Lawrence Berkeley National Laboratory

Recent Work

Title

CORRELATION BETWEEN THE STATIC DIELECTRIC CONSTANT AND THE MINIMUM ENERGY GAP

Permalink

<https://escholarship.org/uc/item/0785n6mq>

Authors

Chadi, D.J.
Cohen, Marvin L.

Publication Date

1974-09-01

CORRELATION BETWEEN THE STATIC DIELECTRIC
CONSTANT AND THE MINIMUM ENERGY GAP

D. J. Chadi and Marvin L. Cohen

September, 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LBL-3190
c.f.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Correlation Between the Static Dielectric Constant
and the Minimum Energy Gap*

D. J. Chadi and Marvin L. Cohen

Department of Physics, University of California

and

Inorganic Materials Research Division,

Lawrence Berkeley Laboratory, Berkeley, California 94720

Abstract

For binary $A^N B^{8-N}$ type crystals we find a striking and useful correlation between the static electronic dielectric constant and $(V^{1/2} E_{\min})^{-1}$ where $E_{\min}$ is the minimum (direct or indirect) energy gap between the valence and conduction bands and V is the volume per valence electron.

For a large series of crystals (with gaps > 0.5 eV) we find that the electronic contribution to the static dielectric constant, $\epsilon_1(0)$, is described to a very good approximation by a relation of the type

$$\epsilon_1(0) - 1 = \frac{\alpha}{V^n E_{\min}} \quad (1)$$

where α is a constant, V is the volume per electron, $n \approx 1/2$, and $E_{\min}$ is the minimum (direct or indirect) energy gap between the valence and conduction bands. We find the constant α to have the same value for 8 electron $A^N B^{8-N}$

crystals with the diamond, zincblende or rocksalt structures; this constant also has the same value for wurtzite crystals with 16 electrons per primitive cell. The choice of $n = 1/2$ gives the best overall results but $n = 1/3$ gives somewhat improved values for the rocksalt crystals.

The relation given by (1) is obviously inadequate for crystals with a small energy gap and it overestimates $\epsilon_1(0)$ for these crystals. Despite this restriction (1) is useful for estimating $\epsilon_1(0)$ for a large number of crystals once $E_{\min}$ and the lattice constant are known. In Table I we have used (1) with $n = 1/2$ to evaluate $\epsilon_1(0)$ for a series of crystals which have energy gaps greater than 0.5 eV. For the rocksalt crystal structures the values of $\epsilon_1(0)$ obtained from (1) using $n = 1/3$ are also given (in parenthesis) in Table I. Most of the lattice constants and the experimental values of $\epsilon_1(0)$ listed in Table I were obtained from Van Vechten.¹ The experimental values of $E_{\min}$ were gathered from a number of sources. For crystals with the diamond, zincblende and rocksalt structure (1) can be expressed conveniently as

$$\epsilon_1(0)-1 = \frac{\beta}{a^{1.5} E_{\min}} \quad (n = 1/2) \quad (2)$$

or

$$\epsilon_1(0)-1 = \frac{\gamma}{a E_{\min}} \quad (n = 1/3) \quad (3)$$

where a is the cubic lattice constant. The value of β was

determined by fitting to the experimental value of $\epsilon_1(0)$ in Si. As seen from Table I the same value of β also gives a very good prediction of $\epsilon_1(0)$ in NaCl. The value of β in Table I is $\beta = 412.1$, where a is measured in Bohr units and $E_{\min}$ in eV. For the rocksalt crystals (3) with $\gamma = 124.5$ (fitted to $\epsilon_1(0)$ for NaCl) gives slightly better results than (2).

In Table I, for the diamond and zincblende crystals the maximum deviation from the experimental value is about 25% and the average deviation is only about 10-15%. This is remarkable in view of the variety of crystal structures and the rather large number of crystals involved. We have been unable to obtain an expression as simple as (2) or (3), with only one adjustable parameter, in which $E_{\min}$ is restricted to be the minimum direct energy gap between the valence and conduction bands. In addition for crystals with indirect energy gaps we find that the choice of (2) or (3) with $E_{\min}$ (indirect) is always better than $E_{\min}$ (direct). This latter observation is particularly difficult to justify or understand theoretically. The formal expression for $\epsilon_1(0)$ is given by

$$\epsilon_1(0)-1 = (\hbar\omega_p)^2 \sum_{v,c} \int_{BZ} d^3k \frac{f_{vc}(\underline{k})}{E_{vc}^2(\underline{k})} \quad (4)$$

where ω_p is the plasma frequency of the valence electrons, f_{vc} is the valence-conduction band oscillator strength and $E_{vc}(\underline{k})$ is the energy difference at $\underline{k}$. The usual approximation

to (4) consists of taking $E_{vc}(k) \approx E_g$, where E_g is an average effective gap. Then using the f-sum rule we obtain the familiar result²

$$\epsilon_1(0)-1 = \left(\frac{\hbar\omega_p}{E_g}\right)^2. \quad (5)$$

This result is very different in its dependence on energy gap and lattice parameters than (1). The only possibility of obtaining a minimum (direct or indirect) energy gap as in (1) starting from (4) appears to be through the matrix elements f_{vc} . At this point, however, we do not have a theory of the dependence of f_{vc} on the lattice constant or the minimum energy gap.

References

- * Supported in part by the National Science Foundation Grant No. 35688, and the U.S. Atomic Energy Commission.
1. J. A. Van Vechten, Phys. Rev. 182, 891 (1969).
 2. J. M. Ziman, Principles of the Theory of Solids, Cambridge University Press, 1964, p. 139.

Table Caption

Table I. The values of $\epsilon_1(0)$ evaluated from $\epsilon_1(0) = \beta/a^{1.5}E_{\min}$ are compared to the experimental values of $\epsilon_1(0)$. For the rocksalt crystals the values of $\epsilon_1(0)$ obtained from $\epsilon_1(0) = \gamma/a E_{\min}$ are given in parenthesis. In the case of the wurtzite crystals the effective lattice constants given in Table I are calculated by assuming the crystals to be zincblende in structure with the volume per atom being the same as in the original wurtzite structure. Crystal with $E_{\min} < 0.5$ eV are not included. The values $\beta = 412.1$ and $\gamma = 124.5$ were used in determining $\epsilon_1(0)$.

Table I

a) Diamond and Zincblende

Compound	Lattice Constant (Bohr units)	$E_{\min}$ (eV)	$\epsilon_1(0)$ calculated	$\epsilon_1(0)$ Expt.
C	6.74	5.33	5.4	5.7
Si	10.26	1.14	12(fitted)	12
Ge	10.69	0.7	17.8	16
GaAs	10.68	1.32	9.9	10.9
GaP	10.30	2.26	6.5	8.5
GaSb	11.56	0.78	14.4	14.4
AlSb	11.59	1.5	8.0	10.2
ZnSe	10.71	2.6	5.5	5.8
ZnS	10.22	3.6	4.5	5.2
ZnTe	11.51	2.2	5.8	7.3
CdTe	12.25	1.5	7.4	7.2
InP	11.09	1.3	9.6	9.6
AlP	10.30	2.4	6.2	8.5
BP	8.58	2	9.2	9
SiC	8.22	~3	~6.8	6.7
AgI	12.23	2.6	4.7	4.9
CuCl	10.22	3.3	4.8	4.8

b) Rocksalt

NaCl	10.64	9	2.3(2.3)	2.3
KBr	12.47	7.7	2.2(2.3)	2.3
RbI	13.87	6	2.3(2.5)	2.6
LiCl	9.69	9.3	2.5(2.4)	2.7
MgO	7.96	7.8	3.3(3.0)	3.0
KF	10.10	10.9	2.2(2.1)	1.8
LiBr	10.4	8	2.5(2.5)	3.2
LiF	7.59	~12	~2.6(2.4)	1.9
RbF	10.66	10.4	2.1(2.1)	1.9
NaBr	11.29	7.5	2.4(2.5)	2.6
AgBr	10.91	2.9	4.9(4.9)	5.0

Table I (continued)

KCl	11.89	8.7	2.2(2.2)	2.2
AgCl	10.48	3.2	4.8(4.7)	4.2
RbCl	12.44	8.2	2.1(2.2)	2.2
NaI	12.23	5.8	2.7(2.8)	3.0
KI	13.35	6.1	2.4(2.5)	2.7
RbBr	12.95	7.5	2.2(2.3)	2.3
CdO	8.87	~2.4	~7.5(6.8)	6.2
LiI	11.34	~5.9	~2.8(2.9)	3.8
SrO	9.75	~6	~3.3(3.1)	3.2
c) Wurtzite				
CuBr	10.87	~3	~4.8	4.4
AlN	8.26	~5.7	~4.0	4.8
GaN	8.48	~3.8	~5.4	5.0
ZnO	8.63	3.44	5.7	4
InN	9.4	~2	~8.1	5.5
CdS	11.05	2.6	5.3	5.4
CdSe	11.49	1.74	7.1	5.8

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720