Homopolar and heteropolar energy gaps of an ionic system

V. Kumar Srivastava

Istituto di Struttura della Materia, Consiglio Nazionale Ricerche,
Via E. Fermi, 38-00044 Frascati, Roma, Italy

A simple method, based on a plasma oscillations theory of solids, is proposed for the calculation of homopolar (E_h) and heteropolar (C) energy gaps of ionic crystals having rocksalt structures. We find that $E_h = K (\hbar\omega_p)_C^{1.6533}$ eV and $C = K_1 b (\hbar\omega_p)_C^{2/3} \exp[-K_2(\hbar\omega_p)_C^{-1/3}]$ eV, where $K = 0.0321$, $K_1 = 9.7798$ and 6.5198 for $A^I B^{VII}$- and $A^{II} B^{VI}$-type compounds, respectively, and $K_2 = 7.2239$. Our calculated values are in excellent agreement with the values reported by different workers.

Frequent attempts have been made at understanding the homopolar (covalent) and heteropolar (ionic) energy gaps in semiconductors. Phillips,[1,2] Van Vechten,[2,3] Levine,[4] and several other workers[5-9] have developed various theories and calculated these gaps for the case of simple compounds. In practice these theories require elaborate computation, and have been developed only for the limited semiconductors. Therefore, I thought it would be of interest to give an alternative explanation for the covalent and ionic energy gaps in semiconducting compounds. In this paper we propose a method based on a plasma oscillations theory of solids for the calculation of the homopolar (E_h) and heteropolar (C) energy gaps in lithium, sodium, potassium, the rubidium halides and some compounds of magnesium, calcium, strontium, and barium having rocksalt structures.

The compounds taken in this paper are not purely ionic, they are partially covalent. Phillips and Van Vechten[1-3] (PV) have calculated the covalent and ionic contribution to the chemical bond in the binary $A^N B^{8-N}$ crystals. Their theory is based on the simple one-electron model originally suggested by Penn.[5] This model has been used to separate the average energy gap into homopolar and heteropolar parts. The average homopolar energy gap E_h is taken to be a function of the nearest-neighbor distance only,[1] while the heteropolar energy gap C is given by a simple expression based on the electronegativity difference between the elements of the compound. Levine[4] has extended the PV theory for ternary compounds, considering also the effect of d core electrons. Several workers[6,7] have correlated these gaps with x-ray chemical-shift data.

Recently the author[10] and Srivastava *et al.*[11] have shown that the plasmon energy of a metal changes when it undergoes a chemical combination and forms a compound. This is due to the fact that the plasmon energy depends on the effective number of valence electrons, which changes when a metal forms a compound. The average energy gaps of alkali halide ($A^I B^{VII}$, Ref. 12) and $A^{II} B^{VI}$ compounds[13] have been calculated by the author using this idea. Further it has been shown by Verma and Agarwal[14] that when the chemical composition of a solid is varied, the energy of the valence bands is shifted since the chemical bonds affect the lattice spacing.

The average energy gap can be separated into the homopolar and the heteropolar parts according to the following relations:[1-3]

$$E_g^2 = E_h^2 + C^2 \ , \tag{1}$$

$$f_i = C^2/E_g^2 , \quad f_C = E_h^2/E_g^2 \ , \tag{2}$$

$$E_h = 39.74/d^{2.48} \ , \tag{3}$$

and

$$C = 14.4 b \left[\frac{Z_A}{r_0} - \frac{n}{m} \frac{Z_B}{r_0} \right] e^{-K_s r_0} \ , \tag{4}$$

where E_g is the average energy gap of a crystal; f_i and f_c are the fractional ionicity and covalency of the bonds; d is the nearest-neighbor distance (bond length), C the heteropolar part of average energy gap for $A_m B_n$ compounds, b the prescreening factor, $e^{-K_s r_0}$ the Thomas-Fermi screening factor, and $r_0 = \frac{1}{2}d$. The numerical factors in Eqs. (3) and (4) and the following ones are given for d expressed in Å and energy in eV.

The most generalized form of the above equations has been discussed by Levine[4] in detail. The equations given by Levine reduce to those of PV when only one type of bond is present in the crystal. In this paper we consider single-bond compounds and hence use the above form of PV's equations.

The physical meaning of Eq. (4) is that C is given by the difference between the screened Coulomb potentials of atoms A and B having core charges Z_A and Z_B. These potentials are to be evaluated at the covalent radii r_0. Only a small part of the electrons are in the bond, the rest screen the ion cores, reducing their charge by the Thomas-Fermi screening factor $e^{-K_s r_0}$, which affects the chemical trend in a compound. This screening factor, as well as the bond length, is related to the effective number of valence electrons in a compound. Also, the plasmon energy depends directly on the effective number of free electrons in the valence band. Thus, there must be some correlation between the physical process which involves the ionic contribution C to the average energy gap E_g and the plasmon energy of a compound $(\hbar\omega_p)_C$.

The free-electron plasmon energy is given by the relation

$$(\hbar\omega_p)^2 = \frac{4\pi e^2}{m} N_e \ , \tag{5}$$

from which we have

$$N_e = \frac{m}{4\pi e^2} (\hbar\omega_p)^2 \ , \tag{6}$$

where N_e is the effective number of free electrons taking part in the plasma oscillations, and e and m are their charge and mass, respectively. Equation (5) is valid for free electrons, but to a first approximation it can also be used for semiconductors and insulators. Raether,[15] and Philipp and Ehrenreich[16] have shown that the plasmon energy for sem-

iconductors and insulators is given by

$$\hbar\omega_{pd} = \frac{\hbar\omega_p}{(1-\delta\epsilon_0)^{1/2}} \quad , \tag{7}$$

where $\delta\epsilon_0$ is a very small correction to the free-electron plasmon energy $\hbar\omega_p$ and can be neglected to a first approximation. Philipp and Ehrenreich[16] have shown that the calculated values of $\hbar\omega_p$ and $\hbar\omega_{pd}$ are in fair agreement with their observed values of plasmon energy in dielectrics. It has also been pointed out by Kittel[17] that the plasmon oscillations in dielectrics are physically the same as in metals.

N_e can be expressed in terms of individual bond properties as

$$N_e = n_v/v_b \quad , \tag{8}$$

where

$$n_v = (Z_A/N_{CA} + Z_B/N_{CB}) \quad , \tag{9}$$

and v_b is the bond volume.

Using Eqs. (8) and (9), the general expression for N_e can be written for single-bond compounds as

$$N_e = \frac{(Z_A/N_{CA} + Z_B/N_{CB})\overline{N}_C Z_M}{V} \quad , \tag{10}$$

where Z_A is the number of the valence electrons of the cation, N_{CA} the coordination number of atom A in the compound, $\overline{N}_C$ the average coordination number, Z_M the number of molecules per unit cell, and V the unit cell volume.

For rocksalt crystals,

$$V = 8d^3, \quad N_{CA} = N_{CB} = \overline{N}_C = 6, \quad (Z_A + Z_B) = 8, \quad Z_M = 4 \quad . \tag{11}$$

Using these values, Eq. (10) yields $N_e = 4/d^3$, from which, with Eq. (6), we find the following relation between d and the plasmon energy

$$d\,(\text{Å}) = 17.669(\hbar\omega_p)^{-2/3} \quad (\hbar\omega_p \text{ in eV}) \quad . \tag{12}$$

The Thomas-Fermi momentum K_s, in terms of the

TABLE I. Homopolar and heteropolar energy gaps of ionic systems.

Metal/ compound 1	$(\hbar\omega_p)$ (eV) (Refs. 12 and 13) 2	b^4 3	This work 4	E_h (eV) Van Vechten (Ref. 3) 5	Levine (Ref. 4) 6	This work 7	C (eV) Van Vechten (Ref. 3) 8	Levine (Ref. 4) 9	This work 10	f_i Phillips (Ref. 1) 11	Levine (Ref. 4) 12
Li	7.99										
LiF	25.96	3.04	6.99	7.0	7.05	22.72	23.0	22.9	0.9136	0.915	0.914
LiCl	17.99	2.73	3.81	3.8	3.84	11.63	11.6	11.8	0.9043	0.903	0.903
LiBr	16.27	2.61	3.23	3.2	3.23	9.41	9.5	9.48	0.8944	0.899	0.9896
LiI	13.25	2.52	2.27	2.6	2.61	6.43	7.4	7.41	0.8889	0.890	0.890
Na	5.92										
NaF	20.11	3.80	4.58	5.0	4.98	19.28	20.9	20.9	0.9462	0.946	0.946
NaCl	15.68	3.40	3.04	3.1	3.04	11.61	11.8	11.6	0.9261	0.935	0.936
NaBr	14.37	3.30	2.63	2.6	2.63	9.76	9.8	9.81	0.9319	0.934	0.933
NaI	12.79	3.23	2.17	2.2	2.16	7.86	7.8	7.83	0.9292	0.927	0.929
K	4.27										
KF	16.83	4.04	3.42	3.5	3.47	15.47	16.1	15.7	0.9538	0.955	0.954
KCl	13.29	3.92	2.31	2.3	2.32	10.18	10.4	10.2	0.9508	0.953	0.951
KBr	12.38	4.03	2.06	2.1	2.06	9.28	9.3	9.29	0.9522	0.952	0.953
KI	11.17	3.83	1.73	1.7	1.74	7.39	7.4	7.41	0.9479	0.950	0.948
Rb	3.86										
RbF	15.03	4.08	2.83	3.0	3.04	13.01	13.9	13.9	0.9554	0.960	0.955
RbCl	12.40	4.18	2.06	2.15	2.07	9.61	9.7	9.68	0.9553	0.955	0.956
RbBr	11.59	4.13	1.84	1.9	1.87	8.84	8.9	8.65	0.9583	0.957	0.955
RbI	10.53	4.09	1.57	1.6	1.58	7.11	7.1	7.16	0.9538	0.951	0.954
Mg	10.89										
MgO	24.27	3.16	6.30	6.3	6.27	14.25	14.5	14.3	0.836	0.841	0.839
MgS	18.28	2.60	2.91	3.7	3.70	7.54	7.1	7.2	0.870	0.786	0.790
MgSe	16.45	2.58	3.29	3.3	3.31	6.36	5.4	6.39	0.788	0.790	0.789
Ca	7.98										
CaO	19.61	4.47	4.40	4.5	4.51	14.55	14.6	14.9	0.916	0.913	0.916
CaS	15.16	4.15	2.87	3.0	2.97	8.95	9.1	9.26	0.906	0.902	0.907
CaSe	14.11	4.11	2.55	2.7	2.71	7.87	8.1	8.36	0.905	0.900	0.905
CaTe	13.89	3.93	2.48	2.3	2.27	7.33	6.7	6.68	0.897	0.894	0.897
Sr	7.02										
SrO	17.35	4.82	3.59	3.8	3.79	12.93	13.4	13.6	0.928	0.926	0.928
SrS	14.32	4.42	2.61	2.6	2.58	8.68	8.5	8.57	0.917	0.914	0.917
SrSe	13.21	4.42	2.29	2.4	2.37	7.58	8.0	7.87	0.916	0.917	0.917
SrTe	12.20	4.2	2.01	2.2	2.16	6.29	6.7	6.8	0.907	0.903	0.908
Ba	6.50										
BaO	15.73	4.90	3.06	$\cdots$	3.20	11.22	$\cdots$	11.7	0.931	$\cdots$	0.931
BaS	12.90	5.05	2.20	$\cdots$	2.23	8.32	$\cdots$	8.44	0.935	$\cdots$	0.935

plasmon energy, can be written as

$$K_s = \left[\frac{4K_F}{\pi a_B}\right]^{1/2} = \left[\frac{4}{a_B}\left[\frac{3m}{(2\pi e)^2}\right]^{1/3}\right]^{1/2} (\hbar\omega_p)^{1/3} \ , \qquad (13)$$

where a_B is the Bohr radius and K_F the Fermi wave vector which is given by the relation

$$K_F^3 = 3\pi^2 N_e \ . \qquad (14)$$

From Eqs. (3) and (12), the homopolar energy gap for A^IB^{VII} and $A^{II}B^{VI}$ compounds having rocksalt structures can be written as

$$E_h = 0.0321(\hbar\omega_p)_C^{1.6533} \text{ eV} \ . \qquad (15)$$

When the values of Eqs. (12) and (13) are substituted in Eq. (4), the expression for the heteropolar energy gap for A^IB^{VII} rocksalt crystals, where $\Delta Z = (Z_A - Z_B) = 6$, can be written as

$$C = 9.7798b \ (\hbar\omega_p)_C^{2/3} \exp[-7.2239(\hbar\omega_p)_C^{-1/3}] \text{ eV} \qquad (16)$$

and that for $A^{II}B^{VI}$ rocksalt crystals, where $\Delta Z = 4$ can be written as

$$C = 6.5198b'(\hbar\omega_p)_C^{2/3} \exp[-7.2239(\hbar\omega_p)_C^{-1/3}] \text{ eV} \ , \qquad (17)$$

where b' is the prescreening factor which includes the effect of the empty conduction d states. Special care of the d states is required in the case of Ca, Sr, and Ba compounds, since they contain low-lying conduction d levels only $\Delta E = 1.75$, 1.8, and 0.6 eV above the ground states in Ca^+, Sr^+, and Ba^+, respectively. Such d states can influence the crystal properties to a substantial degree. Levine[4] has calculated the values of b' for $A^{II}B^{VI}$ compounds in both cases that is, considering the effect of conduction with and without d states. In the present calculation we have taken the former values of the prescreening factor for Ca, Sr, and Ba compounds.

Generalizing Eqs. (15)–(17), the expressions for E_h and

C can be written as

$$E_h = K \ (\hbar\omega_p)_C^{1.6533} \text{ eV} \qquad (18)$$

and

$$C = K_1 b \ (\hbar\omega_p)_C^{2/3} \exp[-K_2(\hbar\omega_p)_C^{-1/3}] \text{ eV} \ , \qquad (19)$$

where K, K_1, and K_2 are the constants depending upon the structure elements and ΔZ. In the present paper we have taken only six- and four-electron rocksalt crystals for which $K = 0.0321$, $K_1 = 9.7798$ and 6.5198, and $K_2 = 7.2239$.

Using Eqs. (2), (18), and (19), the ionicity, homopolar, and heteropolar energy gaps of several alkali halides and several $A^{II}B^{VI}$ compounds have been calculated and presented in Table I. Our calculated values of E_h and C, for most materials, agree within 8% with the previous estimations. The maximum discrepancy for E_h is 12% in the case of LiI. The maximum discrepancy for C is 30% in the cases of MgS and MgSe and 13% for CaO. The calculated values of f_i are also in excellent agreement (within 2%) with the values given by Phillips,[1] Van Vechten,[3] and Levine,[4] except for MgS where the discrepancy is 10%. These discrepancies may be due to strong electropositive Mg^{++} and Ca^{++} ions.

Recently, the author[10, 18] has calculated the plasmon energy of about 150 compounds having different crystal structures. In the present study we find that both E_h and C depend directly on the plasmon energy of the compounds. Thus, this theory can also be extended to other crystal structures.

An excellent agreement between the author's calculated values of E_h, C, and f_i and the values reported by different workers has been found. Thus it is possible to predict the order of homopolar and heteropolar energy gaps and hence the ionicity of semiconducting compounds from their plasmon energies.

---

[1]J. C. Phillips, Phys. Rev. Lett. **20**, 550 (1968); Rev. Mod. Phys. **42**, 317 (1970).

[2]J. C. Phillips and J. A. Van Vechten, Phys. Rev. B **2**, 2147 (1970); Phys. Rev. **183**, 709 (1969).

[3]J. A. Van Vechten, Phys. Rev. **182**, 891 (1969); **187**, 1007 (1969).

[4]B. F. Levine, Phys. Rev. B **7**, 2591 (1973); J. Chem. Phys. **59**, 1463 (1973); Phys Rev. B **7**, 2600 (1973).

[5]D. R. Penn, Phys. Rev. **128**, 2093 (1962).

[6]P. R. Sarode, Phys. Status Solidi B **88**, K35 (1978).

[7]S. V. Adhyapak, S. M. Karnetkar, and A. S. Nigavekar, Nuovo Cimento **35**, 179 (1976).

[8]D. Brust, Phys. Rev. B **5**, 435 (1972).

[9]A. C. Sharma and S. Auluck, Phys. Rev. B **28**, 965 (1983).

[10]K. S. Srivastava, R. L. Shrivastava, O. K. Harsh, and V. Kumar, Phys. Rev. B **19**, 4336 (1979).

[11]K. S. Srivastava, Shiv Singh, A. K. Srivastava, R. S. Nayal, Amita Chaubey, and P. Gupta, Phys. Rev. A **25**, 2838 (1982).

[12]V. Kumar Srivastava, Phys. Status Solidi B **114**, 667 (1982).

[13]V. Kumar Srivastava and A. R. Chetal, Nuovo Cimento D **2**, 1014 (1983).

[14]L. P. Verma and B. K. Agarwal, J. Phys. C **1**, 1658 (1968).

[15]H. Raether, Ergeb. Exakten Naturwiss. **38**, 84 (1965).

[16]H. R. Philipp and H. Ehrenreich, Phys. Rev. **129**, 1530 (1963).

[17]C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1971) (Second Wiley Eastern Reprint, New Delhi, 1974), p. 227.

[18]K. S. Srivastava, R. L. Shrivastava, O. K. Harsh, and V. Kumar, J. Phys. Chem. Solids **40**, 489 (1979).