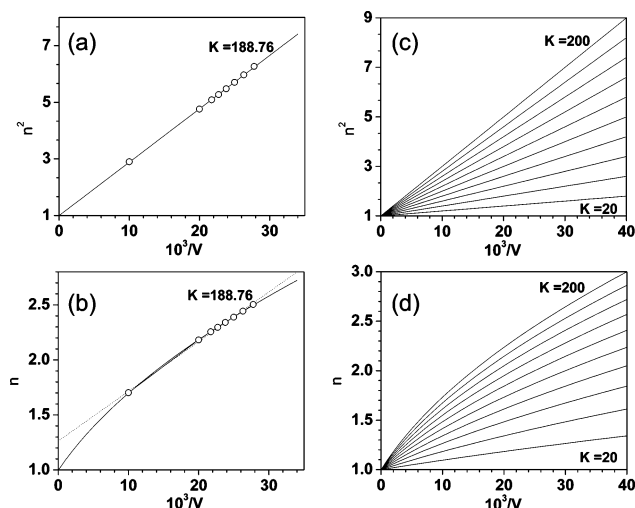where P indicates the principal value. By combining eqs 7 and 8, we obtain

$$\epsilon_1(\omega)_A - 1 = \frac{V_B}{V_A}\frac{2}{\pi}P\int_0^{+\infty}\frac{\omega'\epsilon_2(\omega')_B}{\omega'^2 - \omega^2}\,\mathrm{d}\omega' = \frac{V_B}{V_A}[\epsilon_1(\omega)_B - 1] \qquad (9)$$

Consequently,

$$[\epsilon_1(\omega)_A - 1]V_A = [\epsilon_1(\omega)_B - 1]V_B \qquad (10)$$

which means that

$$[\epsilon_1(\omega) - 1]V = \text{constant} \qquad (11)$$

Volume-Dependence of Index of Refraction

J. Phys. Chem. B, Vol. 110, No. 6, 2006 **2513**

Figure 2. Variation of n^2 and n for the hypothetical CdI$_2$-type structures of TiO$_2$ as a function of $1/V$, where the open circles are the data points obtained from DFT calculations (ref 7). (a) n^2 vs $1/V$, where the solid line is a linear fit with $n^2 = 0.99432 + 188.76/V$. (b) n vs $1/V$, where the solid line represents the equation $\sqrt{0.99432+188.76/V}$, and the dotted line is a linear fit with $n = 1.2625 + 45.167/V$. (c) Plots of $n^2 = 1 + K/V$ as a function of $1/V$. (d) Plots of $\sqrt{1+K/V}$ vs $1/V$. In (c) and (d), the K values were varied from 20 to 200 with the interval of 20.

for any structure of the series. As presented in Figure 1c, the $\epsilon_1(\omega)$ spectra calculated for the two different structures of the CdI$_2$-type TiO$_2$ have a similar shape. The corresponding $[\epsilon_1(\omega) - 1]V$ plots (Figure 1d) show that eq 11 is a very reasonable approximation. It is noticed that eq 11 is similar to the Clausius−Mossotti relation describing nonpolar gases,[9] except that local field effects are neglected. This is not surprising because the value of $\epsilon_1(\omega)$ is known to be affected by local fields at energies higher than approximately 30 eV.[10]

To relate eq 11 to the index of refraction, we note the general relationship

$$\epsilon_1(\omega) = n^2(\omega) - k^2(\omega) \qquad (12)$$

where the extinction coefficient $k(\omega)$ is related to the absorption coefficient $\mu(\omega)$ as $\mu(\omega) = 2\omega k(\omega)/c$, with c being the speed of light in vacuum. An insulator with band gap E_g does not absorb the incident light energy $\hbar\omega$ less than E_g. Namely,

$$k(\omega) = \epsilon_2(\omega) = 0, \text{ if } \hbar\omega < E_g \qquad (13)$$

so that

$$\epsilon_1(\omega) = n^2(\omega), \text{ if } \hbar\omega < E_g \qquad (14)$$

As a result, eq 11 is rewritten as

$$[n^2(\omega) - 1]V = \text{constant} \qquad (15)$$

3. Derivation of the Gladstone−Dale Relation

The GD relation, eq 5, states a linear relationship between n and $1/V$, whereas the new relationship, eq 15, shows a linear relationship between n^2 and $1/V$. To gain insight into this difference, we analyze the indices of refraction calculated for different structures of the CdI$_2$-type TiO$_2$. Figure 2a,b plots the calculated n and n^2 values as a function of $1/V$, respectively. (Details about these calculations were described in ref 7.) Figure 2a shows a perfect linear relationship between n^2 and $1/V$, i.e.,

$$(n^2 - 0.99432)V = 188.76 \qquad (16)$$

with $R^2 = 0.99988$. Therefore, when $1/V \rightarrow 0$, $n^2 \rightarrow 0.994$, and hence, $n \rightarrow 0.997$. The latter is practically 1, i.e., the refractive index expected for the vacuum (i.e., $1/V \rightarrow 0$). This kind of excellent linear relationship is not found in the n vs $1/V$ plot of Figure 2b. However, a set of data points of the n vs $1/V$ plot can be well described by a linear relation between n and $1/V$ if the variation of their formula unit volumes spans a narrow range. For example, the circled data points of Figure 2b is least-squares fitted by

$$(n - 1.2625)V = 45.167 \qquad (17)$$

with $R^2 = 0.99905$. This expression provides a good linear relation between n and $1/V$, although the intercept 1.2625 differs from 1 expected from the GD relation, $(n - 1)V = \text{constant}$. Nevertheless, it is noticed that the linear fit is nearly perfect when the extent of volume variation is small. To realize a nonlinear relationship between n and $1/V$, it is necessary to consider a wide range of volume change. As illustrated in Figure 2c,d, a linear relation between n vs $1/V$ becomes better as the indices of refraction become smaller. It is interesting to note that the initial Gladstone−Dale relation was observed for solutions of organic molecules, which exhibit relatively small refractive indices ($n \approx 1.5$).

It is of interest to consider a mathematical treatment that relates our relation $(n^2 - 1)V = \text{constant}$ to the GD relation $(n - 1)V = \text{constant}$. In general, at a given energy, the linear relation between n^2 and $1/V$ for a series of related systems can be expressed as

$$(n^2 - 1)V = C \qquad (18)$$

where C is a constant relevant for the series. Under the condition of $C/V \ll 1$, this expression is simplified as

$$(n - 1)V \approx C/2 \qquad (19)$$

which provides a theoretical basis for the GD relation, $(n - 1)V = \text{constant}$. However, we note that, for any real systems, the condition $C/V \ll 1$ cannot be met. This explains why the intercept of the linear relation between n and $1/V$ in eq 17 is not 1 but 1.2625. Nevertheless, the volume (or density) variation for most minerals spans a very narrow range. Consequently, the GD relation with the intercept of 1 holds well. This accounts for why the GD relationship holds surprisingly well for most minerals.
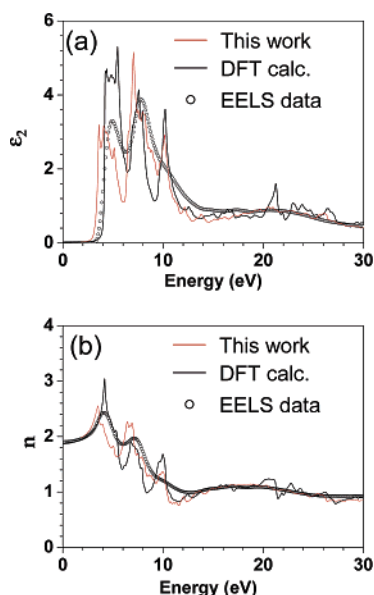
4. Relationship Between Index of Refraction and Formula Unit Volume for Mixtures

In the previous two sections, we have considered how the volume dilution of a component affects the index of refraction. In this section, we consider how the mixing of two different, noninteracting components (say, A and B) affects the index of refraction of the resulting mixture AB. Let the mole fractions of A and B in the mixture AB be x and $1 - x$, respectively. Since the optical entities of A and B are noninteracting, the following is expected from eq 6,

$$\epsilon_2(\omega)_{AB} V_{AB} = x \epsilon_2(\omega)_A V_A + (1 - x) \epsilon_2(\omega)_B V_B \qquad (20)$$

Consequently, the following is expected from eq 11,

$$[\epsilon_1(\omega)_{AB} - 1]V_{AB} = x[\epsilon_1(\omega)_A - 1]V_A + (1 - x)[\epsilon_1(\omega)_B - 1]V_B \qquad (21)$$

2514 *J. Phys. Chem. B, Vol. 110, No. 6, 2006*

Rocquefelte et al.

Figure 3. (a) ϵ_2 and (b) n calculated for TiOF$_2$. The white circles refer to the EELS experimental data (ref 8), the black solid line to DFT calculations (ref 8), and the red solid lines to eqs 20 and 22 for ϵ_2 and n, respectively.

Then, by analogy with eq 15, we obtain the expression

$$[n^2(\omega)_{AB} - 1]V_{AB} =$$
$$x[n^2(\omega)_A - 1]V_A + (1 - x)[n^2(\omega)_B - 1]V_B \quad (22)$$

under the condition that the light source used for index of refraction measurements satisfies the condition $\hbar\omega < E_g$ for both A and B.[11]

To examine how well eqs 20 and 22 work, we consider index of refraction of TiOF$_2$, which can be regarded as derived from TiO$_2$ by replacing one O atom with two F atoms. Thus, from the viewpoint of mixing, TiOF$_2$ is obtained by mixing TiO$_2$ and TiF$_4$ with equal mole fraction (i.e., $x = 0.5$). Figure 3a compares the $\epsilon_2(\omega)$ spectrum (circles) of TiOF$_2$ determined from the EELS experiment with two calculated $\epsilon_2(\omega)$ spectra. One calculated $\epsilon_2(\omega)$ spectrum (black solid line) is obtained from the electronic structure calculated for a model structure of TiOF$_2$ and the other from eq 20 using the $\epsilon_2(\omega)$ spectra of TiO$_2$ and TiF$_4$. It is remarkable that the DFT calculation for a model structure does not give a better agreement with experiment than does the simple mixing formula, eq 20. Figure 3b compares the $n(\omega)$ spectrum from the EELS experiment with the two calculated $n(\omega)$ spectra from the corresponding $\epsilon_2(\omega)$ spectra. Again, the simple mixing formula, eq 22, provides a good description of the observed $n(\omega)$ spectrum.

5. Concluding Remarks

In the present work, we have examined how the volume dilution of an optical entity affects the index of refraction. For closely related insulators made up of an identical light absorbing entity, we showed $[\epsilon_1(\omega) - 1]V =$ constant by combining the approximate relation $\epsilon_2(\omega)V =$ constant with the Kramers–Kronig relation. For the index of refraction $n(\omega)$ determined by the incident light with energy less than the band gap (i.e., $\hbar\omega < E_g$), the relation $[\epsilon_1(\omega) - 1]V =$ constant becomes $[n^2(\omega) - 1]V =$ constant. For a narrow range of change in the formula unit volume, this nonlinear relation between n and $1/V$ is well approximated by a linear relation $[n(\omega) - d]V =$ constant (with $d > 1$), although this expression does not exactly follow the GD relation $[n(\omega) - 1]V =$ constant. We extended the relation, $[n^2(\omega) - 1]V =$ constant, to describe the index of refraction of a mixture of noninteracting optical entities in terms of the indices of refraction of its components. It is striking that one can employ the optical properties of TiO$_2$ and TiF$_4$ to predict the optical properties of TiOF$_2$. Such an observation is hardly expected from sophisticated electronic structure calculations. It is of interest to probe under what conditions such a simple mixing rule is valid. The relation, $[n^2(\omega) - 1]V =$ constant, neglects the local field effect but holds well for a series of closely related solids most probably because the local field is nearly constant.

References and Notes

(1) Gladstone, J. H.; Dale, T. P. *Philos. Trans. R. Soc. London* **1863**, *153*, 317.
(2) Larsen, E. S. *U.S. Geol. Surv. Bull.* **1921**, *679*, 70.
(3) Jaffe, H. W. *Am. Mineral.* **1956**, *41*, 757.
(4) Mandarino, J. A. *Can. Mineral.* **1981**, *19*, 441.
(5) For a recent review, see: Teertstra, D. *Can. Mineral.* **2005**, *43*, 543.
(6) Eggleton, R. A. *Can. Mineral.* **1991**, *29*, 525.
(7) Rocquefelte, X.; Goubin, F.; Koo, H.-J.; Whangbo, M.-H.; Jobic, S. *Inorg. Chem.* **2004**, *43*, 2246.
(8) Rocquefelte, X.; Goubin, F.; Montardi, Y.; Viadere, N.; Demourgues, A.; Tressaud, A.; Whangbo, M.-H.; Jobic, S. *Inorg. Chem.* **2005**, *44*, 3589.
(9) Minkin, V. I.; Osipov, O. A.; Zhadanov, Y. A. *Dipole Moments in Organic Chemistry*; Plenum Press: New York, 1970.
(10) Vast, N.; Reining, L.; Olevano, V.; Schattschneider, P.; Jouffrey, B. *Phys. Rev. Lett.* **2002**, *88*, 037601.
(11) Given the masses (densities) of AB, A, and B as M_{AB}, M_A, and M_B (ρ_{AB}, ρ_A and ρ_B), respectively, eq 22 is rewritten as $[n^2(\omega)_{AB} - 1]/\rho_{AB} = g'_A f_A + g'_B f_B$, where $g'_A = [n^2(\omega)_A - 1]/\rho_A$, $g'_B = [n^2(\omega)_B - 1]/\rho_B$, $f_A = xM_A/M_{AB}$, and $f_B = (1 - x)M_B/M_{AB}$. Thus, the index of refraction for a multicomponent system will be given by $[n^2(\omega) - 1]/\rho_m = \sum_i g'_i f_i$, which is similar to eq 1.