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New one-parameter fits of sub-bandgap optical properties of crystals

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Abstract. Insufficient attention to excitonic processes has been cited in criticism of single-parameter models of the optical properties of solids. On the other hand, the thermally measured energy gap, E_g , has been shown to be a useful predictor of linear and nonlinear susceptibilities of indirect as well as direct gap materials. The explanation for such unanticipated correlations lies in the fact that the virtual excitations that contribute to the real part of the dielectric response include Wannier excitons with polycentric momentum distributions. When these excitations subsequently decay into excitons with better defined momentum, and phonons, Frenkel's selection rule, as discussed by Wannier, applies. In the long wavelength dielectric response no such possibility exists and the dominant excitations, whether in direct or in indirect gap materials, involve k -states at valence band maxima and conduction band minima.

1. Introduction

It is an obvious feature of the dielectric response of insulating crystals that the bandgap and the various linear and nonlinear response functions are inversely related. This qualitative observation suggests the possibility of predicting dielectric response from a single parameter as was indeed proposed by Penn [1]. The Penn gap is an average over the Brillouin zone of the direct gap in accordance with the expectation that the virtual excitations contributing to first-, second- and higher-order polarization energies leave the k -vector as a good quantum number which is approximately conserved under optical excitation. However, since Wannier's paper of 1937 [2] it has been clear that, while Frenkel's selection rule (use of conserved crystal momentum to label excitations) would apply for real absorptive processes, the virtual intermediate states are states for which the k -vector is not a good quantum number. The implication of this for a single parameter model of real dielectric response is that the distinction between direct and indirect processes should not be too rigidly maintained in handling the virtual excitations involved in the real dielectric susceptibility.

The electron and hole wavepackets which together form a Wannier exciton are best considered in momentum space and can be related to the momentum space representation of hydrogen wavefunctions given by Podolsky and Pauling [3]. The implications of this way of looking at things and, in particular, the possibility that it can reconcile band calculations with the bond additivity approximation of Buckingham and Orr [4] are explored in section 2.

In section 3 the bond additivity approximation is applied to data for the second-order nonlinear dielectric susceptibility of zinc-blende and wurtzite polymorphs of ZnS. The data

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appear to be compatible, at least, with the supposition that the dielectric response of a crystal can be approximated by the dielectric response of its bonding electrons taken in pairs.

In the light of the discussion in section 2 of the connection between momentum space representations of the electron and hole wave packets and the minimum exciton energy the selection of gap parameter for a one-parameter fit of dielectric properties of semiconductors and insulators is discussed in section 4. Using data from published compilations one-parameter fits using the thermal energy gap and a certain indirect gap are presented.

Finally, in section 5, the prospect is assessed that some understanding of the dielectric response of glasses, doped and otherwise, can be obtained using the approach outlined here.

2. Exciton intermediate states

In setting out the structure of excitons, Wannier [2] was at pains to make clear that these were the virtual excited states of the crystal. It is the energy of such states that is crucial to the evaluation of perturbative terms of various order that contribute to corresponding dielectric response functions.

'According to Wannier, the exciton is composed of an electron wave packet made up of states from the conduction band, and a hole wave packet taken from the valence band, multiplied by an envelope function depending on the relative electron-hole coordinate $r_e - r_h$.'—J C Phillips [5].

Hydrogen-like wavefunctions in momentum space given by Podolsky and Pauling [3] make the relevant wavepackets easy to visualize. From the general wavefunction

$$\Psi_{nlm}(p, \theta, \phi) = -C \left[\left(\frac{n}{2\pi} \right) (-1)^l \pi 2^{l+4} l! \right] \frac{\zeta^l}{(\zeta^2 + 1)^{l+2}} C_{n-l-1}^{l+1} \left(\frac{\zeta^2 - 1}{\zeta^2 + 1} \right) Y_{lm}(\theta, \phi)$$

where $\zeta = np$, one obtains [6] for the 1s, 2s and 2p states the momentum distributions

$$\begin{aligned} I_{1,0}(p) &= \frac{32}{\pi} p^2 / (p^2 + 1)^4 \\ I_{2,0}(p) &= 32 p^2 (p^2 - 1) / (p^2 + 1)^5 \\ I_{2,1}(p) &= \frac{512}{3\pi} p^4 / (p^2 + 1)^6 \end{aligned}$$

where p is measured in units αmc with α the fine structure constant. When the electron wave packet has a momentum distribution that matches the many-valley conduction band of an indirect gap semiconductor it is plausible that the thermal gap should be predictive of the real optical response. For a many-valley conduction band such as those in silicon and germanium construction of an electron wave packet with a view to minimizing the exciton energy suggests an exciton diameter of the order of the nearest neighbour atomic spacing, that is to say, the length of the bonds between atoms. In saying this it is presumed that the phenomena in question can be understood in terms of states from the first zone and that, consequently, *Umklapp* processes can be ignored. It is, therefore, reasonable to suggest that the excitonic nature of virtual states may validate the bond additivity approximation of polarizability and hyperpolarizability [4] even in its application to condensed matter. Some evidence for the utility of the bond additivity approximation for the dielectric properties of crystals is given in the next section.

The correct characterization of the intermediate states has implications for the discovery of empirical relations between optical constants and bandgap parameters and this is discussed in section 4. More importantly, difficulties in evaluating matrix elements in detailed numerical modelling of the optical response [7] can be seen to arise because of an

inappropriate choice of basis states. Matrix elements for Bloch states must be combined with the correct phases, which for the virtual intermediate states define the exciton wavefunction, if the correct dielectric response functions are to be obtained.

3. Bond additivity for polymorphs of ZnS

The nearest neighbour zinc–sulphur bonds in wurtzite can be assigned a second-order hyperpolarizability on the basis of the second-order dielectric susceptibility tensor elements reported by Patel [8]. On the assumption that the bond hyperpolarizabilities remain the same in the zinc-blende structure, the second-order susceptibility of this polymorph can then be calculated and subsequently compared with experiment. In the wurtzite structure there are seven different zinc–sulphur bond orientations and two independent susceptibility tensor elements while in cubic zinc-blende there are only four bond orientations leading to one independent tensor element. A polar bond between two atoms has two second-order hyperpolarizability constants. Consequently this problem is solvable in the form posed provided that it is well conditioned.

The second-order dielectric susceptibility tensor for wurtzite has the form [9]

$$\begin{array}{cccccc} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{15} & d_{15} & d_{33} & 0 & 0 & 0 \end{array}$$

with $d_{15} = -19 \text{ pm V}^{-1}$ and $d_{33} = +37 \text{ pm V}^{-1}$. Orthogonal transformation gives the bond hyperpolarizabilities β_{15} and β_{33} in a similar tensor as $(\epsilon_0/2n)(-14.4 \text{ pm V}^{-1})$ and $(\epsilon_0/2n)(-22.5 \text{ pm V}^{-1})$ where $2n$ is the number of zinc–sulphur bonds per unit volume of crystal. From this, with further orthogonal transformations, the second-order susceptibility tensor for zinc-blende is

$$\begin{array}{cccccc} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{array}$$

with $d_{14} = +32 \text{ pm V}^{-1}$. This is to be compared with a measured value of $+30 \text{ pm V}^{-1}$ [8].

The bond additivity approximation of dielectric response is attractive for its simplicity and transparency. If the argument for its applicability given in section 2 is indeed valid, then applications such as those described in section 5 will surely follow.

4. Single-parameter prediction of dielectric response

Dielectric susceptibility constants of increasing order arise from correspondingly higher-order corrections to the energy of the material in an external electric field. When the frequency of the field is far below the interband resonance, the corrections contain in their denominators increasing powers of the bandgap energy. One may suppose that such long wavelength susceptibilities of the n th order go inversely as the gap energy to the power n . Figure 1 shows that this is indeed approximately the case when the thermal energy gap is used as the gap parameter. The susceptibility constants used for figure 1 are shown in table 1 which is taken from the compilations in [9]. Where widely different values of a constant are quoted, as for example for $\chi^{(3)}$ of germanium, a geometrical average has been used. The placings of the lines showing inverse linear, quadratic and cubic dependence in

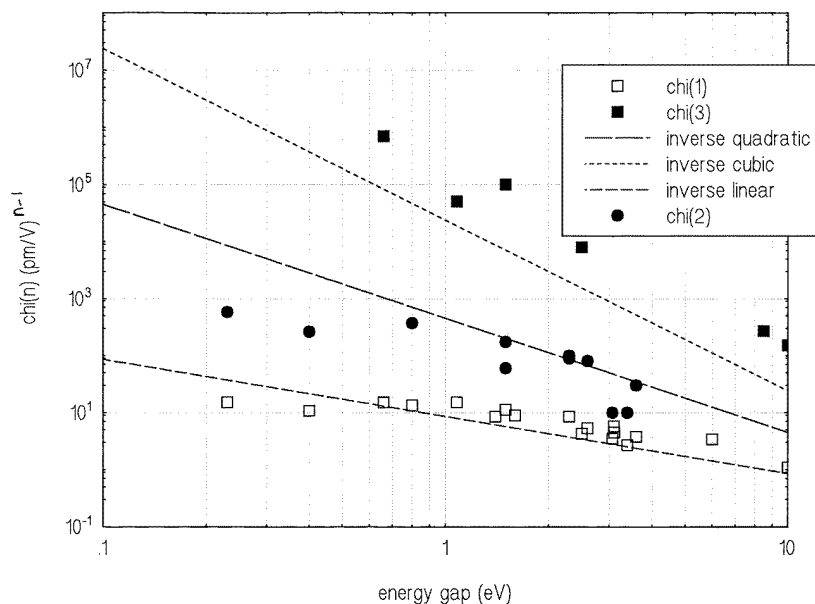


Figure 1. Linear and nonlinear susceptibilities.

Table 1. Nonlinear susceptibilities from the data compiled in [9].

Material	Bandgap E_g (eV)	$\chi^{(1)}$	$\chi^{(2)}$ (pm V ⁻¹)	$\chi^{(3)}$ (pm ² V ⁻²)
BN	6.0	3.4		
AlSb	1.6	8.9		
GaP	2.3	8.6	100	
GaAs	1.5	11.3	173	100 000
GaSb	0.8	13.4	370	
InP	1.4	8.6		
InAs	0.4	10.8	260	
InSb	0.23	15	580	
ZnS	3.6	3.8	30	
ZnSe	2.6	5.3	80	
ZnTe	2.3		90	
CdS	2.5	4.3		8000
CdTe	1.5		60	
KCl	8.5			270
CuCl	3.39	2.7	10	
CuBr	3.07	3.5	10	
CuI	3.11	4.5		
Ge	0.66	15		700 000
Si	1.08	15		51 000
SiC	3.1	5.7		
SiO2	10	1.1		150

figure 1 are not arbitrary but have been determined from bond (hyper)polarizabilities using ea_0 , where a_0 is the first Bohr radius, to estimate the electric dipole matrix elements and the gap energy for the excited state energy.

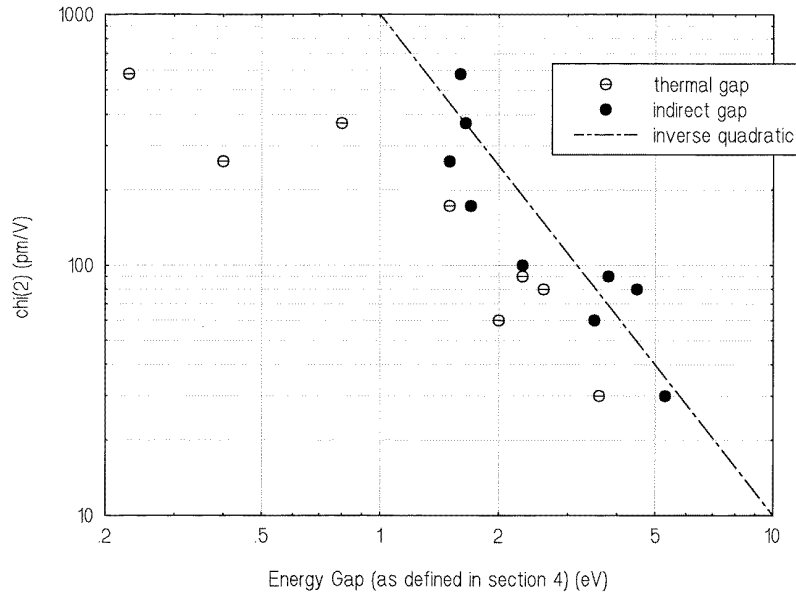


Figure 2. Gap dependence of second-order susceptibility.

Table 2. Bandgap parameters for zinc-blende polymorphs extracted from [10].

Material	Thermal gap (eV)	Indirect gap (eV)	$\chi^{(2)}$ (pm V ⁻¹)
GaP	2.3	2.3	100
GaAs	1.5	1.7	173
GaSb	0.8	1.65	370
InAs	0.4	1.5	260
InSb	0.23	1.6	580
ZnS	3.6	5.3	30
ZnSe	2.6	4.5	80
ZnTe	2.3	3.8	90
CdTe	2.0	3.5	60

While the inverse cubic dependence of the third-order nonlinear dielectric susceptibility in figure 1 is quite convincing, a question remains as to which bandgap parameter gives the best one-parameter fit. From what has been said before the lowest energy virtual intermediate excitations, which are the ones that dominate the perturbative sums, are built from electron and hole wave packets that exploit energy minima in the conduction band and energy maxima in the valence band. This being so, the thermal gap is likely to give a better fit to the dielectric properties than the direct gap. However, an electric dipole selection rule makes direct gap materials exceptional. If the hole wave packet is a 1s state, built from k -states near the zone centre, the electron wave packet for an allowed excitation may be a 2p, but not a 1s or 2s, state. Consequently a conduction band minimum at the zone centre is irrelevant to the construction of the required electron wave packet. What one needs are k -states near conduction band minima away from the zone centre. By choosing an indirect gap parameter, taken from the band structure calculations of Cohen and Bergstresser

[10] and summarized in table 2, one finds that the one-parameter fit of the second-order nonlinear susceptibility, $\chi^{(2)}$, shows the expected inverse gap parameter squared dependence (figure 2).

In this section it has been shown that the thermal energy gap is roughly predictive of low frequency, sub-bandgap, optical constants but that attention to the structure of intermediate states allows even better one-parameter fits to tabulated data.

5. Optical properties of glasses and colour centres

While there are four distinct bond orientations in the zinc-blende structure and seven in wurtzite, high temperature β -quartz has 12 bond orientations. Thus, in crystalline materials, computation of bulk properties using the bond additivity approximation is straightforward if tedious. One reason for wanting to validate the bond additivity approximation is that it offers a way of understanding otherwise intractable problems such as the optical properties of glasses containing point defects. Application of the approximation to the extrinsic properties of crystals and glasses will generally be quite straightforward. Once the structure of a defect has been determined and represented in terms of the new bonds created, fitting of optical properties by bond polarizabilities involves only a small number of tensor transformations and additions.

Table 3. Sources of experimental data on intrinsic and extrinsic contributions to fused silica susceptibilities.

Susceptibility	Intrinsic	Extrinsic			
		Substituted Ge	Ge: lone pair	Ge:E'	OH ⁻
$\chi^{(1)}$	yes [11]	yes [12]		yes [14]	yes [13]
$\chi^{(2)}$ (pm V ⁻¹)			yes [14]		
$\chi^{(3)}$ (pm ² V ⁻²)	yes [9]				

Table 3 shows some properties of fused silica for which experimental data are available which could enable the polarizabilities of various intrinsic and extrinsic bonds to be determined. One problem made accessible by this approach is that of predicting the changes brought about by point defect orientation. Such reorientation is relevant to field and light induced $\chi^{(2)}$ susceptibility in glass waveguides and the production thereby of electro-optic and nonlinear components.

6. Conclusion

The excitonic nature of virtual intermediate states contributing to the long wavelength dielectric response of crystals has been explored in the context of Wannier's description of excitons and Podolsky and Pauling's analysis of hydrogen-like states in momentum space. It has been established that one-parameter fits are able to predict the linear and nonlinear dielectric properties of crystalline insulators. The facts that the bandgap parameter used in such fits needs to reflect the excitonic nature of the intermediate states and that energy considerations favour rather localized electron and hole wave packets suggest the possibility of applying the bond additivity approximation to crystalline media. Further tests of this approximation should now be made to establish its value in understanding the influence of point defects on optical properties of both crystals and glasses.

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