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K. A. SHARIFOV, A. S. ABBASOV

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Abstract

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K. A. SHARIFOV, A. S. ABBASOV

ON THE RELATIONSHIP BETWEEN THE BAND GAP AND THE GIBBS ENERGY OF NONMETALLIC SOLIDS

(Presented by Academician A. N. Frumkin, 27 III 1964)

Recently a number of papers have appeared in the literature on the nature of the relationship between the band gap ΔE of a semiconductor and its energetic (thermodynamic) properties ($^{1-8}$).* This is due to the fact that the band gap ΔE must depend on the strength of the chemical bond, and the stronger the bond, the larger ΔE (^{4}).

Since there are no direct methods for measuring bond energies (strengths) in solids, various authors use some property of a substance that can characterize it approximately. Thus, in ($^{1-3}$) the heat of formation ΔH of the substance is taken. But ΔH is a characteristic of the system, not of the phase (^{4}), and therefore in many cases it proves unsuitable.

The relationship between ΔE and the energy of a single bond (^{7}) would deserve attention if the latter could be calculated satisfactorily. But, as shown in (^{8}), using for this purpose the difference in the electronegativities of the components of a semiconductor ΔX leads to the paradoxical conclusion that ΔE decreases as the ionicity of the bond increases. This is obviously caused by the fact that the bond energy calculated from ΔX in many cases cannot give a satisfactory result, especially for solids. It is appropriate to note here that the literature contains an enormous number of works in which an attempt is made to find a parallel trend between ΔE and ΔX, but their failure can be seen if all the experimental material is considered (and not selectively) (^{9}). And this is quite understandable, for, as Syrkin noted (^{9}), electronegativity is not a quantity into which a definite physical content can be put. A similar assessment of this concept (electronegativity), in still more convincing form, is given in (^{20}). In ($^{4-6,8}$) the atomization energy Ω is used. This concept was introduced by Ormont, and it was shown by him that ΔE must depend on the strength of chemical bonds, which can be characterized by Ω (^{4}). But a careful analysis of the available literature data leads to the conclusion (^{9}) that the relationship between ΔE and Ω is most correctly expressed by the relation

$$\Delta E = q(\Omega - \Omega^0), \tag{1}$$

where q and Ω^0 are constants (depending on T) for chemically and structurally similar substances, such as, for example, $A^{III}B^{V}$ compounds with the sphalerite structure.

It is also necessary to dwell on work (^{10}), in which the crystal-lattice energy ΔU is used. In considering this work, one of us has shown (^{11}) that ΔU has no advantage over Ω for substances far from the ionic state.

If one approaches ΔU in the Born sense, it might be supposed that for homeopolar substances it is better to use Ω, and for ionic crystals ΔU, since the energetic (thermodynamic) strength of a crystal is characterized more accurately by Ω if the homeopolar share of the bond predominates in it, and by ΔU if the bond is ionic (^{4}).

But, as will be shown below, in the case of ionic crystals as well the use of ΔU also raises doubts.

Expression (1) makes it possible, by means of thermodynamic treatment (^{12}), to relate ΔE also to other parameters of the substance (internal energy, heat capacity, Debye temperature).

It has justified itself well on a large amount of experimental material, but proved unsuitable only for a series of PbS (PbS, PbSe, and PbTe). These substances exhibit "anomalous" behavior, consisting in the fact that all their properties change in the order of the positions of the anions in Mendeleev' s table, whereas ΔE of PbSe has not an intermediate but a minimum value.

This "anomaly"raised doubts for us as to the reliability of ΔH for PbSe and PbTe. Calorimetric determination of ΔH by the method (^{13}) gave agreement with (^{14}). The search for the cause of this "misunderstanding" led to the conclusion that, in the more general case, ΔE should be linearly related to the change in the Gibbs energy upon formation of the substance from gaseous components, which, for brevity, we shall call the free energy of atomization ΔG_{at}

$$\Delta E = p(\Delta G_{\text{at}} - \Delta G^0_{\text{at}}), \tag{2}$$

where p and ΔG_{at} are constants, like q and Ω^0 in equation (1), and

$$\Delta G_{\text{at}} = \Omega - T\Delta S, \tag{3}$$

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* In paper (^{1}) the mobility of electrons is considered.

Fig. 1. Dependence of ΔE on ΔG_{at} for some simple and binary substances with the diamond, ZnS, NaCl, and antifluorite structures. 1 –literature data; 2 –our results were used for ΔG_{at}

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where ΔS is the difference between the entropies of the components of the substance in the state of a monatomic gas and the entropy of the substance itself.

It should be borne in mind that there will be few such "anomalies," and therefore both relation (1) and relation (2) are applicable.

Fig. 1. Dependence of ΔE on ΔG_{at} for some simple and binary substances with the diamond, ZnS, NaCl, and antifluorite structures. 1 –literature data; 2 –for ΔG_{at}, our results were used.

The fact that ΔE is linearly related not only to Ω, but also to ΔG_{at}, is not surprising, since in a series of substances of the same type the entropy factor $T\Delta S$ is constant.

Consequently, ΔG_{at} and Ω should also be linearly related to one another, on which one variant of the comparative calculation method is based (15).

The linear relationship between ΔG_{at} and Ω is approximate and therefore expression (1) is also approximate. Taking into account, however, the degree of accuracy of the experimental data entering into the calculation (ΔH, ΔE, heats of sublimation of the elements, etc.), it must be considered that both expression (1) and expression (2) can be successfully used for predicting unknown quantities.

What has been said does not mean that relation (2) is perfectly rigorous, for the accuracy of experiment is still insufficient to assert this. Figure 1 shows the dependence of ΔE on ΔG_{at} for some simple and binary substances with the diamond, ZnS, NaCl, and antifluorite structures. It is interesting that ΔG_{at} performs well also in the case of the "anomalous" PbS series.

Possibly, this regularity is not limited to simple substances, but will also prove valid for substances of more complex composition (ternary, quaternary). As for structure, then, taking into account that the strength of chemi-

···chemical bond strongly depends on its length, it must be assumed that equations (1) and (2) are valid for substances of any isotropic crystalline structure.

This can be verified by considering a series of chemically similar nonisotropic substances (S, Se, Te; P, As, Sb; SnS, SnSe, SnTe).

Fig. 2. Dependence of ΔE on ΔG_{at} (1), on Ω (2), and on ΔU (3) for lead

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

chalcogenides

Fig. 3. Dependence of ΔE on ΔG_{at} (1), on Ω (2), and on ΔU (3) for KCl, KBr, and KJ

By "isotropy" here is meant equality of the distances between particles in the crystal, i.e., crystals of hexagonal ($c/a = 1.63$) and cubic systems.

It should be noted that the literature contains no reliable values of ΔE for typical ionic crystals, while the available data (^{16}) for KCl, KBr, and KJ show that for such substances it is also better to use Ω and ΔG_{at} than ΔU^*, as is evident from Fig. 3. The same idea is supported when considering other alkali halides according to the data of (^{17}).

It must be emphasized that the quantities entering into the calculation show a large scatter among different authors. Therefore, in the present work a minimal number of recent sources has been used ($^{18-21}$). Both ΔE and the thermodynamic quantities were taken at $T = 298^\circ$K.

Thus, from the figures presented it follows that ΔE, as the minimum value of the energy gap, is linearly related to ΔG_{at} (Ω), and this regularity depends neither on the band structure nor on the character of the transition (direct or indirect).

Moscow State University
named after M. V. Lomonosov

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REFERENCES

1. V. P. Zuze, *ZhTF*, **25**, 12, 2079 (1955).
2. S. A. Semenkovich, Abstracts, All-Union Conference on the Nature of the Chemical Bond in Semiconductors, Minsk, 1962.
3. N. Rigon, *Bull. Acad. Polon. Sci. ser. sci. chim.*, **9**, 11, 761 (1961).
4. B. F. Ormont, *DAN*, **124**, 129 (1959).

5. A. M. Evseev, *ZhFKh*, **34**, No. 4, 815 (1960).
6. I. P. Suchet, *C. R.*, **255**, 12, 1444 (1962).
7. P. Manca, *J. Phys. and Chem. Solids*, **20**, 34, 268 (1961).
8. K. A. Sharifov, *Dokl. AzerbSSR*, **19**, No. 3, 23 (1963); **19**, No. 5, 11 (1963).
9. Ya. I. Syrkin, *Usp. khim.*, **31**, No. 4, 404 (1962).
10. N. N. Sirota, *Collected Scientific Works, Moscow Institute of Nonferrous Metals and Gold*, **30**, 117 (1957).
11. K. A. Sharifov, *Dokl. AzerbSSR*, **19**, 9, 15 (1963); **20**, 2 (1964).
12. K. A. Sharifov, *Izv. AN AzerbSSR, ser. phys.-math. and techn. sciences*, No. 1 (1964).
13. S. P. Gadzhiev, K. A. Sharifov, *DAN*, **136**, No. 6, 1339 (1961).
14. O. Kubaschewski, E. Evans, *Metallurgische Thermochemie*, Berlin, 1959.
15. M. Kh. Karapetyants, *ZhFKh*, **30**, 1104 (1956).
16. G. Kuwabara; K. Aoyagi, *J. Phys. and Chem. Solids*, **22**, 333 (1961).
17. R. Hilsch, R. W. Pohl, *Zs. Phys.*, **59**, 812 (1930).
18. D. Long, *UFN*, **80**, 4, 639 (1963).
19. P. Aigrain, M. Balkanski, *Table de constantes de l' UICPA, semiconducteurs*, Paris, 1961.
20. V. P. Spiridonov, V. M. Tatevskii, *ZhFKh*, **37**, No. 6–10, 994, 1236, 1573, 1583, 2174 (1963).
21. A. S. Abbasov, A. V. Nikolskaya et al., *DAN*, **156**, No. 1 (1964); **156**, No. 5 (1964); **156**, No. 6 (1964).

* The above is also valid for lead chalcogenides (Fig. 2), whose ΔU is taken from (^{14}), although they cannot be assigned to typical ionic crystals.

Note: Figure translations are in progress. See original paper for figures.

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