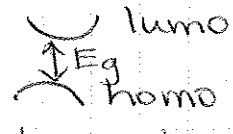
Dielectric Definition of Electronegativity

J.C. Phillips PRL 20, 550-553, 1968.

$A^N B^{8-N}$ empirical → Theory of covalent bonding PRL 19, 415-417, 1967.

→ E_h = covalent energy gap

C = ionic contribution to the energy gap



heteropolar GeAs

$E_g = 4.3$ eV

$E_g = 5.19$
$E_h = 4.3$ eV
$C = 2.9$ eV

Average energy gap E_g

$$E_g^2 = C^2 + E_h^2$$

$$f_i = \frac{C^2}{E_g^2}$$ fraction of ionicity

$$f_c = \frac{E_h^2}{E_g^2}$$

$f_i = 0.785 \pm 0.010$

$\varepsilon_0 \equiv$ macroscopic dialectric constants

Homopolar ε_{00} : $1 + \frac{(\hbar\omega_p)^2}{(E_g)^2} A$ $\quad A \approx 1$

$$\hookrightarrow \varepsilon_0 = 1 + \frac{(\hbar\omega_p)^2}{\left[E_h^2 + C_{\alpha\beta}^2\right]} A$$ $\hbar\omega_p$ = plasma energy

$$C_{\alpha\beta} = 1.5 \left[\left(\frac{Z_\alpha}{r_\alpha}\right) \mp \left(\frac{Z_\beta}{r_\beta}\right) \right] \exp\left(-K_s R\right)$$

r = half the bond length of the Group IV element on the same row.

$R = \frac{r_\alpha + r_\beta}{2}$ K_s = Thomas-Fermi screening wave #

$K_s^2 = \frac{4K_f}{\pi a_0}$ K_f = fermi momentum with appropriate ρ

$(K_f^3 = 3\pi^2 N)$

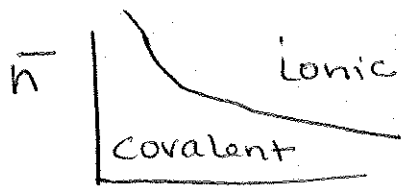
Electronegativity scale:

$$X_\alpha = 3.6\,(Z_\alpha / r_\alpha)(0.9)\exp(-K_s r_\alpha) + 1/2$$

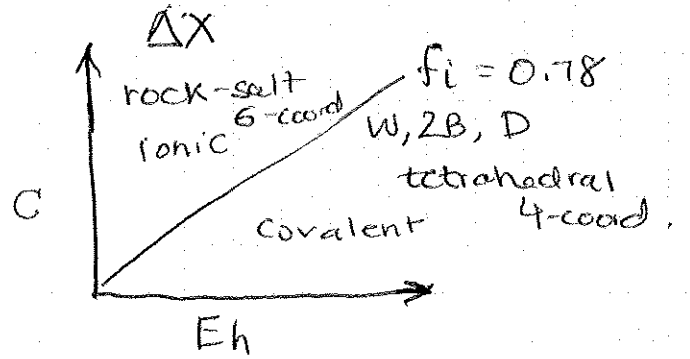
where 3.6 and 1/2 were chosen so that $X_\alpha(C) = 2.5$, $X_\alpha(N) = 3.0$ to agree with Pauling

---

1959 Mooser & Pearson



8 errors in 100 xtals



- much higher fi needed for ionic transition of behavior though

i.e. MgO rocksalt
refractive index decreases with hydrostatic pressure where
alkali-halides ↑

* What else can you predict with these?

* Tetrahedral covalent radii
  - not solely additive like Paulings

* ionic radii
  - b/c different from predicted covalent radii

* Nonlinear optical susceptibilities (Charge transfer polarizability)

  JC Phillips JA Van Vechten
  Phys Rev (183) 709 1969

* Melting temperatures
  JVV PRL (29) 769 1977

* Bandgap energies
  VV Phys Rev (182) 891 1969

  ~~4~~ 442

* Charge distribution & piezoelectric constants
  P & VV PRL (23) 1115 1969

References

General Theory of Dielectric Definition of Electronegativity

J. C. Phillips, *Physical Review Letters* **19**, 415 (1967).
J. C. Phillips, *Chemical Physics Letters* **3**, 286 (1969).
J. C. Phillips, J. A. Van Vechten, *Physical Review Letters* **22**, 705 (1969).
J. C. Phillips, *Reviews of Modern Physics* **42**, 317 (1970).

Covalent radii

J. A. Van Vechten, J. C. Phillips, *Physical Review B* **2**, 2160 (1970).

Melting temperature scaling

J. A. Van Vechten, *Physical Review Letters* **29**, 769 (1972).

Optical susceptibilities

J. C. Phillips, J. A. Van Vechten, *Physical Review* **183**, 709 (1969).

Piezoelectric constants

J. C. Phillips, J. A. Van Vechten, *Physical Review Letters* **23**, 1115 (1969).