

# Correlations Between the Melting Temperature and the Bonding Parameters in AB type Compounds

Haruhito SADAKUNI\*, Shosuke IKEDA and Masaru ANIYA

Department of Physics, Graduate School of Science and Technology, Kumamoto University, Kurokami, Kumamoto 860-8555, Japan

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The aim of the present work is to understand the melting phenomena from a chemical bond point of view. We have studied the chemical trend of the melting temperature of AB type compounds by using the bond orbital model. It has been shown that the dominant interaction parameter determining the melting temperature depends on the types of materials. The peculiar behavior of Cu and Ag halides among the AB type compounds have been pointed out.

KEYWORDS: melting, bond orbital model

## 1. Introduction

Melting is one of the most popular physical phenomena. However, concerning the fundamental aspect of melting phenomena, many questions remains unsolved and not well understood. In order to understand the complicated mechanism of melting, many models have been proposed. For example, the famous empirical model proposed by Lindemann<sup>1)</sup> states that a material melts when the amplitude of the thermal oscillation of the atoms becomes approximately 10% of the equilibrium interatomic separation. Most of the modern approaches to melting are based on lattice dynamical considerations.<sup>2)</sup> In the present report, the melting phenomena are investigated from a chemical bond point of view.<sup>3)</sup> We have studied the chemical trend of the melting temperature by using the bond orbital model.<sup>4)</sup> By using this model, we can consider in a relatively simple way the essence of the nature of the chemical bond. In the past, this model has been used to study the structural stability of many AB type compounds such as NaCl and GaAs.<sup>4,5)</sup>

Among the AB type compounds, the superionic conducting materials such as AgI and CuI are of particular interest, because of their unique lattice dynamical properties. The lattice stability of these compounds is very unique when compared with other AB type compounds. The understanding of this peculiarity is directly related with the understanding of melting. Studies along this line have been performed by our group.<sup>6,7)</sup> The present work is a natural extension of a previous work.<sup>3)</sup>

## 2. Bonding parameter in the bond orbital model

In the bond orbital model, the energy per atom pair in a 4-fold coordinated compound can be written as<sup>3,5)</sup>

$$E^{(4)} = -8 \sqrt{M_2 - \frac{M_4 - M_2^2}{4M_2}} + E_{pro} + 4V(d), \quad (1)$$

where  $M_2$  and  $M_4$  denote the second and the fourth moments of the Hamiltonian,  $E_{pro}$  denotes the promotion energy, and  $V(d)$  denotes the repulsive potential.  $M_2$  and  $M_4$  are written explicitly as

$$M_2 = \sum_i \frac{\varepsilon_i^2}{N}, \quad (2)$$

$$M_4 = \sum_i \frac{\varepsilon_i^4}{N},$$

where  $\varepsilon_i$  is the eigenvalue and  $N$  is the number of orbits. In eq. (1), the first term inside the root sign arises mainly from radial interactions and the second term is related to angular force dependent interactions.

By calculating  $M_2$  with the help of Fig. 1 we obtain<sup>3,5)</sup>

$$M_2 = V_3^2 + \frac{3}{2}(V_{1+}^2 + V_{1-}^2) + \frac{n}{4}V_2^2, \quad (3)$$

where  $n$  denotes the coordination number.

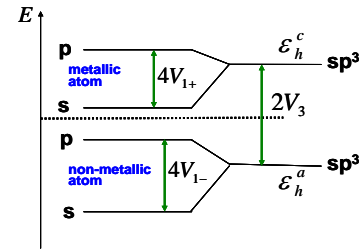


Fig. 1. Energy diagram for a 4-fold coordinated compound.

The quantities  $V_3$  and  $\varepsilon_h$  are defined by

$$V_3 = (\varepsilon_h^c - \varepsilon_h^a) / 2, \quad (4)$$

$$\varepsilon_h = (\varepsilon_s + 3\varepsilon_p) / 4. \quad (5)$$

Here,  $\varepsilon_s$  and  $\varepsilon_p$  are the energies of the s and p electrons whose values are given elsewhere.<sup>4,8)</sup>  $V_2$  arises from the overlap of orbitals between neighboring atoms and is written in terms of the universal tight binding parameters as<sup>4)</sup>

$$V_2 = (V_{ss\sigma}^2 + 2V_{sp\sigma}^2 + V_{pp\sigma}^2 + 2V_{pp\pi}^2)^{1/2} \quad (6)$$

$$= 3.39 \hbar^2 / m_e d^2,$$

where  $d$  denotes the bond length and  $m_e$  denotes the electron mass.

$M_4$  is given by

$$M_4 = M_4(1) + M_4(2) + M_4(3), \quad (7)$$

where

$$M_4(1) = V_3^4 + 9V_3^2(V_{1+}^2 + V_{1-}^2) + 12V_3(V_{1-}^3 - V_{1+}^3) + 21(V_{1+}^4 + V_{1-}^4) / 2, \quad (8)$$

$$M_4(2) = n[0.125 V_2^4 + 0.5 V_2^2 V_3^2 + 0.154 (V_{1+} - V_{1-}) V_2^2 V_3 + 1.808 (V_{1+}^2 + V_{1-}^2) V_2^2 + 0.405 V_{1+} V_{1-} V_2^2], \quad (9)$$

$$M_4(3) = 0.352 V_2^4(d). \quad (10)$$

For 6-fold coordinated compounds, we can assume that s electrons of the metallic and p electrons of the non-metallic atoms participate in the bonding. Under this assumption, the energy per atom pair becomes<sup>3)</sup>

$$E^{(6)} = -6 \sqrt{M_2 - \frac{M_4 - M_2^2}{4M_2}} + 6V(d), \quad (11)$$

where

$$\begin{aligned} V_2 &= 2.01 \hbar^2 / m_e d^2, \\ M_2 &= V_3^2 + 3V_2^2 / 2, \\ M_4 &= V_3^4 + V_2^2 V_3^2 + 11.25 V_2^4. \end{aligned} \quad (12)$$

### 3. Correlations between the melting temperature and the bonding parameters

Fig. 2 shows the correlation between the melting temperature  $T_m$  and the bonding parameter  $M_2$  which denotes the radial component in the bond energy. The Figure indicates that with the exception of Cu and Ag halides,  $T_m$  increases with the increase in  $M_2$ . The result suggests that in Cu and Ag halides, the term  $M_2$  is not the controlling parameter determining the melting.

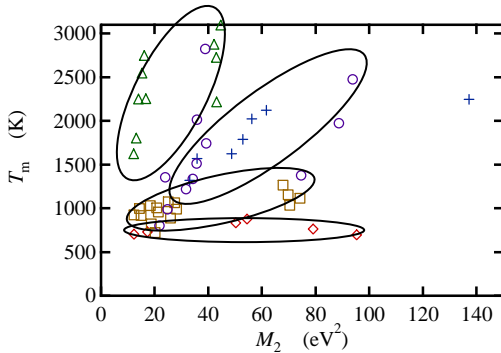


Fig. 2. Relationship between the bonding parameter  $M_2$  and the melting temperature  $T_m$ . The symbols indicate the following compounds. Cu and Ag halides (diamond), alkali halides (square), IIA-VI compounds (triangle), IIB-VI compounds (cross), III-V (circle). The groupings are guides to the eyes.

Fig. 3 shows the relationship between the melting temperature and the energy gap. Here we note a clear separation between the 6-fold and 4-fold coordinated compounds as already pointed out previously.<sup>3)</sup> We note also that Cu and Ag halides occupy a borderline position.

In a previous work,<sup>3)</sup> it has been suggested that the melting temperature is closely related with the angular forces. In Fig. 4, the relationship between  $(M_4 - M_2^2)/4M_2$  and the melting temperature for different group of materials is shown. We can see that in covalent materials such as IIB-VI and III-V compounds,  $T_m$  increases with the increase in  $(M_4 - M_2^2)/4M_2$ .

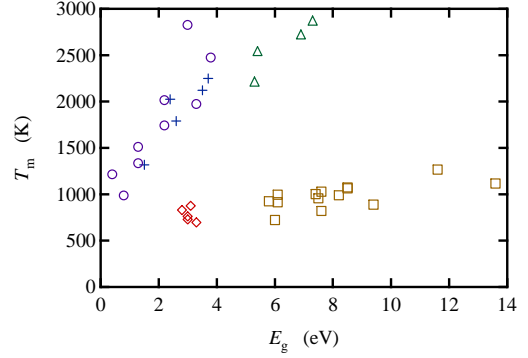


Fig. 3. Relationship between the melting temperature and the band gap  $E_g$ . The meaning of each symbol is the same to those used in Fig. 2.

In the scale shown in Fig. 4, the values of  $(M_4 - M_2^2)/4M_2$  for alkali halides show only a weak material dependence. In an enlarged scale, the gross trend indicates that  $T_m$  increases with  $(M_4 - M_2^2)/4M_2$ . Comparing the result shown in Fig. 2 and 4, we can say that the  $T_m$  in alkali halides is controlled mainly by the term  $M_2$ . For the Cu and Ag halides, analogously to Fig. 2,  $T_m$  is not sensitive to the value of  $(M_4 - M_2^2)/4M_2$ .

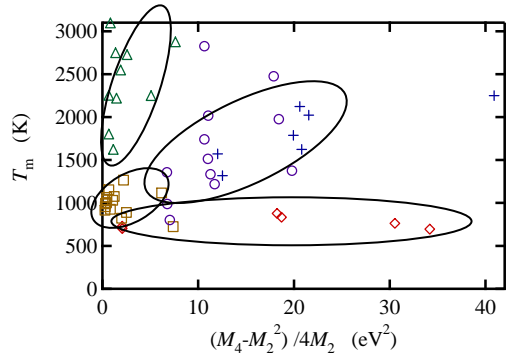


Fig. 4. Relationship between the bonding parameter  $(M_4 - M_2^2)/4M_2$  and the melting temperature. The meaning of each symbol is the same to those used in Fig. 2. The groupings are guides to the eyes.

According to our analysis, the values of  $(M_4 - M_2^2)/4M_2$  for 4-fold coordinated compounds depend mainly on  $V_{1-}$ , whereas for 6-fold coordinated compounds it depends mainly on  $V_2$ . From this observation, we can say that for the 4-fold coordinated compounds, the main factor determining the melting temperature is  $V_{1-}$  of the anion. That is, the melting temperature is related to the band width of the valence band. On the other hand, for the 6-fold coordinated compounds, the controlling parameter of melting is the bond length that enters through  $V_2$ .

Fig. 5 shows the correlation between the melting temperature and the relative stability of a compound. Here,  $|E^{(4)} - E^{(6)}|$  has been obtained by calculating the difference between the energy per atom pair by assuming 4- and 6-fold coordinations. To evaluate the promotion energy, we have used the expression given in previous works.<sup>3, 5)</sup> For the evaluation of the repulsion term  $V(d)$ , we employed the expression derived by Harrison and used frequently by other researchers.<sup>9, 10)</sup>

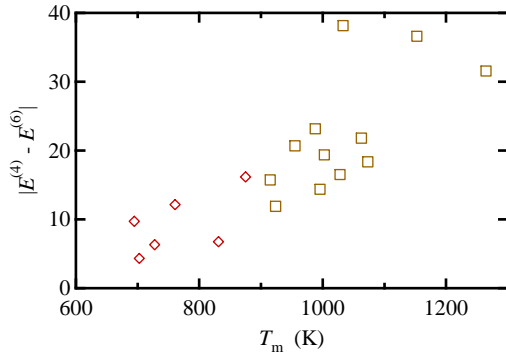


Fig. 5. The correlation between the energy difference  $|E^{(4)} - E^{(6)}|$  and  $T_m$ . Here,  $E^{(4)}$  and  $E^{(6)}$  are the energy per atom pair calculated by assuming 4- and 6-fold coordination. The meaning of each symbol is the same to those used in Fig. 2.

According to Fig. 5, the melting temperature correlates positively with the magnitude of  $|E^{(4)} - E^{(6)}|$ . It should be noted that Ag and Cu halides have small values of  $|E^{(4)} - E^{(6)}|$ . This behavior indicates that the structural stability of these compounds is low in comparison with other materials. In a previous study, it was shown that  $|E^{(4)}|$  calculated for 4-fold coordinated compounds and  $|E^{(6)}|$  calculated for 6-fold coordinated compounds, both increase with the melting temperature.<sup>3)</sup> However, they exhibited different trends. The melting temperature for 4-fold coordinated compounds was more sensitive to the variation of the energy per atom pair than those for 6-fold coordinated compounds. It was also pointed out that superionic materials occupy an intermediate position in the trend between energy per atom pair and melting temperature. This observation and the result shown in Fig. 5 reflect the intermediate nature of the chemical bonding of superionic materials, which is the background of the bond fluctuation model of superionic conductors.<sup>6)</sup>

As shown in Fig. 6, the quantity  $P^{(4)}/P^{(6)}$  varies systematically when plotted against the Phillips' ionicity.<sup>11)</sup> Here,  $P^{(4)}$  and  $P^{(6)}$  are the values of  $(M_4 - M_2^2)/4M_2$  calculated by assuming 4- and 6-fold coordinations. It is interesting to note that  $P^{(4)}/P^{(6)}$  starts to increase rapidly for ionicity larger than 0.8, which is near the critical ionicity 0.785. According to our analysis,  $P^{(4)}/P^{(6)} \approx V_1/V_2$ . That is, the ratio between the main parameters determining the melting temperature in 4- and 6-fold coordinated compounds changes abruptly near the critical ionicity. It is probable that this behavior is related with the superionic behavior that the Cu and Ag halides exhibit, because the ionicities of these compounds are close to the critical value.<sup>11)</sup>

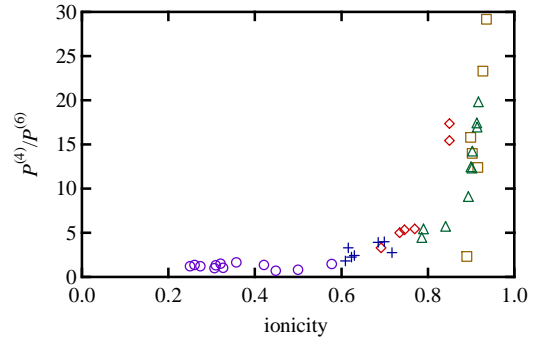


Fig. 6. The correlation between  $P^{(4)}/P^{(6)}$  and the Phillips' ionicity. Here,  $P^{(4)}$  and  $P^{(6)}$  are the values of  $(M_4 - M_2^2)/4M_2$  calculated by assuming 4- and 6-fold coordination. The meaning of the symbols is the same to those used in Fig. 2.

#### 4. Conclusion

In the present report, we have studied how the melting temperature depends on the interaction parameters defined by the bond orbital model. The analysis has revealed that the melting temperature varies systematically with the interaction parameters. It has been shown that the dominant interaction parameter determining the melting temperature depends on the types of the materials. The implication of this finding to understand the superionic behavior has been discussed briefly.

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