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Correlation Between the Static Dielectric Constant

and the Minimum Energy Gap[*]

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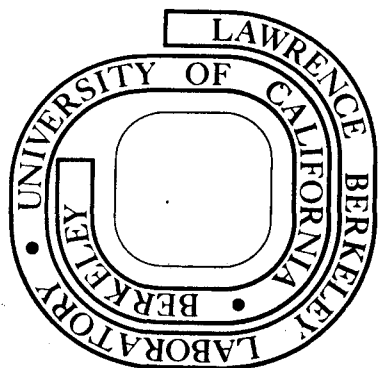
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Abstract

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, $\varepsilon_1(0)$, is described to a very good
approximation by a relation of the type

$$\varepsilon_1(0) - 1 = \frac{\alpha}{V^n E_{min}} \tag{1}$$

where α is a constant, V is the volume per electron, $n \simeq 1/2$,
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 $\varepsilon_1(0)$ for these crystals. Despite this restriction (1) is useful for estimating $\varepsilon_1(0)$ 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 $\varepsilon_1(0)$ for a series of crystals which have energy gaps greater than 0.5 eV. For the rocksalt crystal structures the values of $\varepsilon_1(0)$ 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 $\varepsilon_1(0)$ 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

$$\varepsilon_1(0)-1 = \frac{\beta}{a^{1.5}E_{min}} \quad (n = 1/2) \qquad (2)$$

or

$$\varepsilon_1(0)-1 = \frac{\gamma}{a\,E_{min}} \quad (n = 1/3) \qquad (3)$$

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

determined by fitting to the experimental value of $\varepsilon_1(0)$ in Si. As seen from Table I the same value of β also gives a very good prediction of $\varepsilon_1(0)$ 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 $\varepsilon_1(0)$ 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 <u>direct</u> 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 $\varepsilon_1(0)$ is given by

$$\varepsilon_1(0)-1 = (\hbar\omega_p)^2 \sum_{v,c} \int_{BZ} d^3k \frac{f_{vc}(\underset{\sim}{k})}{E_{vc}^2(\underset{\sim}{k})} \qquad (4)$$

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

to (4) consists of taking $E_{vc}(\underset{\sim}{k}) \simeq E_g$, where E_g is an average effective gap. Then using the f-sum rule we obtain the familiar result[2]

$$\varepsilon_1(0)-1 = \left(\frac{\hbar\omega_p}{E_g}\right)^2 . \tag{5}$$

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

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 $\varepsilon_1(0)$ evaluated from $\varepsilon_1(0) = \beta/a^{1.5}E_{min}$
are compared to the experimental values of $\varepsilon_1(0)$.   For
the rocksalt crystals the values of $\varepsilon_1(0)$ obtained from
$\varepsilon_1(0) = \gamma/a\ E_{min}$ 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 $\varepsilon_1(0)$.

Table I

a) Diamond and Zincblende

Compound	Lattice Constant (Bohr units)	E_{min}(eV)	$\varepsilon_1(0)$ calculated	$\varepsilon_1(0)$ 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

Compound	Lattice Constant (Bohr units)	E_{min}(eV)	$\varepsilon_1(0)$ calculated	$\varepsilon_1(0)$ Expt.
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