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A Thermochemical Approach to the Bandgaps of Semiconducting and Insulating Materials

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Many materials of practical interest are either semiconducting or insulating in nature. One of the most important quantities characterising these materials, therefore, is the energy bandgap. In the present article, procedures available for estimating the bandgaps of binary, inorganic materials from thermochemical and related data have been briefly reviewed with special emphasis on recent work.

It has been shown that heats of formation per equivalent and heats of atomisation per equivalent may be used for approximate prediction of bandgaps of these materials. Theoretical origins of the correlation of bandgaps to heats of formation, heats of atomisation, lattice energies, single bond energies and average bond energies etc., have been indicated.

1. Introduction

A thermodynamic approach to the study of several solid state phenomena is now a well-established procedure and is frequently used by metallurgists, materials scientists, and chemists [1–2]. An important problem in solid state science is the prediction of energy bandgaps [3] of materials. The width of the forbidden gap of a semiconductor or an insulator is, of course, a very fundamental quantity and constitutes the basis for calculating the band structure and related problem of determining the number of intrinsic carriers as well as their temperature-dependence. The object of the present article is to present procedures available for rough computation of bandgaps of binary inorganic compounds from their thermodynamic data [4–7]. These approaches [4–7], even though approximate and only semi-quantitative, are nevertheless very useful since no precise procedures are available for computing the band structure of a variety of practical materials, e.g. refractory oxides, ceramics, polyatomic substances, etc. This is because methods of theoretical physics are either inadequate or too cumbersome for computing the bandgaps of all but the simplest compounds, e.g. Ge. Furthermore, from the sheer pedagogic point of view, the approaches to be described here [5, 6] are extremely instructive for presenting, in a chemist's language, the theoretical origins of correlations between bandgaps and various other quantities, e.g. heats of formation, bond energies and lattice energies, etc.

In the present article, it will be assumed that the reader is familiar with the qualitative aspects of band theory of solids as presented, e.g. in a recent lucid article [3]. Other excellent expositions of band theory of solids at a relatively elementary level are also available in the literature [8–11]. Some familiarity with elementary thermochemistry and the nature of cohesion in ionic solids [8–10] will also be assumed.

2. Prediction of Bandgap from Thermodynamic Data

According to the proposal of Ruppel, Rose and Gerritsen [4], the bandgap energy of several inorganic compounds may be taken as lying between one and two times their heat of formation per *mole* in the standard state (fig. 1). This observation was based on qualitative, intuitive arguments and was used to explain the relationship between energy levels in solids and electrolytes. It was shown by Vijh [5] that this correlation (fig. 1), when applied to polyatomic compounds formed between polyvalent ions gives completely erroneous results. It was argued [5], after ideas of Sanderson [12], that in correlations

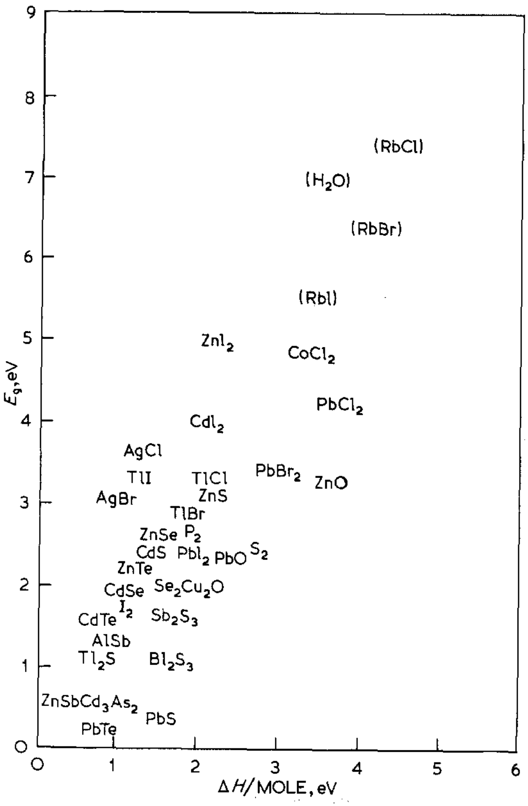

Figure 1 Relationship between bandgaps, E_g, and heats of formation (standard state)per *mole* for several compounds as proposed by Ruppel, Rose and Gerritsen [4].

of the type shown in fig. 1, one must "normalise" the thermodynamic data, i.e. the heats of formation must be taken as per equivalent, i.e. neither as per mole, nor as per atom but as per atomic equivalent. It was observed that this normalisation factor when applied to the proposal of Ruppel *et al* results in a correlation valid for a very large variety of inorganic compounds (fig. 2). Specifically, this improved correlation (fig. 2) results in valid predictions for bandgaps of polyatomic compounds formed between polyvalent ions (table I). Hence, it was concluded that, empirically, bandgap, E_g, is approximately two times the heat of formation per equivalent, ΔH_e; i.e.,

$$E_g \simeq 2\Delta H_e\,. \qquad (1)$$

TABLE I

Compound	E_g (Ruppel *et al*) eV	E_g (Vijh) eV	E_g (experimental) eV
Al_2O_3	17 – 34	5.67	7
Ta_2O_5	21.75 – 43.5	4.35	4.6
TiO_2	9.46 – 19.92	4.73	3.0
Ga_2O_3	11.19 – 22.38	3.73	4.4
In_2O_3	9.63 – 19.26	3.21	2.8

It may be mentioned that suggestions similar to those of Ruppel *et al* were also put forward by Semenkovich [7], and are subject to similar criticism, i.e. his [7] conclusions are also invalid for polyatomic compounds for the reasons mentioned in the foregoing discussion. It follows from equation 1 that for intrinsic semiconductors, ΔH_e is approximately equal to the Fermi energy, E_F, as has been schematically shown in fig. 3 [1, 8–10].

On the basis of some early work on the relationship of bandgaps to crystal binding, Manca [13] showed that for certain restricted classes of semiconductors, the following relationship is obeyed:

$$E_g = a(E_s - b) \qquad (2)$$

where a and b are constants characteristic of a given series of compounds, with the value of a usually close to 2; E_s is a *single* bond energy calculated by Pauling's [14] well-known empirical equation:

$$D(\text{A–B}) = \tfrac{1}{2}\{D(\text{A–A}) + D(\text{B–B})\} + 23(x_A - x_B)^2 \qquad (3)$$

where D(A–B) is the required single bond energy in molecule AB; D(A–A) is the A–A bond strength whereas D(B–B) is the B–B bond strength; X_A and X_B are the electronegativities, on the Pauling scale [14], of atoms A and B respectively. The factor, $23(X_A-X_B)^2$, takes into account the extra strength that results from partial ionicity of the covalent bond between A and B. It may be noted that bond strength has been used here as synonymous with single bond energy.

The value obtained by Pauling's equation gives an estimate of the strength of an *isolated* bond. As was pointed out previously [6], such a quantity would not represent the general magnitude of binding in a complex solid involving many bonds, e.g. Ta_2O_5; the binding in such a substance must be represented by an average bond energy which may be obtained by an appropriate thermochemical cycle as discussed recently by Howald [15]. This average bond energy for, e.g. NaCl, may be obtained by the equation:

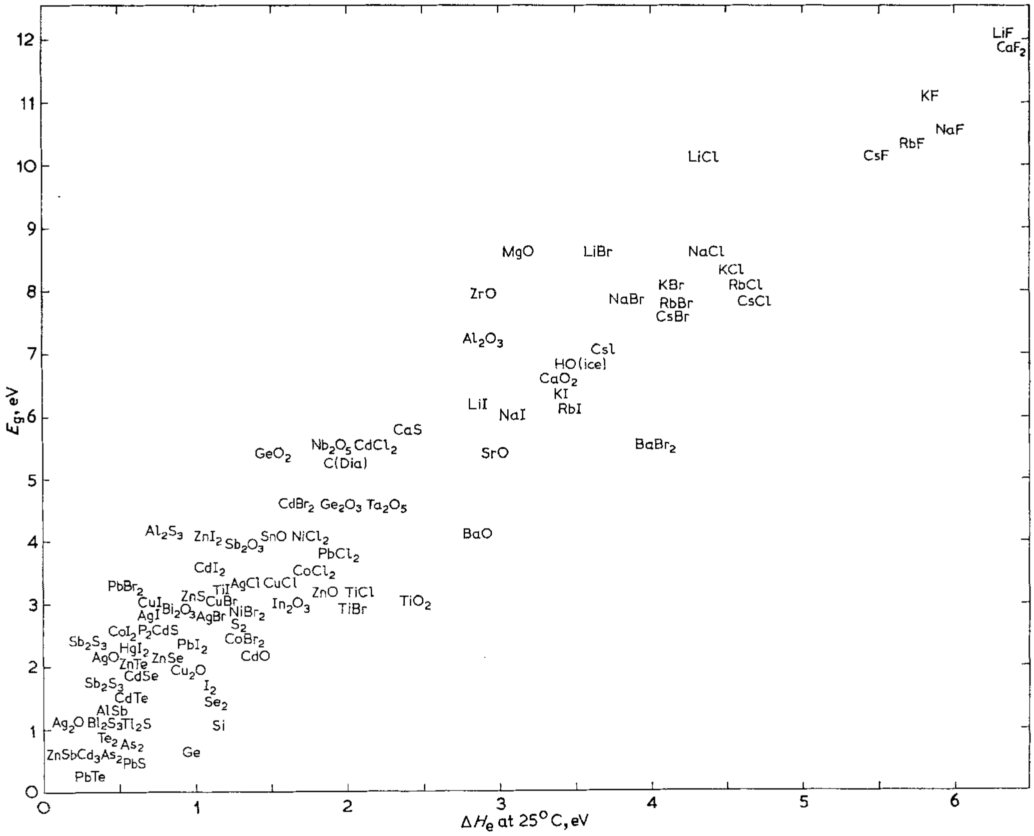

Figure 2 Correlation between bandgaps, E_g, and heats of formation (standard state) per *equivalent* for a large number of inorganic substances [5].

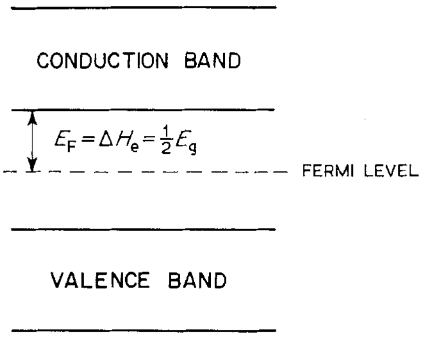

Figure 3 A schematic representation of approximate equivalence of ΔH_e and E_F, the Fermi energy, for intrinsic semiconductors.

$$D(\text{NaCl}) = \Delta H_s + \tfrac{1}{2}\Delta H_{\text{diss}} + \Delta H_f \qquad (4)$$

where D(NaCl) is the energy of the Na–Cl bond; ΔH_s is the heat of sublimation of sodium; ΔH_{diss} is the heat of dissociation of chlorine gas into chlorine atoms; ΔH_f is the heat of formation, in the standard state, of NaCl. For a complex compound like Ta_2O_5, to obtain the bond energy from equation 4, one must take all quantities on the r.h.s. as per equivalent. Further appropriate corrections for co-ordinate valence, spin correlation stabilisation energies and Π bonding etc. must be applied [15]. It may be noted that such corrections are unnecessary for alkali halides, and for other compounds are usually of small magnitude, as discussed by Howald [15]. In effect, an average bond energy is the heat of atomisation per equivalent, to which certain corrections have been applied. In the terminology of Rose [4], an average bond energy would be approximately equivalent to the heat of formation per equivalent in the *atomic* state, i.e. not in the standard state.

By assuming E_s to denote an average bond energy, Vijh examined Manca's equation 2 for the case of several inorganic compounds and found it to be approximately valid (fig. 4). It may be noted that the correlation presented in fig. 4 is rather a general one and includes a wide variety of compounds. Specifically, it includes binary

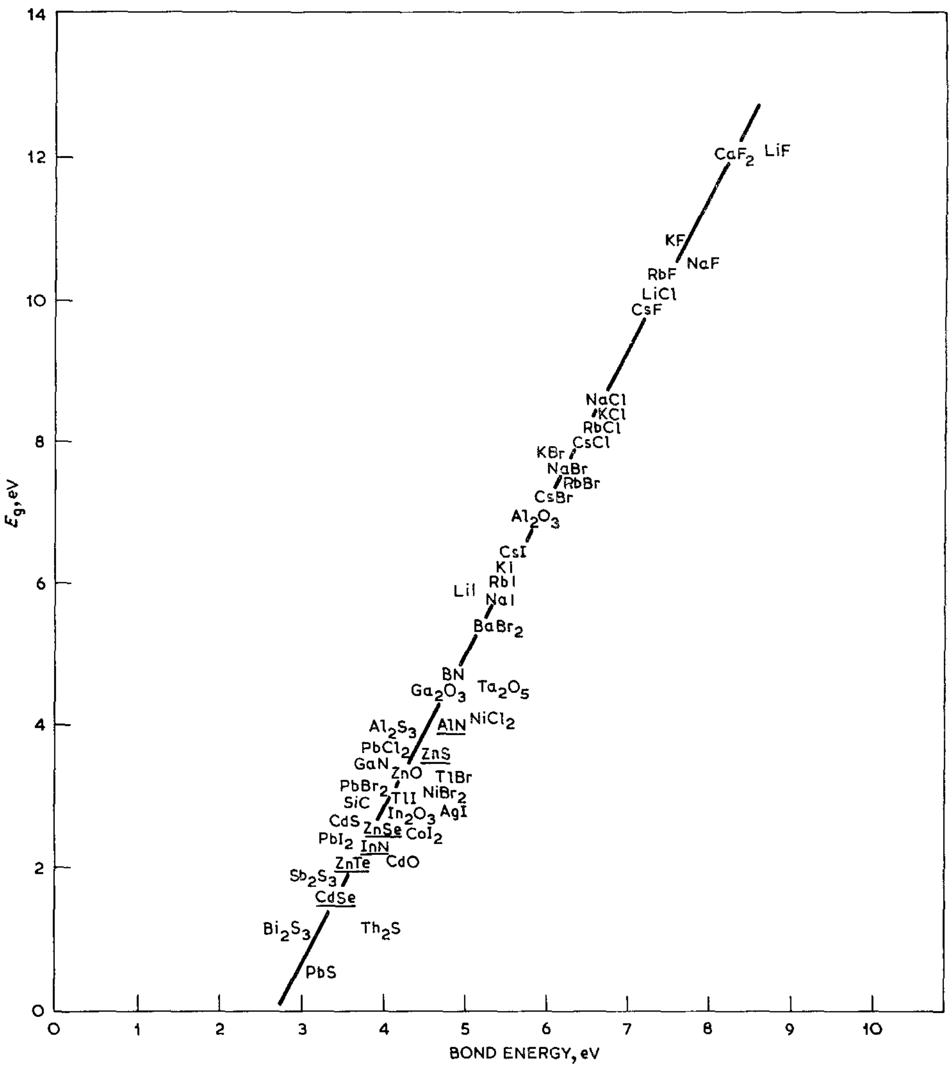

Figure 4 A plot showing correlation between bandgaps, E_g, and average bond energies for several binary compounds.

inorganic substances covering the following type of properties:

(i) Both low and high bandgap semiconductors as well as insulators.

(ii) Several polyatomic compounds formed between *polyvalent* ions.

(iii) Substances which, on the basis of Pauling's criteria, cover a wide range of ionicity. It is realised that Pauling's criteria, strictly speaking, are not applicable to solids. However, Pauling's electronegativity criterion represents a convenient way in terms of a chemist's language, of conveying the fact that fig. 4 includes compounds ranging from the highly covalent (Sb_2S_3) to the extremely ionic (CsF).

(iv) All the important crystal structures have been represented in fig. 4. The examples are zinc blende, wurzite, NaCl, CsCl, cuprite, fluorite and corundum.

Hence it may be concluded that fig. 4 (and equation 2) represents a rather general, though an approximate, basis of predicting bandgaps of substances from thermodynamic data (i.e. equation 4).

An attempt will now be made to point out the possible theoretical basis of figs. 2 and 4, at least for the case of ionic compounds, e.g. alkali halides. As will be shown below the theoretical origins of figs. 2 and 4 (or equations 1 and 2) for the case of highly covalent compounds is not all that clear cut.

3. Theoretical Considerations

In this section, an analysis based on our previous work [6] will be presented; this analysis will attempt to clarify possible theoretical foundations of equations 1 and 2 for the case of alkali halides.

It has been shown by Mark [16] that the bandgap energy, E_g, of, for example, NaCl is given by:

$$E_g = 2M - I_m + A_x \qquad (5)$$

where M is the Madelung energy, I_m is the ionisation potential of Na; A_x is the electron affinity of Cl. Equation 5 may be rewritten as:

$$E_g = 2(U - R) - I_m + A_x \qquad (6)$$

where U is the experimental (thermochemical) lattice energy and R is an energy term which includes repulsive, London, and other components of theoretical lattice energy [8] so that,

$$M = (U - R) \qquad (7)$$

is quite valid.

By a suitable thermochemical cycle, one can show that [8]:

$$\Delta H_f = \Delta H_s + I_m + \tfrac{1}{2}\Delta H_D + A_x + U\,. \quad (8)$$

In equation 8, the various symbols represent the following quantities: ΔH_f is the heat of formation of, for example, of NaCl; ΔH_s is the heat of sublimation of Na; I_m is the ionisation potential of Na; ΔH_D is the energy of dissociation of $Cl_2(g)$ into atoms; A_x is the electron affinity of Cl; U is the lattice energy of NaCl. The quantities defined above are all in per *mole* of the corresponding substance.

On simple rearrangement, equation 6 yields:

$$-\,U = \Delta H_s + I_m + \tfrac{1}{2}\Delta H_D + A_x - \Delta H_f\,. \quad (9)$$

It may be noted that, U, A_x and ΔH_f are exothermic quantities (hence with − sign) and ΔH_s, I_m and ΔH_D are endothermic quantities (hence with + sign) for the case of alkali halides. On substituting for exothermicity and endothermicity in equation 9 one obtains:

$$U = \Delta H_s + I_m + \tfrac{1}{2}\Delta H_D + \Delta H_f - A_x\,. \quad (10)$$

Substituting equation 10 in equation 6

$$E_g = 2\Delta H_s + 2I_m + \Delta H_D + 2\Delta H_f - 2A_x - I_m + A_x - 2R \qquad (11)$$

or,

$$E_g = 2\Delta H_s + I_m + \Delta H_D + 2\Delta H_f - A_x - 2R. \qquad (12)$$

If we make an approximation that I_m is roughly equivalent to A_x in magnitude, we obtain:

$$E_g = 2\Delta H_s + 2\Delta H_f + \Delta H_D - 2R \qquad (13)$$

or,

$$E_g = 2(\Delta H_a - R)\,, \qquad (14)$$

where ΔH_a is the heat of atomisation per *mole*, and for a diatomic molecule formed between uni-univalent ions (e.g. NaCl) is the same thing as heat of atomisation per equivalent, which, of course, is the average bond energy [6, 12, 14, 15.]

For a complex compound involving several ions, either univalent or polyvalent, equation 14 has to be appropriately modified. This is because equations 5 and 6 refer to the transfer of *one* valence electron, e.g. from Na to Cl; for maintaining the validity of equation 11, U in equation 10 must also be taken as per valence electron, i.e. as per equivalent. As a result, the ΔH_a term in equation 14 must be changed from ΔH_a/mole to ΔH_a/eq. for polyatomic compounds. As mentioned above, ΔH_a/eq. is the bond energy E_a. Hence,

$$E_g = 2(E_a - R)\,. \qquad (15)$$

For a given series of compounds, e.g. alkali halides, R may approximately be treated as a constant. Hence, equation 15 may be written in the form:

$$E_g = 2(E_a - b) \qquad (16)$$

where b is a constant. This equation 16 is identical with equation 2 in this article.

The approximation involved in the derivation of equation 13 may now be examined. If I_m is not roughly equivalent to A_x, then R in equation 13 may be converted to R' where,

$$R' = R + \tfrac{1}{2}I_m - \tfrac{1}{2}A_x\,. \qquad (17)$$

For a series of related substances, R' may again be assumed as, *roughly*, a constant. For example, for several alkali halides, R' values are close to 2.5 ± 0.5 eV. It may be mentioned that equation 17 will have to be suitably modified for compounds involving positive electron affinities.

If we rewrite equation 13 by substituting equation 17 in it, we obtain:

$$E_g = (2\Delta H_s + \Delta H_D - 2R') + 2\Delta H_f\,. \quad (19)$$

For several substances, it is observed that, fortuitously, the quantities in the parentheses roughly cancel each other out. For instance, for NaCl, the net value of the quantities in the parentheses in equation 19 would be ca. 0.6 eV. If the magnitude of the quantities in parentheses is small it follows that:

$$E_g \simeq 2\Delta H_f\,. \qquad (20)$$

Like all quantities in such comparisons, ΔH_f must be "normalised", i.e. taken as per equivalent [12, 14, 15]. Hence,

$$E_g \simeq 2\Delta H_f/\text{eq}. \qquad (21)$$

Equation 21 is identical with equation 1 of this article.

From the foregoing it is clear that equations 1 and 2, which have been shown to be obeyed in figs. 2 and 4 respectively, also have some approximate theoretical validity, at least for the case of ionic compounds.

For the case of some covalent compounds included in fig. 4, it is possible that some compensatory effects are involved. For example, increase in cohesive energy due to homopolar binding may roughly cancel out the decrease in lattice energy that would be expected to result from partial ionicity of the compound. In these cases, the analysis presented here, which strictly applies to ionic compounds, would be essentially valid. For other covalent compounds, in principle, one could modify this analysis by writing equation 2 (or equation 16) in the form:

$$E_g = 2(E_s - b) \pm \Delta U\,. \qquad (22)$$

Here ΔU is the difference between theoretical and thermochemical lattice energy, again taken as per equivalent [8]. It may be added, however, that for the compounds in fig. 4, no correction has been applied for covalence. It is fortuitous that several covalent compounds obey equation 2.

Finally, it is obvious that the present theoretical analysis has no validity either for elemental semiconductors or for molecular semiconductors, e.g. anthracene.

4. Conclusions

It has been shown that it is possible to predict, even though somewhat approximately, bandgaps of a wide variety of inorganic compounds from appropriate thermodynamic data. This may be done through application of either of equations 1 or 2. An analysis has been presented which shows the rough theoretical validity of the suggested procedure, at least for the case of ionic compounds. These equations are semi-quantitative in nature, and, are of rather wide applicability, e.g. fig. 2.

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