An Empirical Relation Between the Melting Point and the Direct Bandgap of Semiconducting Compounds

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The melting point is found to vary linearly with the direct bandgap for groups of semiconductors with common anions. Implication of this empirical result is discussed. The linear relation is used to choose between different reported values of melting point for some compounds.

Keywords: Bandgap, entropy of fusion, melting point, semiconductor

INTRODUCTION

Current developments in electron devices are mostly based on semiconducting compounds. A number of physical constants of the compounds are of interest for these applications. However, the various properties being basically determined by the atomic potentials, the different physical constants are expected to be correlated. Correlation between the dielectric constant and the bandgap has been studied by Adachi[1] and a linear relation was suggested, which, however, gave a very approximate fit. Melting point and bandgap, being both related to the binding between the neighboring atoms, are expected to be strongly correlated. As far as the present author is aware, the correlation has not been examined as yet. The purpose of this paper is to examine if the correlation is expressible by a simple formula and to use the formula to choose between different reported values of melting point of some binary compounds. The other objective is to examine the correlation in the light of the theory and to obtain values of the thermodynamic parameters related to melting.

DISCUSSION

There are 39 materials[2] considering the various elemental, III-V, II-VI, and I-VII compounds which have similar bonding and may be expected to have similar properties. However, the melting point and the bandgap of copper and silver compounds do not show much variation, while for beryllium compounds only calculated values are available. On the other hand, grey tin and mercury compounds are semimetals with a near-zero or a negative bandgap. Well-established values of melting point and finite direct bandgap are available only for the semiconducting III-V compounds and zinc and cadmium compounds. The discussion is, therefore, restricted to these compounds only.

We have taken for our consideration the experimental values of the bandgap,[2–5] which are, however, in close agreement with the calculated values. For the melting point also, experimental values are mostly taken, but calculated values[4] are quoted when these are significantly different. The bandgap and the melting point of the 18 materials under consideration are listed in Table I. The melting point increases in general as the bandgap increases. Such variation may be explained by considering that the bandgap should decrease with increase in the atomic number of the constituent atoms. The atomic potentials spread and consequently the potentials of neighboring atoms overlap more and more with increase in the atomic number. Atoms are, therefore, more closely coupled

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Table I. Physical Constants of Semiconducting Compounds

Compound	Direct Bandgap (eV)	Melting Point (K)	Lattice Constant, a (Å)	Entropy of Fusion, ΔS (Cal/gm.mole °K)	$a^2\Delta S$	$C_0\Delta S$ (kCal/gm.mole)
AlN	6.2	3300				
GaN	3.5	2800				
		2000				
InN	2.05	1373				
AlP	3.63	2823	5.46	16.69	498	17.1
		1853				
GaP	2.88	1738	5.45	16.52	491	16.7
InP	1.42	1343	5.86	16.28	559	16.4
AlAs	3.1	2043	5.66	13.83	443	14.8
GaAs	1.51	1511	5.65	13.56	432	14.5
InAs	0.43	1215	6.05	13.01	476	14.0
AlSb	2.38	1338	6.13	16.53	621	12.4
GaSb	0.81	985	6.09	16.17	600	12.2
InSb	0.235	797	6.48	15.57	653	11.7
ZnS	3.8	2196	5.41	16.29	477	17.2
CdS	2.58	1830	5.82	16.21	549	17.1
ZnSe	2.78	1790	5.67	16.29	523	15.7
CdSe	1.85	1512	6.05	16.07	588	15.4
ZnTe	2.34	1570	6.10	16.34	608	14.9
CdTe	1.61	1365	6.48	16.10	676	14.7

Note: Values are taken from Refs. 2–5.

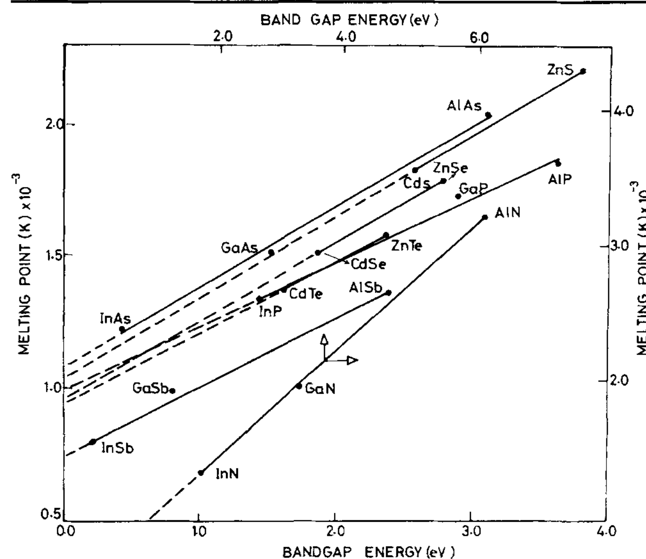

Fig. 1. Melting point vs bandgap; scales for all the compounds except nitrides are as marked on the axes on the left and the bottom. The scale for the nitrides is indicated by the arrows and given by the axes on the right and the top.

and the width of the allowed energy band increases, which results in a decrease of the bandgap. The increasing overlap also causes a decrease in the change in energy between the pre-melting semiconducting phase and the post-melting metallic phase and, therefore, a reduction in the melting point.

The data of Table I are in qualitative agreement with the phenomenological expectation. But, no simple relation correlating the two constants is apparent when all the data are considered collectively. A linear relation gives a root mean square percentage error (RMSPE) of 20% and for some materials the discrepancy is as large as 50%. It is, however, known that compounds with a common anion have similar properties when melted. For example, arsenic segregates in molten arsenides, while phosphorus and antimony remain mixed in phosphides and antimonides. Some regularity may, therefore, be expected when the materials are grouped with a common anion. Physical processes occurring in III-V compounds are, however, known to be very different from those in II-VI compounds. The III-V compounds transform from the semiconducting to the metallic phase before melting at the melting point, whereas II-VI compounds remain semiconducting. These two groups of compounds are, therefore, considered separately.

Data for the III-V compounds with a common anion may be fitted with straight lines as shown in Fig. 1 with a value of RMSPE of 2% or less. Although the fit is obtained with only three points in each group, it may be considered significant as the fit is with a straight line. In the case of phosphides two values of the melting point 2823 and 1853K are available for aluminum phosphide. The latter value fits a straight line with the values for gallium phosphide and indium phosphide with an RMSPE of 1.5%, but the other value is far off. For gallium nitride, also two values, 2800 and 2000K are available. We find that the value of 2000K fits with those of aluminum nitride and indium nitride to give an RMSPE of 1%. In view of the linear relation obtained for other groups, values of 1853 and 2000K may be considered to be appropriate values respectively for AlP and GaN.

The fit to the straight line indicates that the melting point T^F and the direct bandgap E_0, for the III-V

compounds in each group are related linearly as

$$T^F = c_0 + c_1 E_0, \quad (1)$$

where E_0 is the direct bandgap, c_0 and c_1 are constants for each group. Values of these constants are listed in Table II.

Implications of the above linear relation may be discussed on the basis of the theory of melting of semiconductors developed by Van Vechten.[4] It was shown that the melting point, T^F, may be expressed as

$$T^F = \Delta E_m^F/\Delta S + \Delta E/\Delta S \quad (2)$$

where ΔS represents the change in entropy as the state of the semiconductor changes from solid to liquid, ΔE is the change in internal energy as the phase of the semiconductor changes from semiconducting to metallic at the melting point and ΔE_m^F is the change in energy due to change from the solid to the liquid state at the melting point. The contribution arising from the change in volume on melting is considered to be negligible.

The value of ΔE_m^F scales as the inverse square of the lattice constant, a. The value of $a^2\Delta S$ obtained by using the calculated values of ΔS (quoted in Table I from Ref. 4) is found to be within 4.5 and 7.8% of the average value for each group. The term $\Delta E_m^F/\Delta S$ of Eq. (1) is, therefore, expected to be independent of the bandgap for each group and c_0 may be identified with this term. The value of ΔE_m^F may be obtained by using the relation,

$$\Delta E_m^F = c_0 \cdot \Delta S. \quad (3)$$

Values, so obtained, are given in Table I. It should be mentioned that these values are significantly higher than the value of 9.68 kcal/gm.mole obtained for silicon in Ref. 4.

The value of ΔE was shown to be determined by the average bandgap E_g, the average Fermi energy, the direct bandgap E_0 and the critical point energies E_1 and E_2. Values of these constants were evaluated at the melting point by using empirical relations for the temperature dependence, and the computed values of ΔE were found to give values of T^F which agreed with experiments to within 10–20%. The second term $\Delta E/\Delta S$ in Eq. (1) should therefore be related to E_0.

CONCLUSION

Results of the present study indicate that the second term of Eq. (1) may be taken to be proportional to E_0. The proportionality constant for the phosphides and antimonides are nearly the same. The value for arsenides is about 20% larger. This difference may be understood by considering that ΔS for arsenides is smaller.[4]

For the II-VI compounds, there are only two compounds with a finite bandgap, in each group. There is, therefore, no check whether a linear relation fits the data of these compounds. We, however, find that the values of the constant c_1 for these compounds (listed in Table II) are close to the values for the III-V compounds.

The parameter ΔE_m^F may be evaluated for the II-VI compounds also by using the values of c_0 obtained by assuming that the T^F-E_0 relation is linear. Such calculated values are given in Table I. We find that the values are close to those for the III-V compounds.

It may also be noted that, although the nitrides obey a linear relation when the melting point of GaN is taken to be 2000K, the values of c_0 and c_1 are very different from those for the other groups. This result may be explained by considering that the melting points of nitrides are obtained under high pressure, as at ordinary pressures these compounds decompose at a temperature much lower than the melting point. Also, the crystal structure of these compounds are different from that of the other compounds.

Table II. Constants for the Empirical Relation Between Melting Point and Bandgap Energy

Compound	c_0(K)	c_1(K/eV)	RMSPE%
Phosphides	1009.7	239.9	1.5
Arsenides	1073.3	306.7	1.2
Antimonides	751.5	252.4	2.0
Nitrides	421.4	459.6	1.1
Sulphides	1056	300	
Selenide	960.7	298	
Tellurides	914	280	

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