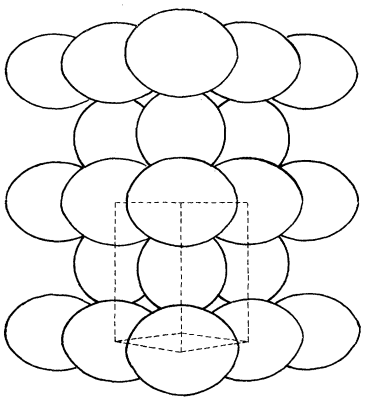

FIG. 2. Perspective drawing of γ N_2 (tetragonal) viewed normal to (110) face showing close packing of prolate molecules.

culated interplanar spacings and reflected intensities for the proposed model of γ N_2. For hcp N_2 at low pressure, the constant B in the Debye-Waller temperature factor has been evaluated[9] as 1.53 Å^2. In keeping with the higher density and larger θ_D of tetragonal N_2, we have used the extimated value $B = 1.4$ Å^2 in computing the expected intensities of Table I.

The structure consists of two types of layers which are perpendicular to the unique axis of the unit cell as shown in Fig. 2. In one of these layers the molecules lie flat in a square array with their long axes parallel and directed along one of the square diagonals. Alternate layers are shifted with the molecules again lying flat and parallel, but with their long axes directed along the other square diagonal and at right angles to molecules in the adjoining layers. This arrangement would seem to minimize the electric-quadrupole-quadrupole energy of the crystal.

A complete treatment of the subject will be submitted to an appropriate journal and will include a discussion of the α and β phases at high pressure and all three phases in nitrogen 15.

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OPTICAL DISPERSION AND THE STRUCTURE OF SOLIDS

S. H. Wemple and M. DiDomenico, Jr.
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 15 September 1969)

A new energy parameter $\mathcal{E}_d$ is introduced to describe dispersion of the electronic dielectric constant. This dispersion energy is found to obey an extraordinarily simple empirical relation in the more than 50 ionic and covalent crystals for which reliable refractive-index dispersion data are available. Based on this result we derive a structure-dependent electronic dielectric response function consisting of constant optical-frequency conductivity with high- and low-frequency cutoffs.

A simple, physically appealing dielectric model of electronegativity and ionicity has been developed recently by Phillips and Van Vechten[1-3] using the concepts of homopolar and heteropolar energy gaps. These authors find that a so called "average energy gap" E_g can be computed for a large group of diatomic crystals using simple empirical expressions. This average gap may be decomposed into a homopolar gap E_h and a heteropolar gap C by the quadrature relation $E_g^2 = E_h^2 + C^2$ and is defined (apart from a factor of order unity) by the equation

$$E_g^2 = (\hbar\omega_p)^2/[\epsilon_1(0)-1], \quad (1)$$

where $\hbar\omega_p$ is the plasma energy of the valence electrons, and $\epsilon_1(0)$ is the static electronic dielectric constant ($\epsilon = \epsilon_1 + i\epsilon_2$).

In this Letter we introduce a new energy pa-

rameter $\mathcal{E}_d$, to describe dispersion of the electronic dielectric constant (or refractive index). This "dispersion energy," which is related to interband transition strengths, obeys an extraordinarily simple empirical relation in over 50 widely different "ionic" and "covalent" nonmetallic crystals. Based on experimental observations we show the following. (1) $\mathcal{E}_d$ is independent of the lowest band gap and internuclear spacing and is essentially the same in all covalent and ionic compounds when normalized by the cation coordination number, anion valency, and number of valence electrons per anion. (2) A realistic model dielectric response function consists of constant optical-frequency conductivity ($\omega\epsilon_2 = \text{constant}$) with high- and low-frequency cutoffs. The dispersion energy is a direct measure of the conductivity. (3) Crystals are found to group into distinct ionic and covalent classes with the transition between the two occurring in AB crystals having the wurtzite structure.

We define the rth moment of the optical spectrum of a crystal by the relation

$$M_r = (2/\pi)\int_{\mathcal{E}_g}^{\infty} \mathcal{E}^{3-2r}\epsilon_2(\mathcal{E})d\mathcal{E}, \tag{2}$$

where $\mathcal{E} = \hbar\omega$, $\epsilon_2(\mathcal{E})$ is the imaginary part of the electronic dielectric function, and $\mathcal{E}_g$ is the lowest band-gap energy. The real part $\epsilon_1(\mathcal{E})$ is represented by a single Sellmeier oscillator at low energies, i.e.,

$$\epsilon_1(\mathcal{E}) - 1 = \mathcal{F}/(\mathcal{E}_0^2 - \mathcal{E}^2). \tag{3}$$

Here $\mathcal{F}$ and $\mathcal{E}_0$ are oscillator-strength and interband-energy parameters. As described in detail elsewhere[4] Eq. (3) is obeyed, for $\mathcal{E} \lesssim \mathcal{E}_g$, in all nonmagnetic materials for which refractive-index dispersion data are available. We emphasize that our use of Eq. (3) does not imply that $\mathcal{E}_0$ can be identified with any particular interband transition or that only a simplified $\epsilon_2(\mathcal{E})$ spectrum is being considered. It is easy to show[4] using the Kramers-Kronig (KK) relation that

$$\mathcal{E}_d^2 \equiv (\mathcal{F}/\mathcal{E}_0)^2 = M_2^3/M_3, \tag{4}$$

$$\mathcal{E}_0^2 = M_2/M_3. \tag{5}$$

We have introduced in Eq. (4) the dispersion energy $\mathcal{E}_d$, which is defined in such a way as to weight most heavily values of $\epsilon_2(\mathcal{E})$ near the band gap. A relation analogous to Eq. (4) can also be written for the Phillips band-gap parameter E_g defined by Eq. (1). The f-sum-rule integral

$$M_1 = (2/\pi)\int_{\mathcal{E}_g}^{\infty} \mathcal{E}\epsilon_2 d\mathcal{E} = (2/\pi)^2(\hbar\omega_p)^2, \tag{6}$$

and the KK relation at $\mathcal{E} = 0$, when substituted into Eq. (1), yield the expression

$$E_g^2 = M_1/M_2. \tag{7}$$

Equation (7) relates E_g to the first and second moments of the ϵ_2 spectrum and thus weights ϵ_2 at higher energies more heavily than the corresponding expression for $\mathcal{E}_d$. We also note that E_g does not depend on the magnitude of ϵ_2 whereas $\mathcal{E}_d$ does, so that interband transition strengths are not contained in the Phillips-model parameter E_g.

We have fitted refractive-index dispersion data taken from a variety of sources[4] to Eq. (3) and have obtained the experimental values of $\mathcal{F}$, $\mathcal{E}_0$, and $\mathcal{E}_d$ listed in Table I.[5] Inspection of Table I shows that $\mathcal{E}_d$ is strikingly constant within the various crystal groupings although $\mathcal{F}$ and $\mathcal{E}_0$ vary widely. For example $\mathcal{E}_d \approx 12.5$ eV in the NaCl-type alkali halides, and $\mathcal{E}_d \approx 25$ eV in 19 oxides having a variety of complex crystal structures. This factor of 2 difference suggests a possible simple connection between $\mathcal{E}_d$ and the anion valency Z_a. Further support for such a relationship is provided by the ratio 2:3:4 between values of $\mathcal{E}_d$ in II-VI, III-V, and IV-IV compounds. A simple relationship between $\mathcal{E}_d$ and the coordination number N_c of the nearest-neighbor cation is also indicated by Table I. For example a ratio of about 8/6 is observed between 8-coordinated and 6-coordinated halides. Furthermore, all the oxides having values clustering around 25 eV are 6-coordinated despite differences in crystal structure. The two 4-coordinated oxides show values approximately 4/6 as large. The above observations suggest that $\mathcal{E}_d \propto N_c Z_a$. Turning to the thallium halides, we observe that $\mathcal{E}_d$ is somewhat higher than in the isostructural 8-coordinated alkali halides. We believe that the higher oscillator strength in the thallium salts is due to the $6s^2$ electrons of the Tl^+ ion. These two electrons plus the eight electrons in the s-p orbitals would yield a total of $N_e = 10$ valence electrons per anion rather than $N_e = 8$ as in the alkali halides. We might then expect a ratio of 10/8 between corresponding values of $\mathcal{E}_d$. This is nearly the ratio observed in Table I. The noble-metal salts appear to fall outside the framework outlined above. For example, the value of $\mathcal{E}_d$ in 6-coordinated AgCl is almost a factor of 2 higher than in the isostructural alkali halides, i.e., $\mathcal{E}_d$ is nearly the same as observed in 6-coordinated oxides. Similarly, in zinc-blende CuCl $\mathcal{E}_d$ has almost the same value as observed in 4-coordi-

Table I. Experimentally determined values of the Sellmeier parameters $\mathcal{E}_0$ and $\mathcal{F}$, the dispersion energy $\mathcal{E}_d$, and the normalized dispersion energy $\mathcal{E}_d/N_c Z_a N_e$. For brevity we have included results for only one light-polarization direction in all anisotropic crystals. The various material groupings are labeled according to anion valency Z_a, nearest-neighbor coordination number N_c, and effective number of valence electrons per anion N_e.

CRYSTAL	$\mathcal{E}_0$(eV)	$\mathcal{F}$(eV²)	$\mathcal{E}_d$(eV)	$\mathcal{E}_d/N_cZ_aN_e$(eV)
NaCl-TYPE (N_c=6, Z_a=1, N_e=8)				
LiF	17.1	255	14.9	0.31
NaF	15	170	11.3	0.24
KF	14.8	183	12.3	0.26
NaCl	10.3	141	13.6	0.28
KCl	10.5	129	12.3	0.26
RbCl	10.4	127	12.2	0.25
CsCl	10.6	149	14.0	0.29
KBr	9.2	114	12.4	0.26
RbBr	9.1	110	12.1	0.25
KI	7.7	99	12.8	0.27
RbI	7.7	94	12.1	0.25
CsCl-TYPE (N_c=8, Z_a=1, N_e=8)				
CsCl	10.6	181	17.1	0.27
CsBr	9.4	159	17.0	0.27
CsI	7.5	114	15.2	0.24
CsCl-TYPE (N_c=8, Z_a=1, N_e=10)				
TlCl	5.8	120	20.6	0.26
TlBr	5.3	115	21.7	0.27
CaF_2-TYPE (N_c=8, Z_a=1, N_e=8)				
CaF_2	15.7	249	15.9	0.25
BaF_2	13.8	219	15.9	0.25
NOBLE METAL SALTS (Z_a=1, N_e=18)				
AgCl (N_c=6)	7.4	163	22	0.20
CuCl (N_c=4)	7.3	132	18.1	0.25
WURTZITES (N_c=4, Z_a=2, N_e=8)				
ZnO	6.4	109	17.1	0.27
CdS	4.9	99	20.4	0.32
CdSe	4.0	82	20.6	0.32
ZnS	6.15	155	25.2	0.39
OXIDES (N_c=6, Z_a=2, N_e=8)				
MgO	11.3	249	22	0.23
CaO	9.9	224	22.6	0.24
Al_2O_3	13.4	370	27.5	0.29
$Y_3Al_5O_{12}$	11.1	282	25.4	0.26
TeO_2	6.24	145	23.2	0.24
$SrTiO_3$	5.68	135	23.7	0.25
$BaTiO_3$	5.57	131	23.3	0.24
$KTaO_3$	6.50	159	23.7	0.25
$KTa_{0.65}Nb_{0.35}O_3$	6.17	144	23.4	0.25
$LiTaO_3$	7.49	196	26.1	0.27
$LiNbO_3$	6.65	172	25.9	0.27
$Ba_2NaNb_5O_{15}$	6.20	153	24.6	0.26
TiO_2	5.24	135	25.7	0.27
$MgAl_2O_4$	12.1	282	23.3	0.24
$CaWO_4$	9.15	213	23.3	0.24
$ZnWO_4$	7.46	194	26.0	0.27
$CaMoO_4$	8.26	190	23.0	0.24
$PbMoO_4$	5.4	122	22.6	0.24
$SrMoO_4$	8.6	183	21.3	0.22
OXIDES (N_c=4, Z_a=2, N_e=8)				
ZnO	6.4	109	17.1	0.27
SiO_2	13.6	250	18.3	0.29
ZINC-BLENDE (N_c=4, Z_a=2, N_e=8)				
ZnS	6.36	164	26.1	0.41
ZnSe	5.54	150	27.0	0.42
ZnTe	4.34	117	27.0	0.42
CdTe	4.13	106	25.7	0.40
ZINC-BLENDE (N_c=4, Z_a=3, N_e=8)				
GaP	4.46	161	36.0	0.38
GaAs	3.55	119	33.5	0.35
DIAMOND-TYPE (N_c=4, Z_a=4, N_e=8)				
C	10.9	541	49.7	0.39
Si	4.0	178	44.4	0.35
Ge	2.7	110	41	0.32

nated oxides. These results can be understood if the d electrons are included[3] in the total N_e, i.e., $N_e \approx 18$ rather than 8.

Based on the experimental results shown in Table I and the observations outlined above we can write the following general empirical expression for $\mathcal{E}_d$, applicable to over 50 nonmetallic-nonmagnetic compounds containing a single anion species[6]:

$$\mathcal{E}_d = \beta N_c Z_a N_e \text{ eV}, \tag{8}$$

where N_e is the number of effective valence electrons per anion, e.g., $N_e = 8$ in an s-p valence band; $\beta_i = 0.26 \pm 0.04$ eV for the ionic compounds[7] (halides and oxides); $\beta_c = 0.39 \pm 0.04$ eV for the covalent compounds[8] (all nonhalide, zinc-blende, and diamond structures); and β ranges between these extremes in simple AB-wurtzite crystals. The wurtzite structure can thus be viewed as transitional between two well-defined ionic and covalent crystal classes. The transitional character of wurtzites has also been observed experi-

mentally within the dielectric model of Phillips and Van Vechten.[2] Furthermore, Kurtin, McGill, and Mead[9] have deduced the existence of distinct ionic and covalent crystal classes based on observations of the barrier energies at metal-semiconductor interfaces, exciton strengths, and the relative importance of "direct" and "nondirect" transitions. These authors also find that wurtzite crystals tend to be distributed near the transition region between ionic and covalent classes. Their results imply, however, that ZnS is nearly ionic whereas we would place this material in the covalent class.

We now propose a dielectric model that can account for the empirical results summarized by Eq. (8). Because $\mathcal{E}_d$ is found experimentally to be independent of the band gap $\mathcal{E}_g$, a strong constraint is imposed on the form of the fundamental ϵ_2 spectrum [see Eqs. (2) and (4)]. We propose the following simple model ϵ_2 spectrum which satisfies this constraint:

$$\mathcal{E}\epsilon_2 = \sigma\hbar/\epsilon_0, \quad \mathcal{E}_g < \mathcal{E} < b\mathcal{E}_g,$$
$$\epsilon_2 = 0, \quad \mathcal{E} < \mathcal{E}_g \text{ and } \mathcal{E} > b\mathcal{E}_g. \tag{9}$$

In Eq. (9) the coefficient b is an arbitrary normalized bandwidth parameter, σ has units of conductivity, and ϵ_0 is the free-space permittivity. Our model dielectric response function thus consists simply of a constant optical-frequency conductivity σ with high- and low-frequency cutoffs. We show this spectrum in Fig. 1 for $b = 4$. We also show the single Sellmeier oscillator that produces equivalent dispersion of the refractive index for $\mathcal{E} \lesssim \mathcal{E}_g$. Our model spectrum should be contrasted to the results of the Penn model[10]

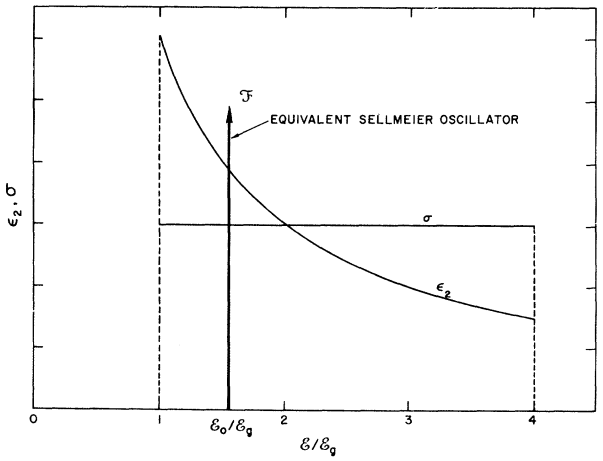

FIG. 1. Model dielectric functions ϵ_2 and σ together with equivalent Sellmeier oscillator for $b = 4$.

for which $\mathcal{E}\epsilon_2$ is singular at $\mathcal{E} = \mathcal{E}_g$ and falls off very rapidly with increasing energy.[11] Experimentally observed ϵ_2 spectra are more realistically described by the constant-σ model. It is also significant to note that the Penn model gives $\epsilon_1(0) - 1 = (\hbar\omega_p)^2/E_g^2$ with no theoretical connection between the parameters $\hbar\omega_p$ and E_g, whereas our model gives $\epsilon_1(0) - 1 = \mathcal{E}_d/\mathcal{E}_0$ as a consequence of the observed relation between $\mathcal{F}$ and $\mathcal{E}_0$. Structure associated with interband critical points or exciton bands is, of course, generally superimposed on the constant-σ "bond-breaking" background. This structure apparently has little influence on the moment integrals contained in Eq. (4).

Substituting the model spectrum given by Eq. (9) into Eqs. (4), (5), and (7) yields:

$$\mathcal{E}_d = (2\sqrt{3}/\pi)(\hbar/\epsilon_0)\sigma(b-1)/(1+b+b^2)^{1/2}, \tag{10}$$
$$E_g = \sqrt{b}\,\mathcal{E}_g, \tag{11}$$
$$(\mathcal{E}_0/E_g)^2 = 3b/(1+b+b^2). \tag{12}$$

Therefore in terms of our model the dispersion energy $\mathcal{E}_d$ is a measure of the optical-frequency conductivity σ and is consequently an interband oscillator-strength parameter. The parameter E_g of the Phillips model retains its significance as a band-gap parameter and is simply the geometric mean of the upper and lower cutoff energies. Combining Eqs. (10) and (8) we find that

$$\sigma/N_c Z_a N_e = (\pi/2\sqrt{3})(\epsilon_0/\hbar)\beta(1+b+b^2)^{1/2}/(b-1). \tag{13}$$

Because $\beta_i \approx 0.26$ eV in ionic crystals and $\beta_c \approx 0.39$ eV in covalent crystals, it is tempting to ascribe this difference solely to differences in bandwidth and thus to assign the same universal numerical value to the quantity $\sigma/N_c Z_a N_e$ in all ionic and covalent crystals. In order to estimate the bandwidth parameter we make use of Eqs. (12) and (13) and the following experimental observations: (1) $\beta_c \approx 1.5\beta_i$, and (2) $\mathcal{E}_0 \approx 0.8E_g$ for covalent crystals (compare values of $\mathcal{E}_0$ shown in Table I with values of E_g tabulated by Van Vechten[3]). We then find that $b_c \approx 3.4$ and $b_i \approx 2.1$, and, as expected, $b_c > b_i$. Equation (13) now becomes

$$\sigma/N_c Z_a N_e = 80 \pm 12\ (\Omega\ \text{cm})^{-1}. \tag{14}$$

Equation (14) expresses the striking result that both the magnitude and dispersion of refractive indices in over 50 widely different nonmetallic ionic and covalent crystals can be related to es-

sentially the same normalized value of optical-frequency conductivity. In our model only bandwidth differences distinguish ionic from covalent crystals. Neither the energy gap nor the internuclear spacing enter into the computation of σ. The bandwidth parameters b_c and b_i measure the width of those parts of the conduction and valence bands which play important roles in determining crystal structure. For the more covalent crystals Phillips[12] has correlated crystal structure with a dielectrically defined bond ionicity. Here we have found from a spectroscopic analysis of covalent and ionic crystals that the N_c and Z_a of Pauling's classical resonating-bond theory[13] play an important role. In both cases the usual picture of crystal structure as determined only by the energies of occupied valence states is discarded in favor of relationships between structure and the optical spectrum.

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[5]We have excluded from Table I all small-band-gap semiconductors since it is difficult to determine with sufficient accuracy the free-carrier and/or photoionization contribution to the observed refractive-index dispersion for such materials. The results tabulated for Ge may in fact be influenced by such extrinsic effects.

[6]In magnetic transition-metal compounds we would expect weaker oscillator strength for transitions from the occupied d or f orbitals. For example, in EuO $\mathcal{E}_d = 9$ eV rather than approximately 25 eV as observed in 6-coordinated nonmagnetic oxides. In complex crystals containing anion radicals we find, for example, that $\mathcal{E}_d \approx 16$ eV for several phosphates and $\mathcal{E}_d \approx 20$ eV for a group of iodates and carbonates.

[7]Based on available refractive-index data the β values for LiF and AgCl fall slightly outside the limits given for β_i.

[8]The β value for Ge lies slightly below the lower bound given for β_c. This may be due to a small free-carrier contribution to the refractive index data.

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REFLECTION SPECTRUM OF SOLID ARGON IN THE VACUUM ULTRAVIOLET*

R. Haensel and G. Keitel

Physikalisches Staatsinstitut, II. Institut für Experimentalphysik der Universität Hamburg, Hamburg, Germany

and

E. E. Koch and M. Skibowski

Sektion Physik der Universität München, München, Germany

and

P. Schreiber

Deutsches Elektronen-Synchrotron, Hamburg, Germany

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The reflectance of solid Ar has been measured at 20°K for an angle of incidence of 15° in the photon energy range from 10 to 30 eV using the synchrotron radiation of DESY. The reflectance data reveal a spin-orbit-split exciton series with sharp maxima converging to about 14 eV together with broader peaks above 14 eV due to transitions between the valence and conduction band. The results are compared with the absorption spectrum associated with the $2p$ core levels.

Several optical[1,2] and electron-energy-loss[3] measurements have been performed on solid Ar in order to study its electronic transitions from the valence band. These investigations were confined to the spectral region below 14 eV. They were made with limited resolution so that the existence of an exciton series converging to the band gap could not clearly be proved. Thus these measurements led to some uncertainty in the determination of the series limit.[4]