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Volume-Based Thermoelasticity: Consequences of the (Near) Proportionality of Isothermal Compressibility to Formula-Unit Volume

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Groups of structurally related materials, including the alkali halides, exhibit a proportionality of isothermal compressibility to formula-unit volume. The relationship has recently been explored by Glasser and by Recio et al. In this paper, we present the consequences of such proportionality on the relationships of Born−Landé and Born−Mayer parameters to the formula-unit volume. These relationships have then been tested separately on (i) alkali (excluding cesium) halides and (ii) cesium halides. We conclude that the equations fit the NaCl-type materials satisfactorily, but less well for the CsCl-type materials, and that the Born−Mayer equation is more applicable. These results confirm the conclusion that volume is intimately linked to thermodynamic quantities, as already demonstrated by our development of volume-based thermodynamics (VBT).

1. Introduction

The role of formula-unit volume, V_u, in providing a series of simple correlations between molar thermodynamic quantities for condensed-phase materials, mainly, although not exclusively, for ionic salts and minerals, continues to expand. [In previous publications, formula-unit volume has been symbolized V_m. However, it is now internationally agreed that sub-m represents a molar quantity, in this case, molar volume V_m = volume/amount of substance. V_u and V_m are simply related by $V_u = V_m/L$, where L is the Avogadro constant.] In previous publications, we have reported, following Mallouk and co-workers,[1,2] general correlations[3−8] between the following:

(a) Standard molar entropy, $S_m°$, and formula-unit volume, V_u, in the form[3−5]

$$S_m° \approx a_1 V_u + b_1 \qquad (1)$$

where a_1 and b_1 are constants. For this relationship and similar ones below, standard molar thermodynamic quantities (with a superscript °) appertain to a standard pressure of 100 kPa and a temperature of 298 K; formula unit volume has been measured under ambient conditions.

(b) Lattice potential energy, U_{POT}, and V_u in the form[6−8]

$$U_{POT} \approx 2I(a_2 V_u^{-1/3} + b_2) \qquad (2)$$

where a_2 and b_2 are constants and I, the lattice ionic strength factor is equal to $^1/_2\sum_i n_i z_i^2$ in which n_i is the number of ions of charge number z_i in the formula unit. Volume-based thermodynamics (VBT) have also been explored for sequences of transition metal oxides[9] where it was reported that, for compounds Ti_xO_y (for a range of values $1 < x < 20$ with compatible values of y), V_xO_y (for a range of values $1 < x < 7$ with compatible values of y), Mo_xO_y (for a range of values $1 < x < 9$ with compatible values of y), and Pr_xO_y (for a range of values $1 < x < 12$ with compatible values of y), correlations can be found in the forms

standard enthalpy of formation,

$$\Delta_f H° \approx a_3 V_u + b_3 \qquad (3)$$

$$S_m° \approx a_4 V_u + b_4 \qquad (4)$$

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standard Gibbs energy of formation,

$$\Delta_f G^\circ \approx a_5 V_u + b_5 \tag{5}$$

where a_3, b_3, a_4, b_4, a_5, and b_5 are constants and squares of correlation coefficients r^2 are usually greater than 0.999. Most recently,[10,11] isothermal compressibility, β (measured under ambient conditions), and formula-unit volume within groups of materials have been related in the linear form

$$\beta = k'(2V_u/N) + c' \equiv k'V_{pr} + c' \tag{6}$$

where k' and c' are constants for a related set of compounds and N is the number of atoms in the formula unit. In some compound sets, c' is close to, and not statistically significant from, zero; in such cases, linear relation becomes proportionality. For the alkali halides, $N = 2$, and thus $V_{pr} = V_u$. The introduction of V_{pr} (defined as $2V_u/N$) by Anderson and Nafe[12] effects a so-called "normalization to binary". This enables, in the wider application of our work beyond alkali halides, formula units having different values of N to be treated within the same broad linear relationship.

Such correlations are extremely useful since they provide information concerning thermodynamic and thermoelastic properties which are *independent* of detailed structural information. This is philosophically related to the fact that even if our current theories concerning *microscopic* properties of atoms and molecules proved to need revision, this would not affect the *macroscopic* properties which are the subject of thermodynamics.[13]

V_u is directly derivable from X-ray diffraction information, since

$$V_u = V_{cell}/Z = abc(1 - \cos^2\alpha - \cos^2\gamma - \cos^2\varepsilon + 2\cos\alpha\cos\gamma\cos\varepsilon)^{1/2}/Z \tag{7}$$

where V_{cell} is the unit cell volume of the crystal; Z is the number of formula units found within the unit cell; a, b, and c are the cell constants; and α, γ, and ε are the unit cell angles.

In a study of the 16 alkali halides possessing the NaCl structure (i.e., LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, and RbI), Glasser has noted[9]

$$\beta/\text{GPa}^{-1} = 0.908\,(V_u/\text{nm}^3) \tag{8}$$

with $r^2 = 0.989$, while for the Cs halides, which possess the CsCl structure

$$\beta/\text{GPa}^{-1} = 0.807\,(V_u/\text{nm}^3) \tag{9}$$

with $r^2 = 0.968$. Significantly, these correlations are seen to pass through the origin.

In the case of the dihalides, MX_2 (M = Ba, Ce, Cd, Eu, Sr, Pb paired with X = F and M = Sr, X = Cl)

$$\begin{aligned}\beta/\text{GPa}^{-1} &= 0.576\,(V_{pr}/\text{nm}^3) - 0.005\\ &= 0.384\,(V_u/\text{nm}^3) - 0.005\end{aligned} \tag{10}$$

with $r^2 = 0.981$ and again passing close to the origin. The overall least-squares fit for materials other than alkali halides took the form (with $r^2 = 0.914$)

$$\beta/\text{GPa}^{-1} = 0.317\,(V_{pr}/\text{nm}^3) \tag{11}$$

and for close-packed oxides

$$\beta/\text{GPa}^{-1} = 0.108\,(V_{pr}/\text{nm}^3) + 0.003 \tag{12}$$

Such a pattern of linear behavior has been explored by Recio et al.,[14-18] whose approach partitions the unit cell volume of crystalline solids into separate volume regions by analysis of the topology of the electron density contours and the electron localization functions (ELF). These separate volumes correspond essentially to either the ion constituents or to their valence electron shells, and each is found to contribute additively to the bulk compressibility. It emerges that the larger the volume of a component, the greater is its compressibility. The bulk compressibility, β, is simply the sum of the individual ion contributions, and so an ion with a larger volume will contribute to a greater extent to the compressibility, independently of the compressibilities of the remaining atoms.[18]

Oxide ions, in materials such as spinels, were found, by Recio et al., to be much more voluminous (and thus more compressible) than the accompanying, more rigid, cations. Thus, the summed (bulk) compressibility, β, is dominated by that of the oxide ions—resulting in very similar compressibilities (and, indeed, molar volumes, V_m) for the oxide spinels. By contrast, volume in the alkali halides is shared more equally between cations and anions, resulting in compressibilities (and molar volumes) which depend on the particular combination of cation and anion (i.e., on the chemical composition), with β increasing as V_m increases.

The present approach begins with fundamental equations of physics and then derives, as a consequence of the observed (near) proportionalities given above, testable relations between Born–Landé/Born–Mayer parameters and formula-unit volumes. Experimental validity or otherwise of these derived relationships then establishes the applicability or otherwise of Born–Landé/Born–Mayer equations to particular sets of crystalline solids.

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2. Relationship for a Crystalline Solid between Isothermal Compressibility and Closest Ion Separation

Isothermal compressibility, β (a weak function of temperature and pressure), is defined by the equation

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,n} = -\frac{1}{V_{\mathrm{m}}}\left(\frac{\partial V_{\mathrm{m}}}{\partial p}\right)_{T} \tag{13}$$

where T = thermodynamic temperature, V = volume, V_{m} = molar volume (volume/chemical amount, n), and p = pressure. The corresponding bulk modulus, K, the reciprocal of isothermal compressibility, is then defined by the equation

$$K = \frac{1}{\beta} = -V_{\mathrm{m}}\left(\frac{\partial p}{\partial V_{\mathrm{m}}}\right)_{T} \tag{14}$$

but at T = 0 K

$$\begin{aligned} p &= -\left(\frac{\partial A}{\partial V}\right)_{T,n} = -\left(\frac{\partial A_{\mathrm{m}}}{\partial V_{\mathrm{m}}}\right)_{T} \\ &= -\left(\frac{\partial U_{\mathrm{m}}}{\partial V_{\mathrm{m}}}\right)_{T} + T\left(\frac{\partial S_{\mathrm{m}}}{\partial V_{\mathrm{m}}}\right)_{T} = -\left(\frac{\partial U_{\mathrm{m}}}{\partial V_{\mathrm{m}}}\right)_{T} \end{aligned} \tag{15}$$

where A = Helmholtz energy, A_{m} = molar Helmholtz energy, U_{m} = molar internal energy, and S_{m} = molar entropy, so that

$$K = V_{\mathrm{m}}\left(\frac{\partial^2 U_{\mathrm{m}}}{\partial {V_{\mathrm{m}}}^2}\right)_{T} \tag{16}$$

For a crystalline solid, MX, such as an alkali halide

$$V_{\mathrm{m}}(= LV_{\mathrm{u}}) = CLr^3 \tag{17}$$

where C = 2 for NaCl structures and $8/3^{3/2}$ (= 1.540) for CsCl structures, L = Avogadro constant, and r = closest ion separation. Now

$$\left(\frac{\partial U_{\mathrm{m}}}{\partial V_{\mathrm{m}}}\right)_{T} = \left(\frac{\partial U_{\mathrm{m}}}{\partial r}\right)_{T}\left(\frac{\partial r}{\partial V_{\mathrm{m}}}\right)_{T} \tag{18}$$

and

$$\left(\frac{\partial^2 U_{\mathrm{m}}}{\partial {V_{\mathrm{m}}}^2}\right)_{T} = \left(\frac{\partial U_{\mathrm{m}}}{\partial r}\right)_{T}\left(\frac{\partial^2 r}{\partial {V_{\mathrm{m}}}^2}\right)_{T} + \left(\frac{\partial^2 U_{\mathrm{m}}}{\partial V_{\mathrm{m}}\partial r}\right)_{T}\left(\frac{\partial r}{\partial V_{\mathrm{m}}}\right)_{T} \tag{19}$$

Furthermore

$$\left(\frac{\partial U_{\mathrm{m}}}{\partial r}\right)_{T} = 0 \tag{20}$$

for a crystal in its equilibrium state (at 0 K), so for this situation

$$\begin{aligned} \left(\frac{\partial^2 U_{\mathrm{m}}}{\partial {V_{\mathrm{m}}}^2}\right)_{T} &= \left(\frac{\partial^2 U_{\mathrm{m}}}{\partial V_{\mathrm{m}}\partial r}\right)_{T}\left(\frac{\partial r}{\partial V_{\mathrm{m}}}\right)_{T} \\ &= \left(\frac{\partial^2 U_{\mathrm{m}}}{\partial V_{\mathrm{m}}\partial r}\right)_{T}\left(\frac{\partial V_{\mathrm{m}}}{\partial r}\right)_{T}\left(\frac{\partial r}{\partial V_{\mathrm{m}}}\right)_{T}\left(\frac{\partial r}{\partial V_{\mathrm{m}}}\right)_{T} \\ &= \left(\frac{\partial^2 U_{\mathrm{m}}}{\partial r^2}\right)_{T}\left(\frac{\partial r}{\partial V_{\mathrm{m}}}\right)_{T}^{2} = \left(\frac{\partial^2 U_{\mathrm{m}}}{\partial r^2}\right)_{T}\frac{1}{9C^2L^2r^4} \end{aligned} \tag{21}$$

and therefore

$$K = \frac{1}{\beta} = CLr^3\left(\frac{\partial^2 U_{\mathrm{m}}}{\partial r^2}\right)_{T}\frac{1}{9C^2L^2r^4} = \left(\frac{\partial^2 U_{\mathrm{m}}}{\partial r^2}\right)_{T}\frac{1}{9CLr} \tag{22}$$

3. Application to Alkali Halide Crystals Satisfying Born–Landé and Born–Mayer Equations

The above equations will now be considered in relation to the Born–Landé and Born–Mayer equations for 1:1 crystalline $\mathrm{M^+X^-}$ solids (specifically alkali halides). We shall assume that eq 22 above applies at ambient temperatures and not exclusively at 0 K (but see Appendix 1).

(a). Born–Landé Equation. The Born–Landé equation for singly charged ionic crystals takes the form

$$U_{\mathrm{m}} = -\frac{LMe^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n} \tag{23}$$

where M = Madelung constant, e = elementary charge, ε_0 = permittivity of free space, B = repulsion parameter, and n = Born exponent. [The charge number product $|z_+z_-|$ has been omitted from the numerator of the first quotient because this product is equal to 1 for $\mathrm{M^+X^-}$ crystals. However, if the equations in this paper are adapted to crystals where $|z_+z_-|$ is greater than 1, e^2 should be replaced by $|z_+z_-|e^2$.] The equation strictly applies to potential energy only, and we therefore assume here that kinetic energy associated with zero-point vibration can be ignored in comparison, more particularly in connection with the following manipulations. Differentiation with respect to r, the anion–cation lattice separation, leads us to

$$\left(\frac{\partial U_{\mathrm{m}}}{\partial r}\right)_{T} = \frac{LMe^2 r^{-2}}{4\pi\varepsilon_0} - nBr^{-n-1} \tag{24}$$

This derivative is zero at the equilibrium value of r, viz, r_0. (Strictly this also requires zero external pressure, but ambient pressure, under which compressibility is measured, is assumed to be a good approximation.) Setting the right-hand side of eq 24 to zero, we have

$$B = \frac{LMe^2 {r_0}^{n-1}}{4\pi\varepsilon_0 n} \tag{25}$$

Substituting B back into eq 24 gives

$$\left(\frac{\partial U_{\mathrm{m}}}{\partial r}\right)_{T} = \frac{LMe^2}{4\pi\varepsilon_0}(r^{-2} - {r_0}^{n-1}r^{-n-1}) \tag{26}$$

Further differentiation leads to

$$\begin{aligned} \left(\frac{\partial^2 U_{\mathrm{m}}}{\partial r^2}\right)_{T} &= \frac{LMe^2}{4\pi\varepsilon_0}[-2r^{-3} + (n+1){r_0}^{n-1}r^{-n-2}] \\ &= \frac{LMe^2}{4\pi\varepsilon_0}[-2{r_0}^{-3} + (n+1){r_0}^{-3}] \\ &\text{at } r = r_0 \\ &= \frac{(n-1)LMe^2}{4\pi\varepsilon_0}{r_0}^{-3} \end{aligned} \tag{27}$$

Table 1. Composite Table of Original Formula-Unit Volume and Compressibility Values[10] for Alkali Halides Together with Various Born−Landé and Born−Mayer Parameters

MX	V_u/nm^{3a}	β/GPa^{-1}	$n(\mathrm{st})^{19}$	n(calc)	$V_u^{1/3}/\mathrm{nm}$	ρ/nm	$V_u^{1/3}/\rho$	X/nm^{4b}
LiF	0.0163	0.0147	6	5.981	0.2535	0.0288	8.796	0.6585
LiCl	0.0337	0.0322	7	6.989	0.3230	0.0321	10.066	1.4425
LiBr	0.0416	0.0389	7.5	7.565	0.3465	0.0321	10.791	1.7426
LiI	0.0543	0.0522	8.5	7.979	0.3787	0.0335	11.313	2.3384
NaF	0.0247	0.0206	7	7.187	0.2912	0.0282	10.315	0.9228
NaCl	0.0449	0.0402	8	8.034	0.3554	0.0312	11.382	1.8009
NaBr	0.0533	0.0490	8.5	8.253	0.3763	0.0323	11.658	2.1951
NaI	0.0679	0.0622	9.5	8.891	0.4080	0.0327	12.461	2.7864
KF	0.0382	0.0316	8	8.213	0.3368	0.0290	11.608	1.4156
KCl	0.0623	0.0522	9	8.927	0.3964	0.0317	12.507	2.4728
KBr	0.0718	0.0659	9.5	9.023	0.4156	0.0329	12.628	2.9522
KI	0.0882	0.0833	10.5	9.351	0.4451	0.0341	13.041	3.7516
RbF	0.0446	0.0357	8.5	8.850	0.3546	0.0286	12.410	1.5993
RbCl	0.0715	0.0612	9.5	9.591	0.4151	0.0311	13.344	2.7416
RbBr	0.0840	0.0730	10	9.506	0.4327	0.0327	13.237	3.2702
RbI	0.0989	0.0909	11	9.915	0.4625	0.0336	13.752	4.0721
CsF	0.0542	0.0400	9.5	10.828	0.3784	0.0277	13.658	1.8074
CsCl	0.0702	0.0549	10.5	11.110	0.4125	0.0295	13.983	2.4806
CsBr	0.0788	0.0632	11	11.245	0.4287	0.0303	14.140	2.8557
CsI	0.0953	0.0796	12	11.481	0.4568	0.0317	14.412	3.5967

[a] This is symbolized as V_m in previous papers by these authors. In this paper, V_m is reserved, in accordance with international (IUPAC) convention, for molar volume. [b] $X = 1000(-2C^{1/3}V_u^{-4/3} + V_u^{-1}/\rho)^{-1}$.

Hence, via eq 22

$$K = \frac{1}{\beta} = \frac{1}{9CLr_0}\left(\frac{\partial^2 U_m}{\partial r^2}\right)_{T,r=r_0}$$

$$= \frac{(n-1)Me^2}{36\pi\varepsilon_0 C} r_0^{-4} \tag{28}$$

From eq 17

$$V_{m0}(= LV_u) = CLr_0^3 \tag{29}$$

where sub-0 indicates a minimum energy value (implied for the formula-unit volume V_u)

$$r_0^{-4} = C^{4/3}V_u^{-4/3} \tag{30}$$

Combining eqs 28 and 30

$$K = \frac{1}{\beta} = \frac{(n-1)Me^2C^{1/3}}{36\pi\varepsilon_o} V_u^{-4/3} \tag{31}$$

and therefore

$$\beta = \frac{36\pi\varepsilon_0}{e^2}\frac{1}{MC^{1/3}}\frac{V_u^{4/3}}{n-1} \tag{32}$$

Rearrangement of either eq 31 or eq 32 gives

$$n - 1 = \frac{36\pi\varepsilon_0}{e^2}\frac{1}{MC^{1/3}}\frac{V_u^{4/3}}{\beta} \tag{33}$$

from which, using experimental values of β, n may be calculated; these values are given as n(calc) in Table 1. It should be noted that there also exists, for the alkali halides, integral or half-integral "semi-theoretical" values of n;[19] these values are given as n(st) in Table 1. The relationship between n(st) and n(calc) is shown in Figure 1.

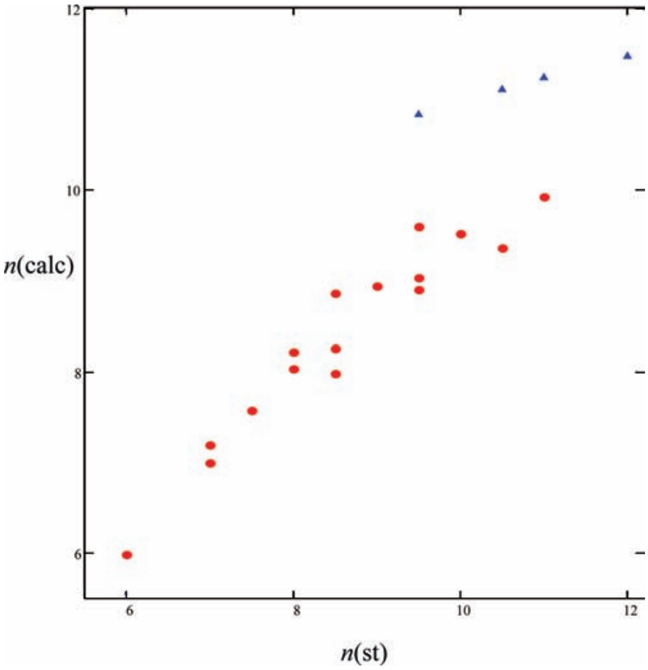

Figure 1. Relation between n(calc) and n(st) for NaCl-type structures (●) and CsCl-type structures (▲).

For a set of crystalline solids M^+X^- with the same values of M and C such as the Li, Na, K, Rb halides ($M = 1.74756$, $C^{1/3} = \sqrt[3]{2} = 1.25992$)—the NaCl series—or the Cs halides ($M = 1.76267$, $C^{1/3} = 2/\sqrt{3} = 1.15470$)—the CsCl series—the composite of an experimental proportionality of β to V_u **and** conformity of the particular set of solids to the Born−Landé equation would require, by eq 33, $n - 1$ to be directly proportional to $V_u^{1/3}$. [Provided that the proportionality constants of β to V_u are the same—not the case for the two sets of alkali halides—one could combine solids with different M and C values

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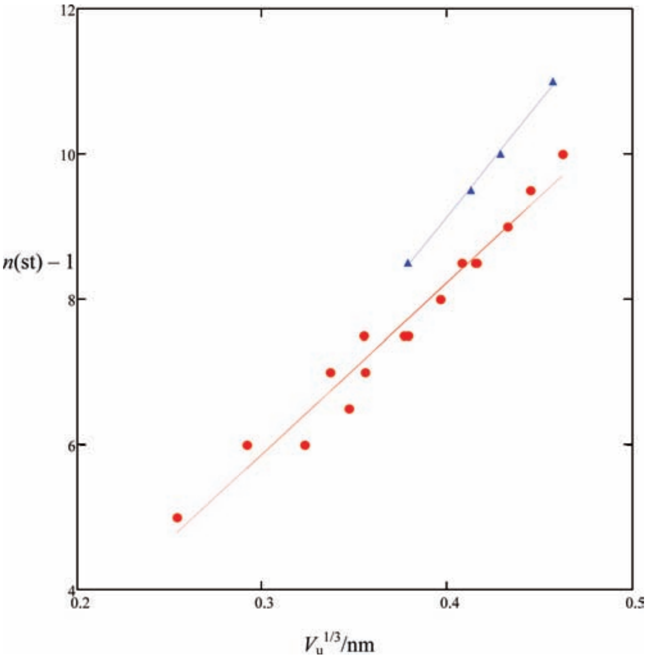

Figure 2. Plot of n(st) − 1 versus $V_u^{1/3}$. (●) NaCl series: Pearson r^2 = 0.963 for 14 degrees of freedom. Least squares fitted line is n(st) − 1 = −1.2(±1.0) + 23.5(±2.6)$V_u^{1/3}$/nm. Figures in parentheses are estimated 95% deviations. (▲) CsCl series: Pearson r^2 = 0.996 for 2 degrees of freedom. Least squares fitted line is n(st) − 1 = −3.6(±2.2) + 31.7(±5.2)$V_u^{1/3}$/nm. Figures in parentheses are estimated 95% deviations.

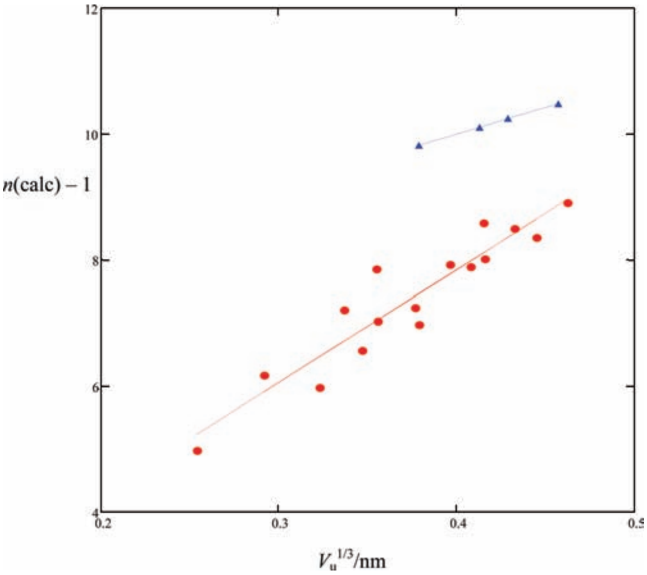

Figure 3. Plot of n(calc) − 1 versus $V_u^{1/3}$. (●) NaCl series: Pearson r^2 = 0.883 for 14 degrees of freedom. Least squares fitted line is n(calc) − 1 = 0.7(±1.4) + 17.8(±3.7)$V_u^{1/3}$/nm. Figures in parentheses are estimated 95% deviations. (▲) CsCl series: Pearson r^2=0.996 for 2 degrees of freedom. Least squares fitted line is n(calc) − 1 = 6.676(±0.045) + 8.33(±0.11)$V_u^{1/3}$/nm. Figures in parentheses are estimated 95% deviations.

by testing the proportionality of $MC^{1/3}(n-1)$ to $V_u^{1/3}$.] Least squares plots of $n-1$ against $V_u^{1/3}$ are presented in Figures 2 and 3 for (i) both the NaCl and CsCl series and (ii) both "semi-theoretical" and calculated [by eq 33] values of n. For all four combinations, significant correlation is exhibited (as indicated both by correlation coefficients and by 95% confidence intervals on the slopes). However (as indicated by 95% confidence intervals on the intercepts), only the n plots for the NaCl series pass significantly through, or very close to, the origin, thereby corresponding to, or very near, proportionality. For both CsCl series plots, the intercepts deviate substantially from zero. This suggests that the Born−Landé equation is a good approximation for the whole of the NaCl series but not so for the CsCl series.

Born−Mayer Equation. The Born−Mayer equation for singly charged ionic crystals takes the form

$$U_m = -\frac{LMe^2}{4\pi\varepsilon_0 r} + D\exp\left(-\frac{r}{\rho}\right) \tag{34}$$

where D and ρ are new constants. [The charge number product $|z_+z_-|$ has been omitted from the numerator of the first quotient because this product is equal to 1 for M^+X^- crystals. However, if the equations in this paper are adapted to crystals where $|z_+z_-|$ is greater than 1, e^2 should be replaced by $|z_+z_-|e^2$.] Again, this equation omits the kinetic energy of zero-point vibration. An interesting further point is that, unlike the B factor in the Born−Landé equation, the D factor in this (unextended) form of the Born−Mayer equation only includes repulsion from nearest neighbor cation−anion pairs.

$$\left(\frac{\partial U_m}{\partial r}\right)_T = \frac{LMe^2 r^{-2}}{4\pi\varepsilon_0} - \frac{D}{\rho}\exp\left(-\frac{r}{\rho}\right) \tag{35}$$

The above derivative is equal to zero at the equilibrium value of r, r_0, so that

$$D = \frac{LMe^2 r_0^{-2}}{4\pi\varepsilon_0}\rho\exp\left(\frac{r_0}{\rho}\right) \tag{36}$$

and back-substitution of D into eq 35 leads to

$$\left(\frac{\partial U_m}{\partial r}\right)_T = \frac{LMe^2}{4\pi\varepsilon_0}\left[r^{-2} - r_0^{-2}\exp\left(\frac{r_0 - r}{\rho}\right)\right] \tag{37}$$

Differentiating further, we have

$$\left(\frac{\partial^2 U_m}{\partial V_u^2}\right)_T = \frac{LMe^2}{4\pi\varepsilon_0}\left[-2r^{-3} + \frac{r_0^{-2}}{\rho}\exp\left(\frac{r_0 - r}{\rho}\right)\right] \tag{38}$$

where at $r = r_0$

$$\left(\frac{\partial^2 U_m}{\partial V_u^2}\right)_T = \frac{LMe^2}{4\pi\varepsilon_0}\left[-2r_0^{-3} + \frac{r_0^{-2}}{\rho}\right] \tag{39}$$

and hence

$$\begin{aligned} K &= \frac{1}{\beta} = \frac{1}{9CLr_0}\left(\frac{\partial^2 U_m}{\partial V_u^2}\right)_{T,\, V_u = V_{u0}} \\ &= \frac{Me^2}{36\pi\varepsilon_0 C}\left(-2r_0^{-4} + \frac{r_0^{-3}}{\rho}\right) \\ &= \frac{Me^2}{36\pi\varepsilon_0}\left(-2C^{1/3}V_u^{-4/3} + \frac{V_u^{-1}}{\rho}\right) \end{aligned} \tag{40}$$

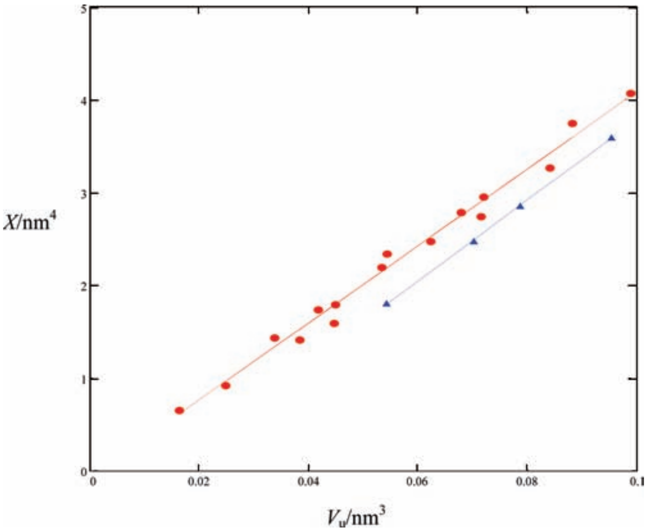

Figure 4. Plot of $X = 1000[-2C^{1/3}V_u^{-4/3} + (V_u\rho)^{-1}]^{-1}$ versus V_u. (●) NaCl series: Pearson $r^2 = 0.988$ for 14 degrees of freedom. Least squares fitted line is $1000[-2C^{1/3}V_u^{-4/3} + (V_u\rho)^{-1}]^{-1}/\text{nm}^4 = -0.06(\pm 0.16) + 41.5(\pm 2.6)V_u/\text{nm}$. Figures in parentheses are estimated 95% deviations. (▲) CsCl series: Pearson $r^2 = 1.000$ for 2 degrees of freedom. Least squares fitted line is $1000[-2C^{1/3}V_u^{-4/3} + (V_u\rho)^{-1}]^{-1}/\text{nm}^4 = -0.56(\pm 0.18) + 43.6(\pm 2.4)V_u/\text{nm}$. Figures in parentheses are estimated 95% deviations.

or

$$\beta = \frac{36\pi\varepsilon_0}{Me^2}\left(-2C^{1/3}V_u^{-4/3} + \frac{V_u^{-1}}{\rho}\right)^{-1} \tag{41}$$

Rearrangement of either eq 40 or eq 41 gives

$$\rho = \left(\frac{36\pi\varepsilon_0 V_u}{Me^2\beta} + 2C^{1/3}V_u^{-1/3}\right)^{-1} \tag{42}$$

from which ρ may be calculated; these values are given as in Table 1.

From eq 41, it would appear that, for β to be approximately proportional to V_u, we would require that

$$V_u^{-1}/\rho \gg 2C^{1/3}V_u^{-4/3} \tag{43}$$

or that

$$V_u^{1/3}/\rho \gg 2C^{1/3} \tag{44}$$

where $2C^{1/3} = 2.52$ for NaCl structure halides and $4/(3)^{1/2} = 2.31$ for CsCl structure halides (CsF, CsCl, CsBr, and CsI).

As shown in Table 1, the values of $V_u^{1/3}/\rho$ vary from 8 to 14 for the NaCl series and between 13 and 15 for the CsCl series. At first sight, and in neither case, do these values appear sufficiently large to convince anyone that the Born–Mayer equation predicts proportionality of β to V_u. However, plots of $1000(-2C^{1/3}V_u^{-4/3} + V_u^{-1}/\rho)^{-1}$ [tabulated as X in Table 1; the 1000 multiplier is merely a convenient scaling factor] against V_u for both NaCl and CsCl series in Figure 4 are very close to linearity, but only for the NaCl series can the plot be permitted to pass with reasonable statistical confidence through the origin. Together with the experimental proportionality between β and V_u as found by Glasser,[10] this reasonably supports the applicability of the Born–Mayer equation to the NaCl series but not so for the CsCl series.

There are many other types of 1:1 species, and in order to study these by the methods discussed for the alkali halides, we would need to specify the Madelung constant, M, in eqs 23 and 34 for the new structure as well as define the value of C, determined by internal geometry, in eq 17.

4. Conclusion

A comparison of Figures 3 and 4 shows that the Born–Mayer equation fits the NaCl-structured materials rather better than the Born–Landé equation. This is not unexpected since the exponential repulsion term in the Born–Mayer equation is believed to better represent the repulsion than the power-law term in the Born–Landé equation.

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Appendix 1

Considering the equations derived in section 2 of this paper and the avoidance of the precise requirement that $T = 0$ K.

$$K = V_m\left(\frac{\partial^2 A_m}{\partial V_m^2}\right)_T \tag{A1}$$

Now

$$A_m = U_m - TS_m \tag{A2}$$

so that

$$\left(\frac{\partial A_m}{\partial V_m}\right)_T = \left(\frac{\partial U_m}{\partial V_m}\right)_T - T\left(\frac{\partial S_m}{\partial V_m}\right)_T \tag{A3}$$

and

$$\left(\frac{\partial^2 A_m}{\partial V_m^2}\right)_T = \left(\frac{\partial^2 U_m}{\partial V_m^2}\right)_T - T\left(\frac{\partial^2 S_m}{\partial V_m^2}\right)_T \tag{A4}$$

One of the Maxwell relationships states

$$\left(\frac{\partial S_m}{\partial V_m}\right)_T = \left(\frac{\partial p}{\partial T}\right)_{V_m} \tag{A5}$$

so that

$$\begin{aligned}\left(\frac{\partial^2 S_m}{\partial V_m^2}\right)_T &= \left(\frac{\partial}{\partial V_m}\left(\frac{\partial p}{\partial T}\right)_{V_m}\right)_T \\ &= \left(\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V_m}\right)_T\right)_{V_m} \\ &= -\left(\frac{\partial}{\partial T}\left(\frac{K}{V_m}\right)\right)_{V_m} = -\frac{1}{V_m}\left(\frac{\partial K}{\partial T}\right)_{V_m}\end{aligned} \tag{A6}$$

Combining eqs A1, A4, and A6

$$K = V_{\mathrm{m}}\left(\frac{\partial^2 U_{\mathrm{m}}}{\partial {V_{\mathrm{m}}}^2}\right)_T + T\left(\frac{\partial K}{\partial T}\right)_{V_{\mathrm{m}}} \tag{A7}$$

or

$$K - T\left(\frac{\partial K}{\partial T}\right)_{V_{\mathrm{m}}} = V_{\mathrm{m}}\left(\frac{\partial^2 U_{\mathrm{m}}}{\partial {V_{\mathrm{m}}}^2}\right)_T \tag{A8}$$

This requires knowledge not only of K but also of its temperature derivative. If K can be treated as being independent of T

$$K = V_{\mathrm{m}}\left(\frac{\partial^2 U_{\mathrm{m}}}{\partial {V_{\mathrm{m}}}^2}\right)_T \tag{A9}$$

which was our original starting point at eq 16 (strictly true only for $T = 0$ K).

Interestingly, an experimental study of the high-temperature (300−700 K) elasticity of sodium chloride[20] shows that the temperature dependence of bulk modulus (K) at a constant molar volume V_{m} (equal to the ambient value) is essentially zero over the whole temperature range covered. This gives strong support to approximating eq A8 by eq A9, i.e., by eq 16. Further support for neglecting temperature dependence of the *constant-volume* bulk modulus has been given by Thakur and Dwary[21] and by Recio et al.[22]

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