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Decisive importance of the bulk modulus and the anharmonicity in the calculation of migration and formation volumes

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In the calculation of migration and formation volumes, various relations between defect parameters and elastic constants have been proposed. Recent experiments by Samara on ionic crystals agree with the view that migration and formation parameters are connected to the bulk modulus rather than to another combination of elastic constants. This has been previously proposed by the authors on intuitive grounds; the anharmonicity was found to be a pertinent factor. In the Appendixes the proposal receives a well-founded proof for the migration and formation process.

The calculation from first principles of migration (v^m) and formation (v^f) volumes in a crystal is a very difficult problem. The calculation of v^m for the cation vacancy motion in alkali halides has led to values which were in strong disagreement with the experimental results reported by Yoon and Lazarus.[1] A similar sharp disagreement between experiment[2] and theory[3] exists for formation volumes in ionic crystals. This discrepancy has repeatedly been attributed to the neglect of anharmonic effects.[4] For example, for Schottky defects in alkali halides, the omission of anharmonic effects leads to negative formation volumes whereas the experimental results by Lazarus and co-workers[1,2] give large positive values. Most recent microscopic calculations[5] that included anharmonic terms immediately solved the problem. The importance of anharmonicity emerges clearly from the application of a connection between the Gibbs energy g of a defect and the bulk properties[4] (from now on called the $cB\Omega$ model)

$$g^m = c^m B\Omega \tag{1a}$$

and

$$g^f = c^f B\Omega , \tag{1b}$$

where B is the isothermal bulk modulus, Ω the mean volume per atom, and the superscripts f and m stand for formation and migration processes, respectively; the values of c^m and c^f are given by[4]

$$c^m = \left(\frac{dB}{dP} - 1\right)^{-1} \frac{v^m}{\Omega} \tag{2a}$$

and

$$c^f = \left(\frac{dB}{dP} - 1\right)^{-1} \frac{v^f}{\Omega} . \tag{2b}$$

Obviously for activation (act) processes we have[4]

$$g^{\text{act}} = c^{\text{act}} B\Omega , \tag{3}$$

where

$$c^{\text{act}} = \left(\frac{dB}{dP} - 1\right)^{-1} \frac{v^{\text{act}}}{\Omega} . \tag{4}$$

The reliability of the $cB\Omega$ model has been already checked in a large number of cases comprising formation, migration, and activation processes and a variety of type of defects.[4] These equations were initially proposed on intuitive grounds. In Appendix A we derive the $cB\Omega$ model for migration processes from the assumption that in ionic crystals the TO modes are mainly responsible for this process. In Appendix B we derive Eq. (1b), i.e., the same model for formation processes, from general thermodynamical grounds; it contains an integration constant which, however, is easily excluded with the help of microscopic concepts. The existence of this latter equation is important because it was previously thought[6] that a connection of formation parameters to the bulk properties could have no justification.

For reasons of brevity we replace with i the superscript which refers to formation (f), to migration (m), or to activation (act) processes. By inserting the appropriate value of c^i from Eqs. (2a), (2b), or (4) into Eqs. (1a), (1b), or (3) we get

$$\frac{v^i}{g^i} = \left(-\frac{1}{B} + \frac{1}{B}\frac{dB}{dP}\bigg|_T\right). \tag{5}$$

This equation shows that the ratio v^i/g^i is independent of the defect mechanism and is characteristic of the bulk material. The basic physical point that emerges from Eq. (5) is that the anharmonicity of solids plays an extremely important role in the calculation of defect volumes. This is obvious because in the harmonic case the elastic constants do not depend on pressure (i.e., $dB/dP = 0$), and therefore Eq. (5) leads to a negative value of v, which the experimental data definitely contradict.

During the last months, experimental data for defect volumes in ionic crystals have been reported.[7,8] It is therefore of interest to examine here whether these recent data are in accord with Eq. (5).

According to Zener,[9] the temperature and pressure derivatives of the Gibbs energy g are connected to $(d\mu/dT)_P$ and $(d\mu/dP)_T$, respectively, where μ is the shear modulus. More recently, Flynn[6] has proposed—instead of μ—another effective elastic constant $\tilde{c}$, given by

$$\frac{15}{2\tilde{c}} = \frac{3}{C_{11}} + \frac{2}{C_{11} - C_{12}} + \frac{1}{C_{44}} .$$

In this case the connection between v and g becomes

$$\frac{v^m}{g^m} = -\frac{1}{B} + \frac{1}{\tilde{c}} \frac{d\tilde{c}}{dP}\bigg|_T . \qquad (6)$$

The problem is now to decide which of the two equations, (5) or (6), describes accurately the experimental data. Such a decision will best be possible in a material in which the quantities $(1/B)(dB/dP)_T$ and $(1/\tilde{c})(d\tilde{c}/dP)$ differ considerably. This is the case for PbF_2, for which the elastic data (under pressure) have just been reproted by Rimai and Sladek[10] at 296K. These data lead to $B = 6.3 \times 10^{11}$ dyn/cm^2, $\tilde{c} = 6.255 \times 10^{11}$ dyn/cm^2, $(dB/dP)_T = 7.13$, and $(d\tilde{c}/dP)_T = 2.56$ (these values correspond to the adiabatic elastic constants but their differences from the isothermal ones are very small). By using these values in Eqs. (6) and (5) we get for v/g the values 2.5×10^{-12} cm^3/erg from Flynn's formula (6) and 9.7×10^{-12} cm^3/erg from Eq. (5) of the $cB\Omega$ model.

This difference by a factor of 4 is sufficient for a choice to be made. Experimental values of v/g for PbF_2 can be extracted from the recent conductivity experiments under pressure of Samara.[7] He reported the values $h^{m,\text{vac}} = 0.26 \pm 0.02$ eV and $v^{m,\text{vac}} = 1.9$ cm^3/mole for the migration enthalpy and volume of a fluorine vacancy (vac); further, he gave the values $h^{m,\text{int}} = 0.52 \pm 0.03$ eV and $v^{m,\text{int}} = 3.5$ cm^3/mole for the migration of a fluorine interstitial (int). As the migration entropy s for both mechanisms should lie in the region 2–3 K we get for the Gibbs energy—by using the relation $g = h - Ts$—the values $g^{m,\text{vac}} \simeq 0.21$ eV at $T = 300$ K and $g^{m,\text{int}} \simeq 0.44$ eV at $T = 400$K. The experimental values of the ratio v/g are, therefore, in cm^3/erg,

$$\frac{v^{m,\text{vac}}}{g^{m,\text{vac}}} \simeq 9.4 \times 10^{-12} \text{ and } \frac{v^{m,\text{int}}}{g^{m,\text{int}}} \simeq 8.3 \times 10^{-12} .$$

These results show that within the experimental error of about 15% the quantity v/g is not only independent of the mechanism but also agrees with the value predicted from Eq. (5). We see also that the experimental value of v/g is appreciably higher than that resulting from Eq. (6) (see Table I). It should be noted that if one uses Zener's formula, i.e., $(1/\mu)(d\mu/dP)_T$, instead of $(1/\tilde{c})(d\tilde{c}/dP)_T$ a similar disagreement between theory and experiment results. We conclude therefore that in cubic PbF_2 the migration Gibbs energy g^m seems to be connected to the bulk modulus B and not to $\tilde{c}$ or to μ.

Another interesting point should be noted. When the cubic PbF_2 transforms into the orthorhombic structure, the migration volumes $v^{m,\text{vac}}$ and $v^{m,\text{int}}$ become approximately equal, whereas in the cubic structure they differ by a factor of 2.[7] This fact is again in accordance with Eq. (5) because in the orthorhombic structure the experimental enthalpies $h^{m,\text{vac}} = 0.36 \pm 0.02$ eV and $h^{m,\text{int}} = 0.41 \pm 0.02$ eV (and therefore approximately the Gibbs migration energies) are approximately equal, thus giving approximately the same values for $v^{m,\text{vac}}$ and $v^{m,\text{int}}$.

Up to this point we have checked the reliability of Eq. (5) for migration processes. We proceed now to the activation in state II, i.e., anion Frenkel pair formation and fluorine vacancy migration.[7] Reference (7) gives $h^{\text{act}} = 0.73$ eV and $v^{\text{act}} = 4$ cm^3/

TABLE I. Experimental and calculated values of the quantity v/g in cubic PbF_2.

	v/g Experimental (10^{-12} cm^3/erg)	v/g Calculated from $cB\Omega$ model (10^{-12} cm^3/erg)	v/g Calculated from Flynn's formula [Eq. (6)] (10^{-12} cm^3/erg)
Migration of anion vacancy	9.4	9.7	2.5
Migration of anion interstitial	8.3	9.7	2.5
Activation (anion Frenkel defect and anion vacancy migration)	10.9	9.7	

mole, by using a typical value $s^{\text{act}} \simeq 4k$ we get, at 340 K $g^{\text{act}} \simeq 0.61$ eV and hence $v^{\text{act}}/g^{\text{act}} = 10.9\times10^{-12}$ cm^3/erg, which is in fine agreement with the value 9.7×10^{-12} cm^3/erg predicted from Eq. (5).

We conclude the discussion of PbF_2 by noting that recent, very careful conductivity measurements under pressure by Oberschmidt and Lazarus[11] agree with Samara's values thus confirming our present considerations.

Other interesting recent experimental results are the measurements of Samara[8] on CsCl and TlBr. In Table II we give all the data required for the calculation. We find again a good agreement between the experimental v/g values with those predicted from Eq. (5). On the other hand, Flynn's equation (6) gives for a migration process values that are 20–30% lower than those predicted from Eq. (5), thus being far from the experimental values if one considers the experimental error of 10–15%.

We would like to summarize the success of the $cB\Omega$ model by using a large body of earlier experimental data. For purpose of convenience we write Eq. (5) in a slightly different form as follows. At $T = 0$ the expressions (1a) and (1b) give $h_0^i = c^i B_0 \Omega_0$ and hence $c^i = h_0^i / B_0 \Omega_0$ (the subscript zero denotes values at absolute zero). By considering that[4] $h_{\text{expt}}^i = h_0^i B_0^{SL} / B_0$ we have $c^i = h_{\text{expt}}^i / B_0^{SL} \Omega_0$, where h_{expt}^i is the experimental enthalpy value and B_0^{SL} the bulk modulus of the harmonic crystal, i.e., the intercept of the extension of the linear part of the graph $B = f(T)$ with the vertical axis. Therefore Eq. (5) is equivalently written as

$$\frac{v^i}{c^i B \Omega} = -\frac{1}{B} + \frac{1}{B} \left. \frac{dB}{dP} \right|_T ,$$

or by inserting the above value of c^i,

$$v^i = \frac{h_{\text{expt}}^i}{B_0^{SL}} \left(\frac{dB}{dP} - 1 \right) \exp\left(\int_0^T \beta \, dT \right) , \tag{7}$$

where $\Omega/\Omega_0 = \exp(\int_0^T \beta \, dT)$ and β is the volume thermal-expansion coefficient.

Equation (7) can be checked for a large number of solids and types of defects. In Table III we have compiled a large number of references which lead to the required experimental data for the application of Eq. (7). In Fig. 1 we have plotted the experimental values of the defect volumes versus the calculated values of the right-hand side of Eq. (7). According to this equation all points should lie on a straight line with a slope of 1. One sees that this is satisfied for a large number of solids and types of defects. The nine points for PbF_2, TlBr, and CsCl, which as mentioned agree with the $cB\Omega$ model, have not been inserted either to avoid com-

TABLE II. Calculated and experimental values of v/g in TlBr and CsCl. (The conversion of the adiabatic values to the isothermal ones has been done with the help of the relation $B_s/B = 1 + TV\beta^2 B_s / C_p$.)

		T (K)	B (kbar)	$\frac{dB}{dP}$	v, expt. (cm^3/mole)	v/g, from Eq. (5) (10^{-12} cm^3/erg)	h (eV)	s (k)	v/g, expt. (10^{-12} cm^3/erg)
TlBr	Schottky formation	700	135 [a]	~8.2 [b]	44.4 [c]	8.6	1.10 [c]	~5 [d]	9.2
	Cation vacancy migration	300	213 [e]	7.5 [b]	13.7 [c]	4.8	0.56 [c]	~2 [d]	4.5 ~ 5.1
	Anion vacancy migration	300	213 [e]	7.5 [b]	6.8 [c]	4.8	~0.25 [c]	~1 [d]	4.5 ~ 5.1
CsCl	Schottky formation	700	123 [f]	6.9 [g]	80–87 [c]	7.7	2.1 ~ 2.3 [c]	~5 [d]	7.4
	Cation vacancy migration	300	173 [h]	6.2 [g]	18 [c]	4.8	0.62 [c]	~2 [d]	5.2 ~ 5.5
	Anion vacancy migration	300	173 [h]	6.2 [g]	5.5 ~ 9.0 [c]	4.8	0.2 ~ 0.3 [c]	~1 [d]	5.2 ~ 5.5

[a] R. Bechmann and R. F. S. Hearmon, in *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology* (Springer, Berlin, 1969), Group III, Vol. 2, p. 31. For 700 K the value of adiabatic bulk modulus, $B_s = 150$ kbars is quoted; it has to be decreased by ~10% to give the isothermal value.

[b] In Ref. a the value $dB_s/dP = 7.15$ at room temperature (RT) is quoted which gives $dB/dP = 7.5$ (at RT); the value at 700 K has been estimated by assuming that $(d/dT)(dB/dP)$ in TlBr is the same as that given for NaCl by H. Spetzler *et al.*, J. Phys. Chem. Solids 33, 1727 (1972).

[c] Reference 8.

[d] Estimated value, because in Ref. 8 the entropies are not given.

[e] By applying a correction of 5% to the value $B_s = 224$ kbars given in Ref. a for 300 K.

[f] By applying a correction of 10% to the value $B_s = 136$ kbars given in Ref. a.

[g] V. K. Gard, D. S. Puri, and M. P. Verma, Phys. Status Solidi B 82, 481 (1977); they give, for 300 K, the value 5.9 which leads to $dB/dP = 6.2$; by following the same procedure as in Ref. b the value $dB/dP = 6.9$ is obtained for 700 K. In Ref. a, for RT, the value $dB_s/dP = 5.7$ is given, which is practically the same with that quoted by Gard *et al.*

[h] By applying a correction of 5% to the value $B_s = 182$ kbars given in Ref. a.

TABLE III. Various defect volumes in solids.

Dots of Figs. 1 and 2	Kind of defect	Solids	Data for enthalpy	Data for volume	Data for elastic constants
1,2,3	Formation of Schottky defect	KCl, NaCl, KBr	a	b	a
4	Formation of Schottky defect	LiF	c	c	d
5,6	Formation of (cation) Frenkel defects	AgCl, AgBr	e	f	g
7	Migration of a cation vacancy	NaCl	h	b	i
8	Migration of a cation vacancy	AgBr	e,j	j	k
9	Migration of anion bound vacancy	CaF_2	l	l	m
10	Activation of monovacancy	Cu	n	o	p,q
11	Activation of monovacancy	Ag	r	o,s	t,q
12	Activation of monovacancy	In	u	v	w
13	Formation of monovacancy	In	x	y	w,z
14	Activation of monovacancy	Na	aa	aa	bb
15	Activation of monovacancy	K	a	a	a
16	Activation of monovacancy	Pb	a	a	a
17	Activation of monovacancy	Sn	cc	dd	w
18	Activation of silver ion	B4-AgI at RT	ee	ee	ff,gg,hh
19	Activation of silver ion	B4-AgI at 400 K	ee	ee	ff,gg,hh

[a] Quoted in Ref. 4.

[b] Reference 1.

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[cc] F. H. Huang and H. B. Huntington, Phys. Rev. B 9, 479 (1974).

[dd] N. H. Nachtrieb and C. Coston, in *Physics of Solids at High Pressure*, edited by C. T. Tomizuka and R. M. Emrick (Academic, New York, 1965), pp. 336–48.

[ee] D. C. Allen and D. Lazarus, Phys. Rev. B 17, 1913 (1978).

[ff] G. H. Shaw, J. Geophys. Res. 83, 3519 (1978).

[gg] G. H. Shaw, J. Phys. Chem. Solids 41, 155 (1980).

[hh] For details of the application of $cB\Omega$ model to B4-AgI see P. Varotsos and K. Alexopoulos, Phys. Rev. B 21, 4898 (1980).

plicating the figure or because they lie beyond the region of coordinates. In order to realize the "order" introduced by the $cB\Omega$ model we plot, in Fig. 2, the experimental defect volumes versus the corresponding enthalpies.

By summarizing all the above applications of the $cB\Omega$ model to experimental data and the proofs given in the Appendices A and B we can say that

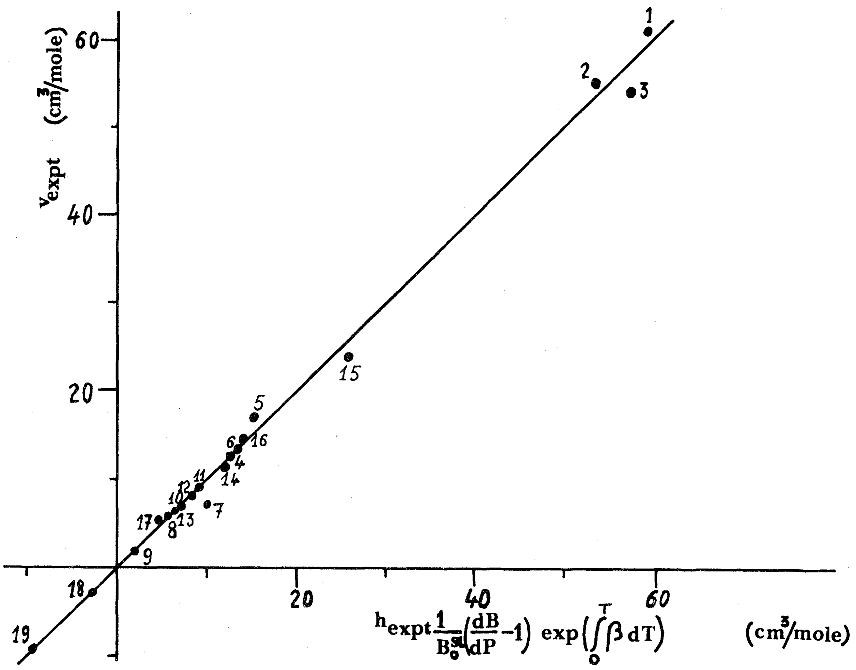

FIG. 1. Experimental defect volumes versus the quantity $(h_{\text{expt}}/B_0^{SL})(dB/dP-1)\exp\left(\int_0^T \beta dT\right)$. According to the $cB\Omega$ model all points should lie on the straight line with a slope of 1.

sufficient evidence has been accumulated in order to state the following.

(i) The migration volume is connected to the pressure derivative of the bulk modulus and not to the derivative of another combination of elastic constants.

(ii) The defect formation parameters are actually connected to the bulk properties in contrast to previous suggestions.

APPENDIX A: DERIVATION OF EQUATION (1a)

The dynamical theory predicts that the quantities v and g for migration are connected through the relation[6]

$$v^m = \frac{2\gamma_i}{B} g^m , \tag{A1}$$

where γ_i is the Gruneisen constant of that mode (or modes) which is mainly responsible for the migration process. In the case of ionic crystals these should be the TO modes because they mainly reflect vibrations of the anion sublattice that are in antiphase with the cation sublattice. Therefore from a physical point of view one should set for ionic crystals $\gamma_i = \gamma_{\text{TO}}$; then Eq. (A1) becomes

$$v^m = \frac{2\gamma_{\text{TO}}}{B} g^m . \tag{A2}$$

It should be mentioned here that the prominent role of optical modes in the migration event has been stressed by Glyde,[13] Flynn,[6] and Van Vechten;[14] especially the prominent role of TO modes has been also noticed recently by Dryden and Heydon,[15] Samara,[7] and Fontanella and co-workers.[16,17]

A connection between γ_{TO} and elastic constants has recently been proposed[18] by one of the authors:

$$\gamma_{\text{TO}} = \frac{1}{2} \frac{dB}{dP}\bigg|_T - \frac{1}{6} . \tag{A3}$$

The validity of Eq. (A3) has been checked in a large number of ionic crystals thus justifying its use. It is based on a connection between ω_{TO} and B which has been theoretically predicted and experimentally confirmed.[18] By inserting Eq. (A3) into Eq. (A2) we get

$$\frac{v^m}{g^m} = \left(\frac{dB}{dP}\bigg|_T - \frac{1}{3}\right)\bigg/ B . \tag{A4}$$

As $(dB/dP)_T$ takes large values[12] (from 5 to 8) we can approximate $dB/dP - \frac{1}{3} \simeq dB/dP - 1$, and hence Eq. (A4) immediately leads to

$$\frac{v^m}{g^m} = \left(\frac{dB}{dP}\bigg|_T - 1\right)\bigg/ B \tag{A5}$$

or

$$\frac{dg^m}{g^m} = \frac{d(B\Omega)}{B\Omega}\bigg|_T ,$$

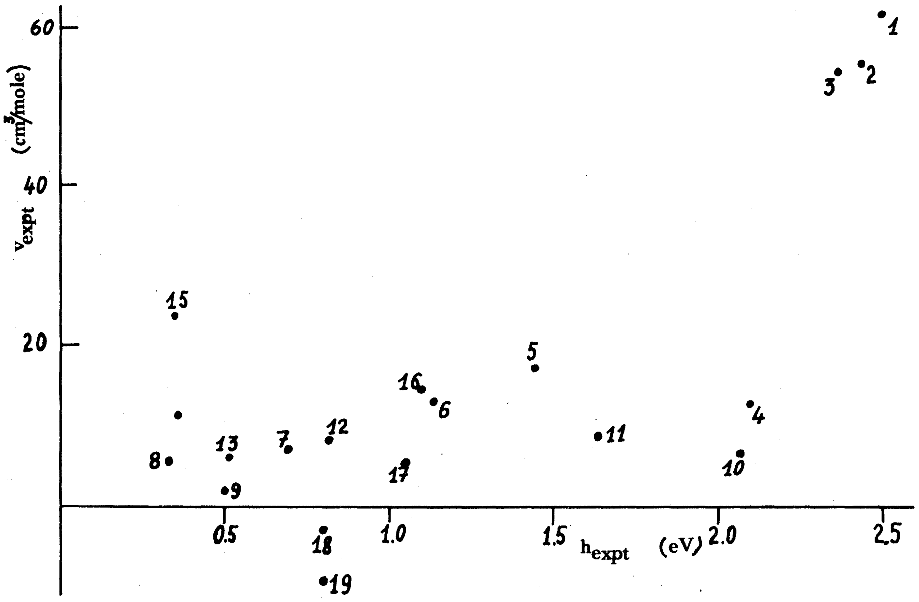

FIG. 2. Experimental defect volumes versus the corresponding enthalpy. The large scatter observed in this figure immediately vanishes when the values of the horizontal axis are multiplied by the quantity $(1/B_0^{SL})(dB/dP-1)\exp(\int_0^T \beta\, dT)$ (see Fig. 1), indicated by the $cB\Omega$ model.

which is exactly Eq. (5) derived from the $cB\Omega$ model.

In the case of monatomic crystals, Eq. (A5) can be easily derived in a similar way if one combines Eq. (A1) with the equation

$$(\gamma_i \simeq)\gamma = \frac{1}{2}\frac{dB}{dP}\bigg|_T - \frac{1}{6}. \tag{A6}$$

[Equation (A6) has been derived by Slater[19,20] within the Debye approximation of solids.]

APPENDIX B: DERIVATION OF THE $cB\Omega$ MODEL FOR A FORMATION PROCESS

The definition of the formation volume v^f implies that $v^f = (dg^f/dP)_T$ and hence

$$v^f = \frac{dg^f}{dP}\bigg|_T = \frac{dg^f}{d(B\Omega)}\bigg|_T \frac{d(B\Omega)}{dP}\bigg|_T. \tag{B1}$$

By recalling the definition of the isothermal bulk modulus $B = -\Omega(dP/d\Omega)_T$ we immediately verify that

$$\frac{d(B\Omega)}{dP}\bigg|_T = \Omega\left(\frac{dB}{dP}\bigg|_T - 1\right). \tag{B2}$$

The combination of (B1) and (B2) gives the thermodynamical identity

$$\frac{dg^f}{d(B\Omega)}\bigg|_T = \left(\frac{dB}{dP}\bigg|_T - 1\right)^{-1}\frac{v^f}{\Omega}. \tag{B3}$$

Now the formation Gibbs energy at a given (e.g., ambient) pressure P_a can be calculated from

$$g^f = \frac{dg^f}{d(B\Omega)}\bigg|_{T,P=P_\alpha} B\Omega + \Lambda, \tag{B4}$$

where Λ is a constant which does not depend on $B\Omega$, i.e., for a given pressure it may depend only on temperature. By introducing Eq. (B3) into Eq. (B4) we get

$$g^f = Bv^f \bigg/ \left(\frac{dB}{dP}\bigg|_T - 1\right) + \Lambda \tag{B5}$$

or equivalently

$$g^f = c^f B\Omega + \Lambda, \tag{B6}$$

where c^f is given by Eq. (2b).

Let us exclude now the existence of the constant Λ in the case of ionic crystals, which seems to be the most difficult case. In these crystals the current method of microscopic calculation of g^f at absolute zero (i.e., the enthalpy h_0) is a refinement of the classical Mott-Littleton model.[21] For instance, in alkali halides with NaCl structure, by employing nearest neighbor (NN) Born-Mayer repulsive interactions φ_{+-} the energy of formation per Schottky defect is given by the expression[22] (zeroth-order approximation)

$$2Z_1\frac{e^2}{r_0} - 12\varphi_{+-}(r_0) - \frac{e^2}{r_0}\left(M_+\sum_+ F^2 + M_-\sum_- F^2\right), \tag{B7}$$

where r_0 is the NN equilibrium distance, Z_i the Madelung constant, M_+, M_- are the dipoles described by Mott and Littleton, and F stands for the monopole field arising from the defects. By using the explicit results for M_+ and M_- and the lattice sums for $\Sigma_+ F^2$ and $\Sigma_- F^2$ the last term given in the large parentheses is of the form $(1/4\pi)(1-1/\epsilon)\times A$, where ϵ is the static dielectric constant and A is simply a numerical constant (according to the recent work of Tharmalingam[22] it is equal to 16.5323).

By writing the equilibrium conditions[23] the term e^2/r_0 and $\varphi_{+-}(r_0)$ can be finally written as

$$\frac{e^2}{r_0} = 18 Z_1^{-1}\left(\frac{1}{\rho} - \frac{2}{r_0}\right)^{-1} B\Omega\,, \quad \varphi_{+-} = 18 z^{-1} \frac{\rho}{l}\left(\frac{l}{\rho} - 2\right)^{-1} B\Omega\,,$$

where $z = 6$ and $\varphi_{+-} = A\exp(-l/\rho)$. By inserting the above values into the expression (B7) we see immediately that the energy of formation per Schottky defect is directly proportional to $B\Omega$ without any additive constant. This immediately tells that the integration constant Λ in Eq. (B6) is zero.

We have therefore arrived at the following conclusion: The relation $g^f = c^f B\Omega$ (or $g^f = Bv^f/[(dB/dP)-1]$) is a purely thermodynamical result apart from the point that microscopic concepts exclude the existence of an integration constant. It should be stressed that in writing Eq. (B4) the second term of expanding g^f in a Taylor series with respect to $B\Omega$ ($T = \text{const}$) has been deleted as being negligible (for $\Delta P/B < 0.1$) in comparison to the first one; the deletion is directly justified from the fact that the compressibility of the formation volume cannot exceed the bulk compressibility by no more than a few times and further that dB/dP varies only slightly on compression.

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