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Relationship between energy gaps and melting temperatures in various classes of materials

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An interesting relationship between the energy gaps and melting temperatures in a variety of classes of materials is found. The relationship suggests the existence of two different processes for the melting phenomenon which depend on the nature of the chemical bond. By using the bond orbital theory, it is shown that the relationship is correlated with the total energy of the compounds considered. A brief discussion on the melting of superionic conductors is also given.

I. INTRODUCTION

Despite the fact that the solid-liquid transition is one of the most familiar, there is still little knowledge of this phenomenon on a microscopic level.¹ To date, a large number of diverse ideas have been proposed in order to understand the solid-liquid transition. However, we are still far from a consensus on which of the several mechanisms is responsible for initiating the melting process as the temperature is raised. In most of the investigations, the efforts have been centered upon a search for some sort of lattice instability occurring at elevated temperatures. One of the oldest and the most influential of such investigations is that due to Lindemann.² Lindemann assumed that a solid melts when the mean-square amplitude of vibration of atoms about their equilibrium position becomes larger than a certain fraction of the lattice parameter. The Lindemann criterion has been applied and tested by various researchers,³⁻⁶ who have confirmed its validity.

The understanding of why such a simple melting criterion is obeyed in terms of the electronic structure of the material is of great interest. However, to the author's knowledge only a few works have been published in this context.^{7,8} The present report is a contribution to understanding in this field. It is shown that there is an interesting relationship between the energy gaps and melting temperatures in a variety of materials which includes semiconductors, ionic solids, and ferroelectrics. The relationship shows two main features which may be interpreted successfully by considering the different types of bonding involved. In the following, we first give the relationship. After that, a simple explanation based on bond orbital theory is given.

II. RELATIONSHIP BETWEEN ENERGY GAPS AND MELTING TEMPERATURES

Most of the theoretical investigations on the solid-liquid transition are discussed by making use of the notions of lattice dynamics. Furthermore, the scope of the works are limited to a restricted number of substances of the same class. The finding that is presented below, suggests that from the point of view of the electronic structure, the melting phenomenon can be understood on general grounds, irrespective of the material considered.

The interesting relationship between the energy gaps

and melting temperatures is shown in Fig. 1. Two groups of materials are discernible. One of these consists mainly of alkali halides and alkaline-earth halides, which are well-known ionic substances (group I). In this group the halides of copper, silver, and thallium, and other compounds such as CdI_2 and CsAu are also included. The other group, although somewhat dispersed, includes substances of a varied nature such as semiconductors, insulators, and ferroelectrics (group II). Some compounds such as Al_2O_3 , MgSe , Al_2S_3 , SiC , and AlP deviate considerably, but may be considered to belong to the group II. In order to avoid unnecessary congestion, many other compounds, the data for which are available in the literature,^{9,10} are not plotted in Fig. 1. The omitted compounds were confirmed to belong to one of the two groups. With few exceptions, the values of the energy gaps reported in Fig. 1 are those measured at room temperature. We have neglected the small temperature dependence which is irrelevant for our purposes.

At this point it would be interesting to note from Fig. 1, the behavior of a special group of compounds known as cation superionic conductors. The good ionic conductors such as AgI , CuI , CuBr , and RbAg_4I_5 pertain to group I, whereas mixed conductors such as Cu_2S , Cu_2Se , Ag_2S , Ag_2Se , and Ag_2Te pertain to group II. Compounds such as AgI , although belonging to group I, are found close to compounds of group II. This behavior reminds the classification of solids in terms of Phillips' ionicity.¹¹ According to his theory, compounds of copper and silver halides have ionicities near to the critical value $f_i = 0.785$. Concerning the $A^N B^{8-N}$ compounds, at the critical value of ionicity a phase transition from fourfold to sixfold coordination occurs. The peculiar location of copper and silver halides in Fig. 1 could be related to this fact.

The concept of ionicity introduced by Phillips has been used successfully to classify and explain many properties and chemical trends of $A^N B^{8-N}$ type compounds.¹¹ However, the relationship shown in Fig. 1 as a whole is not explained by taking a simple parameter such as ionicity, even restricting our data to $A^N B^{8-N}$ compounds. Rather, it seems to correlate with the valence bandwidth. The compounds in group I have a narrow valence bandwidth compared to those in group II. This observation provides a simple physical interpretation: Group II compounds are more favored to form hybrid orbitals which lead to a large noncen-

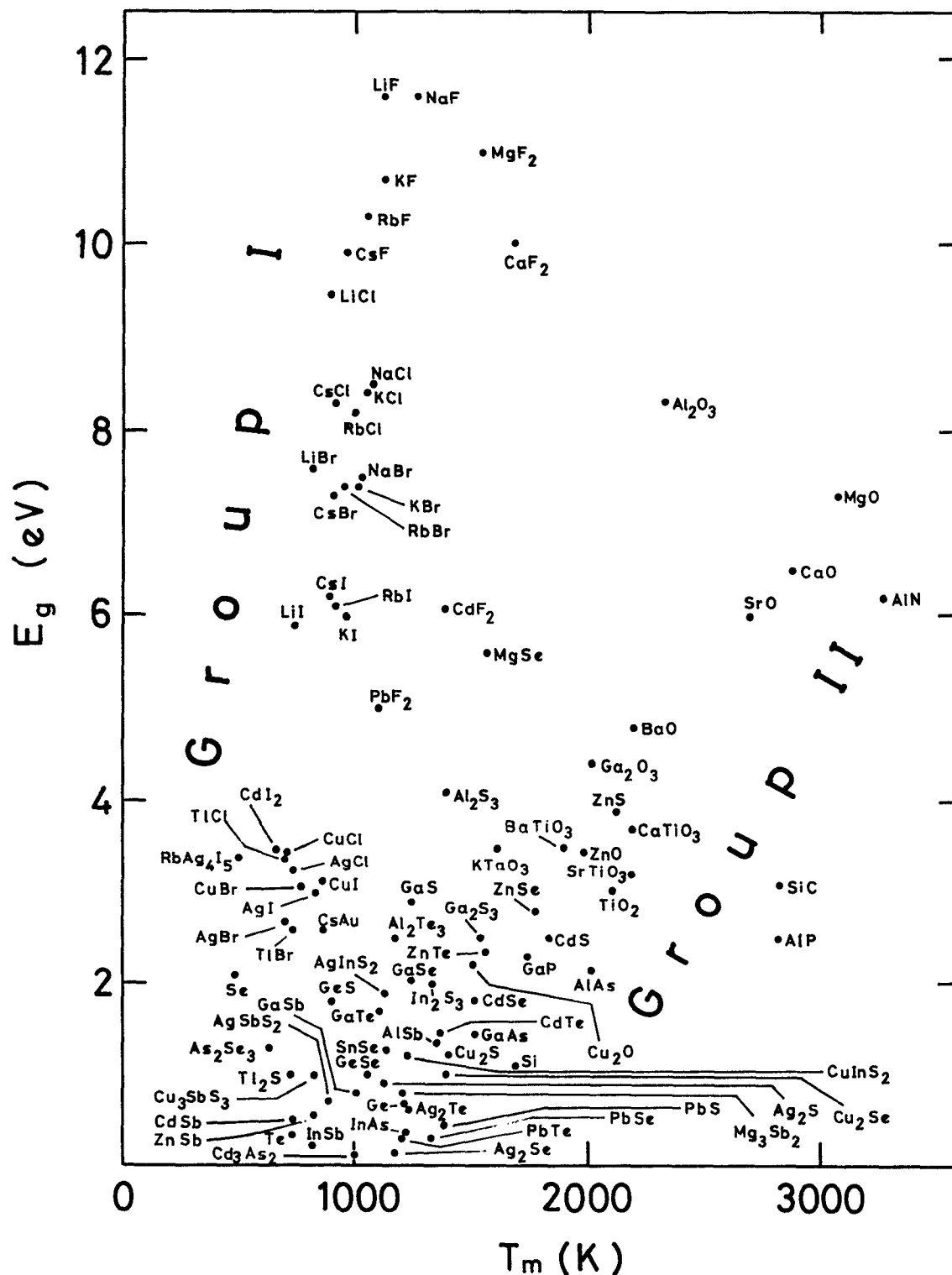


FIG. 1. Empirical relationship between energy gaps and melting temperatures.

tral force constant between the atoms. Since melting is expected to be related to the shear instability, these compounds can resist strong thermal disturbance of the ions. On the other hand, the bond nature of the compounds of group I are more sensitive to the thermal disturbance of the ions than those of group II. Indeed, it is known that the valence band of alkali halides and alkaline-earth halides is mainly formed

from the outermost p orbitals. Consequently, the thermal disturbance of the atoms decreases considerably, the overlap integral of the wave function between neighboring atoms, resulting in a relatively low melting temperature in comparison to those of group II. In the last statement we are referring of course to a comparison between compounds of both groups which have nearly the same energy gaps. Such com-

parison is meaningful because it is known that a linear relationship exists between the energy gaps and the heat of formation.¹² The fact that compounds such as CuCl, CuI, AgBr, AgI, TlCl, PbF₂, CdF₂, MgSe, etc., occupy a somewhat intermediate position in Fig. 1 is due to the presence of hybridization such as Cl(3*p*)-Ag(4*d*) in AgCl, F(2*p*)-Cd(4*d*) in CdF₂, F(2*p*)-Pb(*s*) in PbF₂, etc., as has been evidenced in band-structure calculations.^{13,14} MgSe is a compound which can exist in both phases: fourfold or sixfold coordination.¹¹

By examining Fig. 1, we observe another interesting feature. The oxides of alkaline-earth elements which are well-known ionic compounds belong to group II rather than to group I, in contradiction with our naive expectation. This fact can be understood along the lines discussed above. The electronic structure of these compounds show insulating characteristics, such as large band gaps, as well as semiconducting characteristics, such as large valence bandwidths.¹⁵

It must be mentioned that a relationship between energy gaps and melting temperatures of elemental and III-V semiconductors has been reported by Ferrante and Tosi.¹⁶ However, the interpretation given in this report is new and independent of theirs.

III. EXPLANATION BASED ON BOND ORBITAL THEORY

The aforementioned discussions are rather qualitative and speculative. In order to gain more insight into our findings and give a more quantitative discussion, we have calculated the total energy by making use of the bond orbital theory developed by Harrison and his co-workers.¹⁷

In Sec. II we have already mentioned that there is an empirical relationship between the energy gaps and the heat of formation.¹² This prompted us to calculate the total energy of the compounds and compare them with the data shown in Fig. 1. We have chosen the bond orbital theory because it is a convenient theory for studying the general chemical trends of the compounds in a relatively simple way. Although the bond orbital theory has been shown to be applicable to a variety of compounds,¹⁷ we have limited its application to $A^N B^{8-N}$ compounds, which is sufficient for our purposes.

In the following, an expression of the total energy is given. We will follow the approach given recently by Harrison¹⁸ in a somewhat modified form. The formulation is in terms of tight-binding atomic states. In tight-binding theory of *sp*-bonded systems, the electronic eigenstates are written in terms of a minimal basis set consisting of a single *s* state and three *p* states on each atom.¹⁷ A principal contribution to the total energy is the sum of the eigenvalues of the occupied states.¹⁸ Since we are interested in $A^N B^{8-N}$ compounds, we shall consider that the occupied states consist of the lowest half of the eigenvalues. A simple expression for the average of the lower half of the eigenvalues, as measured from the average of all the eigenvalues, is given by¹⁸

$$\epsilon_b^2 = M_2 - (M_4 - M_2^2)/4M_2, \quad (1)$$

where

$$M_2 = \sum_i \epsilon_i^2/N = \sum_{ij} H_{ij}H_{ji}/N \quad (2)$$

and

$$M_4 = \sum_i \epsilon_i^4/N = \sum_{ijkl} H_{ij}H_{jk}H_{kl}H_{li}/N. \quad (3)$$

Here, ϵ_i is the eigenvalue and H_{ij} is the Hamiltonian matrix element. Harrison¹⁸ has shown that the first term of Eq. (1) gives the radial interaction and the second term leads to angular forces.

The universal tight-binding parameters for interaction between nearest-neighbor orbitals has the form¹⁷

$$V_{ll'm} = \eta_{ll'm} \hbar^2/m_0 d^2. \quad (4)$$

Here, *l* and *l'* indicate the orbitals coupled and *m* indicates the component of angular momentum around the internuclear axis. In Eq. (4), *d* is the internuclear distance and *m*₀ is the electron mass. The coefficients are¹⁸ $\eta_{ss\sigma} = -1.32$, $\eta_{sp\sigma} = 1.42$, $\eta_{pp\sigma} = 2.22$, and $\eta_{pp\pi} = -0.63$.

A. Fourfold coordinated compounds

For the fourfold coordinated compounds, consider the energy diagram illustrated in Fig. 2. $4V_{1+}$ and $4V_{1-}$ denote the *sp* splitting of the metallic and nonmetallic atoms, respectively. $2V_3$ represents the energy separation between the *sp*³ hybrids localized on the metallic and nonmetallic atoms. More specifically,

$$V_3 = (\epsilon_h^m - \epsilon_h^n)/2, \quad (5)$$

where

$$\epsilon_h^m = (\epsilon_s^m + 3\epsilon_p^m)/4 \quad (6a)$$

and

$$\epsilon_h^n = (\epsilon_s^n + 3\epsilon_p^n)/4. \quad (6b)$$

Here the superscripts *m* and *n* denote the metallic and nonmetallic atoms, respectively. The subscripts denote the orbitals *s* and *p*. For the values of ϵ_s and ϵ_p , we will use those tabulated by Harrison.¹⁹

With the help of the energy diagram shown in Fig. 2, we can immediately calculate the terms M_2 through Eq. (2), which gives

$$M_2 = \sum_i \epsilon_i^2/N = V_3^2 + 3(V_{1+}^2 + V_{1-}^2)/2 + nV_2^2/4. \quad (7)$$

Here *n* is the number of nearest neighbors. The first two terms on the right-hand side is the contribution from the

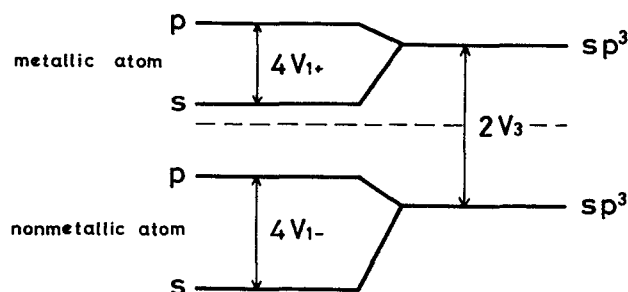


FIG. 2. Energy diagram for a fourfold coordinated compound. The dashed line represents the average of the atomic terms.

diagonal terms of the Hamiltonian matrix. The last term represents the contribution from off-diagonal terms and arises from the coupling between orbitals on neighboring atoms which is given by

$$V_2 = (V_{ss\sigma}^2 + 2V_{sp\sigma}^2 + V_{pp\sigma}^2 + 2V_{pp\pi}^2)^{1/2} = 3.39\hbar^2/m_0d^2. \quad (8)$$

In Eq. (8) we have used the fact that, for a particular pair of neighboring atoms, the coupling can be taken as σ oriented or π oriented.¹⁸

The evaluation of M_4 is more complicated. The sum of

the diagonal terms gives

$$\begin{aligned} M_4(1) = \sum_i H_{ii}^4/4 = & V_3^4 + 9V_3^2(V_{1+}^2 + V_{1-}^2) \\ & + 12V_3(V_{1-}^3 - V_{1+}^3) \\ & + 21(V_{1+}^4 + V_{1-}^4)/2, \end{aligned} \quad (9)$$

where the 1 in the parentheses indicates one-atom terms.

There are off-diagonal terms involving two and three neighboring atoms. By carefully collecting a large number of terms from Eq. (3), the term involving two atoms may be written as¹⁸

$$\begin{aligned} M_4(2) = & (V_{ss\sigma}^4 + 4V_{ss\sigma}^2V_{sp\sigma}^2 + 4V_{ss\sigma}V_{sp\sigma}^2V_{pp\sigma} + 2V_{sp\sigma}^4 + 4V_{sp\sigma}^2V_{pp\sigma}^2 + V_{pp\sigma}^4 + 2V_{pp\pi}^4)/4 \\ & + V_{ss\sigma}^2[V_3^2 + 3V_3(V_{1-} - V_{1+}) + 9(V_{1+}^2 + V_{1+}V_{1-} + V_{1-}^2)]/2 \\ & + V_{sp\sigma}^2[V_3^2 + V_3(V_{1-} - V_{1+}) + 5(V_{1+}^2 + V_{1-}^2) - 3V_{1+}V_{1-}] \\ & + (V_{pp\sigma}^2 + 2V_{pp\pi}^2)[V_3^2 - V_3(V_{1-} - V_{1+}) + V_{1+}^2 + V_{1+}V_{1-} + V_{1-}^2]/2. \end{aligned} \quad (10)$$

Since Eq. (10) has been evaluated by considering only one pair of atoms, we must multiply Eq. (10) by the number of neighbors, $n = 4$ in our case. Moreover, by using Eq. (8), Eq. (10) is rewritten as

$$\begin{aligned} M_4'(2) = & n[0.125V_2^4 + 0.5V_2^2V_3^2 + 0.154(V_{1-} - V_{1+}) \\ & \times V_2^2V_3 + 1.808(V_{1+}^2 + V_{1-}^2)V_2^2 \\ & + 0.405V_{1+}V_{1-}V_2^2]. \end{aligned} \quad (11)$$

Following the method used by Harrison,¹⁸ the term involving three atoms leads to

$$\begin{aligned} M_4(3) = & (V_{ss\sigma}^2 + V_{sp\sigma}^2)^2 + 2(V_{sp\sigma}^2 + V_{pp\sigma}^2)V_{pp\pi}^2 + V_{pp\pi}^4 \\ & + 2V_{sp\sigma}^2(V_{ss\sigma} - V_{pp\sigma})^2 \cos \theta \\ & + (V_{sp\sigma}^2 + V_{pp\sigma}^2 - V_{pp\pi}^2)^2 \cos^2 \theta \\ = & (0.150 + 0.382 \cos \theta + 0.324 \cos^2 \theta) \\ & \times V_2^2(d_1)V_2^2(d_2), \end{aligned} \quad (12)$$

where d_1 and d_2 are the two internuclear distances involved and θ is the angle subtended by the two ligands at the central atom. For the tetrahedral structure, there are six combinations of ligand pairs each with $\cos \theta = -\frac{1}{3}$. Moreover, by adopting $d_1 = d_2 = d$, Eq. (12) may be rewritten as

$$M_4'(3) = 0.352V_2^4(d). \quad (13)$$

Consequently, the required fourth moment M_4 is given by

$$M_4 = M_4(1) + M_4'(2) + M_4'(3). \quad (14)$$

To obtain the total energy, we must add an overlap repulsion which, in the tight-binding context, arises principally from nonorthogonality of neighboring orbitals.¹⁸ Apart from the overlap repulsion, in order to obtain the energy relative to isolated atoms, we must add a promotion energy, which is the energy required to form an sp^3 configuration from an isolated atom configuration. The promotion energy per atom pair is given by¹⁸

$$\begin{aligned} E_{\text{pro}} = & \begin{cases} 8V_1 & \text{(column IV compounds)} \\ 5V_{1+} + 3V_{1-} + 2V_3 & \text{(III-V compounds)} \\ 6V_{1+} + 2V_{1-} + 4V_3 & \text{(II-VI compounds)} \\ 3V_{1+} + V_{1-} + 6V_3 & \text{(I-VII compounds).} \end{cases} \end{aligned} \quad (15)$$

The energy per atom pair is written as

$$\begin{aligned} E_{\text{pair}} = & -8\epsilon_b + nV_0(d) + E_{\text{pro}} \\ = & -8[M_2 - (M_4 - M_2^2)/4M_2]^{1/2} \\ & + 4V_0(d) + E_{\text{pro}}, \end{aligned} \quad (16)$$

where $V_0(d)$ is the overlap repulsion. The coefficients 8 and 4 are the number of electrons participating in the bonding and the coordination number, respectively.

B. Sixfold coordinated compounds

For sixfold coordinated $A^N B^{8-N}$ compounds, we can assume that electrons participating in the bonding are the s electrons of the metallic atom and the p electrons of the non-metallic atom. Then, in the present case, the only term that survives is $V_{sp\sigma}$. Moreover, the sp splitting of the atoms vanishes, i.e., $V_{1+} = V_{1-} = 0$.

By taking into account the change in the coordination number, the relations deduced in the preceding subsection are modified to become

$$V_2 = \sqrt{2}V_{sp\sigma} = 2.01\hbar^2/m_0d^2, \quad (17)$$

$$M_2 = V_3^2 + 3V_2^2/2, \quad (18)$$

$$M_4(1) = V_3^4, \quad (19)$$

$$M_4(2) = V_{sp\sigma}^2(V_{sp\sigma}^2/2 + V_3^2), \quad (20a)$$

$$M_4'(2) = 6V_2^2(0.125V_2^2 + 0.5V_3^2), \quad (20b)$$

$$M(3) = V_{sp\sigma}^4(1 + \cos^2 \theta), \quad (21a)$$

$$M'_4(3) = 4.5V_2^4, \quad (21b)$$

$$M_4(4) = 2V_{sp\sigma}^4, \quad (22a)$$

$$M'_4(4) = 6V_2^4, \quad (22b)$$

$$M_4 = V_3^4 + 3V_2^2V_3^2 + 11.25V_2^4. \quad (23)$$

In the case of sixfold coordinated compounds, we have also the contribution from a term involving four atoms, which is denoted above by $M_4(4)$. In Eq. (21b) we have taken into account the fact that, for a sixfold coordinated compound, there are twelve pairs of atoms at $\theta = 90^\circ$ and three pairs at

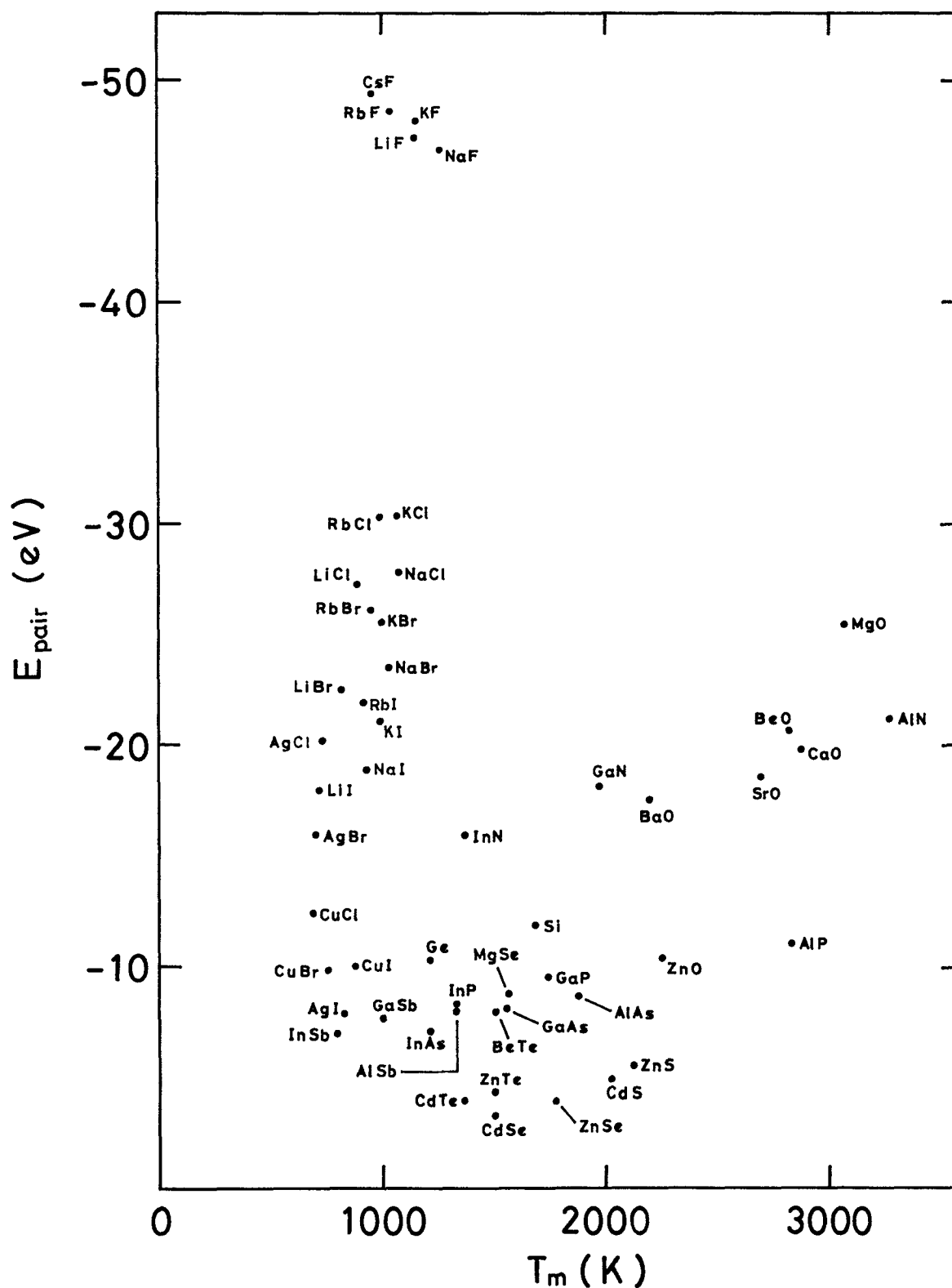


FIG. 3. Energy per atom pair calculated by using the bond orbital theory. The energy per atom pair is plotted against the melting temperature in order to compare with the empirical relationship shown in Fig. 1.

$\theta = 180^\circ$. Equation (22b) arises by noting that there are twelve $V_{sp\sigma}$ bonded loops consisting of four atoms which are associated with a particular atom.

In the case of sixfold coordinated compounds we do not need a promotion energy. Consequently, the energy per atom pair is given by

$$E_{\text{pair}} = -6[M_2 - (M_4 - M_2^2)/4M_2]^{1/2} + 6V_0(d). \quad (24)$$

C. Application

With the results enumerated in Secs. III A and III B, we are prepared to evaluate the total energy of $A^N B^{8-N}$ compounds and interpret the empirical relationship shown in Fig. 1. The atomic term values used here are those tabulated by Harrison.¹⁹

For the overlap repulsion we have used those results determined empirically or semiempirically.²⁰⁻²⁴ We have avoided the determination of V_0 within the same formulation because adjustment must be made in any case. According to Harrison's guiding study,¹⁸ V_0 is given by

$$V_0(d) = A/d^3 + B/d^{12}, \quad (25)$$

where A and B are obtained by fitting the observed lattice spacing and the bulk modulus. Except for the copper and silver halides, the repulsive energy that we have used is in good agreement with those reported by Harrison.¹⁸ As mentioned briefly in Sec. II, these compounds are sufficiently unusual. The aforementioned disagreement must be taken as a starting point for a more careful study. The repulsive potential that we have used for these compounds is that used in a molecular dynamics study.²⁴

In Fig. 3 we show the distribution of the calculated values E_{pair} , by using Eqs. (16) and (24). For the alkali halides, AgCl and AgBr, we have applied the formulae of Sec. III B. For the other compounds the expressions of Sec. III A have been used. We can observe that the overall behavior resembles that shown in Fig. 1. The group of semiconductors is found to be more dispersed when compared to the corresponding group II of Fig. 1. However, we must take this as a surprising result, because of its simplicity.

BaO, SrO, CaO, and MgO are well-known ionic compounds. However, the evaluation of E_{pair} by using the relations of Sec. III B, gives a different chemical trend as shown in Table I. The results shown in Fig. 3 have been evaluated as in the case of semiconductors. That is, the s and p electrons of the oxygen atom and s electrons of the metallic atom are considered to be participating in the bonding. This approach is supported by band-structure studies. The electronic structure of these compounds show characteristics of both ionic and semiconducting solids. In Table I, we have included MgSe which is a structurally unstable compound. We can observe that the participation of the selenium $4s$ electrons in the bonding, lowers the energy per atom pair by about 2 eV. Since the compounds listed in Table I are sixfold coordinated, in order to evaluate E_{pair} we must use $n = 6$ in the relations of Sec. III A. The other modifications which arise from terms involving three and four atoms are expressed as¹⁸

$$M'_4(3) + M'_4(4) = 2.7V_2^4. \quad (26)$$

TABLE I. Energy per atom pair as evaluated without the participation of the oxygen $2s$ electron (or the selenium $4s$ electron) in the bonding (E'_{pair}), and with its participation (E_{pair}). The promotion and repulsive (Ref. 21) energies are also given for a reference. The energy unit is in eV.

Compound	E'_{pair}	E_{pair}	E_{pro}	V_0
MgO	-25.46	-25.55	46.32	1.63
CaO	-28.84	-19.98	56.08	1.55
SrO	-30.32	-18.57	55.60	1.41
BaO	-31.61	-17.51	54.76	1.36
MgSe	-6.76	-8.80	28.94	1.31

IV. CONCLUSION

In the present study we have reported an interesting relationship between energy gaps and melting temperatures which has been found in varied classes of materials. The relationship divided the materials into two main groups which have been interpreted successfully by considering the nature of the bonding. We have shown that the two groups are correlated with the total energies of the compounds. The total energy has been evaluated by making use of the bond orbital theory developed by Harrison.^{17,18}

As discussed in Sec. II, the empirical relationship shown in Fig. 1 suggests the different behavior of compounds pertaining to group I and II as against the thermal disturbance of the atoms. A theoretical formulation of this picture will lead, the author believes, to a microscopic understanding of Lindemann's law. To this object we have to develop a dynamical theory of chemical bonding.

As we have previously mentioned, a group of materials named superionic conductors occupies a particular location in Fig. 1. Many properties of these compounds have been found to show behavior intermediate between solids and liquids.²⁵ Such peculiarities lead Ginoza *et al.*²⁶ to suggest that these compounds melt in a characteristic way. However, according to our interpretation of Fig. 1, the melting mechanism of these compounds do not differ from that of alkali halides. The author believes that the "superionic melt" discussed by Ginoza *et al.*²⁶ is due to another mechanism. A view that the author would like to suggest is that the "superionic melt" is a manifestation of the local change of the chemical bond which fluctuates in time.²⁷ We are planning a more detailed study in this connection.

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