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Article

Volume-Based Thermoelasticity: Compressibility of Inorganic Solids

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Thermodynamic properties such as entropy, among others, have been shown to correlate well with formula volume, thus permitting prediction of these properties on the basis of chemical formula and density alone, with no structural detail required. We here extend these studies to the thermoelastic property of isothermal compressibility, β. We show that compressibility is strongly linearly correlated with formula volume per atom pair, V_{pr}, for binary solids, with the alkali halides having a proportionality constant of 0.908 GPa^{-1} V_{pr}^{-1} while 1:1 monoxides, monochalcogenides, monopnictides, and chalcopyrites (ABX_2, which may be considered as AX plus BX) have a common compressibility proportionality constant of 0.317 GPa^{-1} V_{pr}^{-1}. Oxides with closely packed oxygen lattices (such as Al_2O_3), garnets (such as $Y_3Fe_5O_{12} = 4M_2O_3$), spinels ($MgAl_2O_4 = MgO \cdot Al_2O_3$), and other oxides (e.g., $FeTiO_3 = FeO \cdot TiO_2$) have compressibilities which are only slightly dependent on volume, at about 0.108 GPa^{-1} V_{pr}^{-1} + 0.003 GPa^{-1}.

Introduction

Knowledge of the thermodynamic and thermoelastic properties[1−4] of materials is fundamental to understanding and prediction of their behavior and applications. Although there are extensive tables of thermoelastic values,[3] printed, electronic, and online, these are inevitably incomplete because of the accelerating pace of discovery and synthesis (CAS[5] has recently recorded its 50 millionth entry) as opposed to the slow rate of recording of experimental data, brought about by the difficulty of measurement which requires expertise in a generally unfashionable area of research.

Ab initio and semiempirical computational procedures which are required for the calculation of thermodynamic values are both demanding in expertise and expensive (and the results perhaps not always completely reliable). It is therefore not inappropriate that empirical procedures are widely applied to generate provisional results not otherwise available and to check published values, which themselves are not always accurate. Indeed, Julian Schwinger (Nobel Prize in physics, 1965) has remarked:[1] "There is more joy in heaven in a good approximation than in an exact solution."

Over the past few years, colleagues and I have introduced the topic of Volume-Based Thermodynamics (VBT)[6] wherein we have developed a number of simple correlations between thermodynamic quantities and the molar (formula unit) volumes of condensed-phase materials, mainly (but not exclusively) ionic solids, and including many minerals. Thus, we have discovered linear correlations between entropies and volumes, between enthalpies of formation and volumes,[6b] and also between lattice energies and volumes—where lattice energies are modulated by an ionic strength factor which accounts for charge differences among the solids.[6c]

In the present paper, we extend our thermodynamic studies to the thermoelastic property of isothermal compressibility, represented variously by the symbol β or κ:

$$\beta, \kappa = -\frac{1}{V}\left(\frac{\partial V_m}{\partial p}\right)_T = \frac{1}{B}, \frac{1}{K_T}$$

Here, the bulk modulus, B or K_T, which is the reciprocal of the coefficient of isothermal compressibility, represents the resistance to bulk compression of the material and is the form generally favored by geophysicists.

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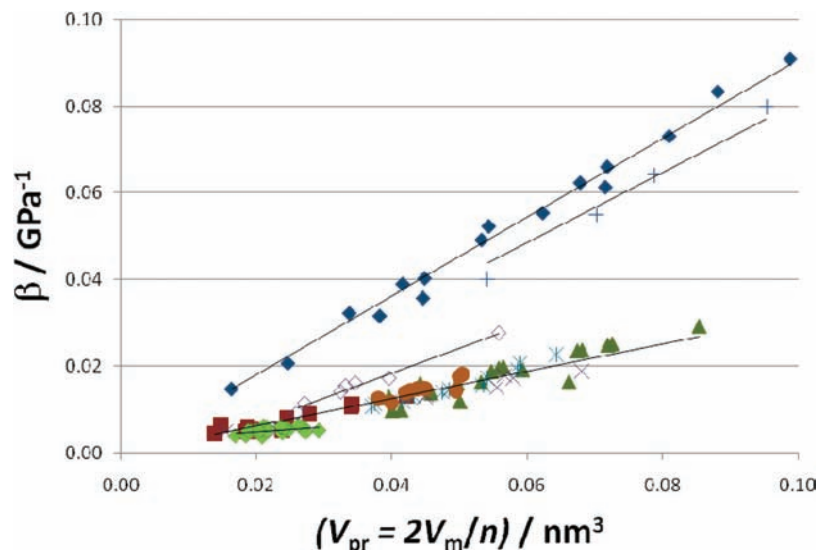
Figure 1. Compressibility, β/GPa^{-1}, versus formula volume per ion-pair ($V_{pr} = 2V_m/n$)/nm^3 for: alkali halides (Li, Na, K, Rb − filled diamonds; fitted equation: $\beta = 0.908V_{pr}$, $R^2 = 0.989$); Cs halides (pluses; fitted equation: $\beta = 0.807V_{pr}$, $R^2 = 0.968$); dihalides (open diamonds; fitted equation: $\beta = 0.576V_{pr} - 0.005$, $R^2 = 0.981$). Overall least-squares fit for non-alkali halides (4th line shown, details in Figure 2): $\beta = 0.317V_{pr}$, $R^2 = 0.914$. Overall least-squares fit for closely packed oxides (bottom line shown - details in Figure 2): $\beta = 0.108V_{pr} + 0.003$.

Isothermal compressibility is studied as contributing to the central group of thermoelastic properties which characterize materials. Principal thermoelastic properties are as follows:

- the coefficient of cubic thermal expansion,

$$\alpha = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p$$

- "thermal pressure", based upon the Maxwell relation

$$\left(\frac{\partial S}{\partial V_m}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \alpha K_T = \frac{\alpha}{\beta}$$

thus named since the derivative $(\partial p/\partial T)_V$ represents the increase in pressure, p (at fixed volume, V), arising from a rise in absolute temperature, T

- the Grüneisen ratio (or Grüneisen parameter), γ, a dimensionless quantity relating the macroscopic thermal and elastic properties of a solid

$$\gamma_{th} = \alpha K_T V_m/C_v = \alpha V_m/\beta C_v$$

where C_v = heat capacity under conditions of constant volume, and

$$C_v = C_p - \alpha^2 V_m K_T T = C_p - \alpha^2 V_m T/\beta$$

The Grüneisen parameter is defined variously; in particular it has definitions in the macroscopic domain as well as in the microscopic domain, where it relates to vibrational frequencies within the solid. In the macroscopic version above, γ_{th} measures the change in pressure resulting from an increase in energy density at constant volume. It is useful in thermodynamics and of great significance in condensed matter physics and geophysics because it enters into equations of state (EoS) for

matter in condensed phases. It is of particular interest in respect of high-temperature and -pressure conditions, for example, in the study of the earth's interior and, more generally, in the study of the extra-terrestrial planets.[1,2] It is very approximately independent of temperature and generally decreases in value as the volume decreases.[1]

More than four decades ago, Anderson and Nafe[7] demonstrated for many materials of interest that the logarithm of the bulk modulus, $\ln(K_T)$, is proportional to the logarithm of their formula unit volumes per atom pair, $\ln(V_{pr})$, with fitted intersections dependent on a modified ion-charge product. The present work develops these results, in the form of a more direct presentation in terms of compressibility rather than the bulk modulus, uses current data, simplifies and rationalizes some of the observed relations, and considers the analysis of more complex materials, all independent of detailed structural information.

Compressibility versus Formula Volume

Since isothermal compressibility, β, is the reciprocal of bulk modulus, logarithms may conveniently be avoided by plotting β versus V_m. In Figure 1 we plot β versus $2V_m/n$, where n is the number of atoms per formula unit, for an extensive range of two-atom solids, including alkali halides (F, Cl, Br, I), Cs halides, monoxides (O), monochalcogenides (S, Se, Te), monopnictides (N, P, As, Sb), and chalcopyrites (formula ABX_2, whose composition we may conveniently regard as a sum of AX and BX): the multiplying factor $2/n$ converts the formula volumes to volumes per atom pair, V_{pr}. We also include data for a set of dihalides, MX_2, per atom pair. The data for the plot are listed in Supporting Information, Table S1.

The slope of the least-squares line for the alkali (except Cs) halides is well-established at 0.908 GPa^{-1} V_{pr}^{-1} ($R^2 = 0.989$). Anderson and Nafe[7] report this data set as linear

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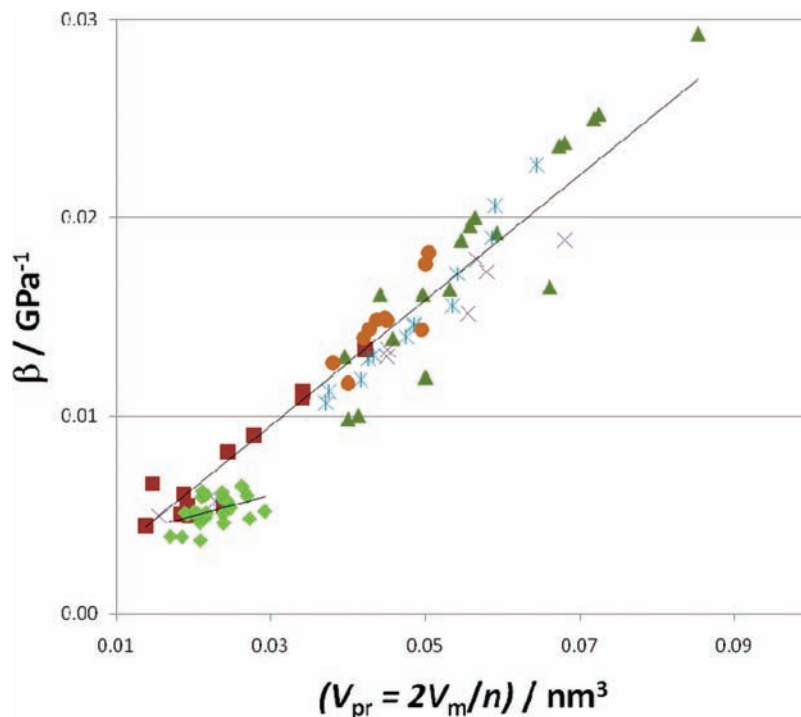(7) Anderson, O. L.; Nafe, J. E. *J. Geophys. Res.* **1965**, *70*, 3951–3963.

Figure 2. Compressibility, β/GPa^{-1}, versus formula volume per ion-pair, $(V_{pr} = 2V_m/n)/\mathrm{nm}^3$. This figure is duplicated with 10% compressibility error bars as Supporting Information, Figure S1. Overall least-squares fit for other than alkali halides (upper line shown): $\beta = 0.317V_{pr}$, $R^2 = 0.914$; overall least-squares fit for closely packed oxides (lower line shown): $\beta = 0.108V_{pr} + 0.003$. Fitted least-squares equations (lines not shown) for: monoxides (squares: fitted equation: $\beta = 0.312V_{pr}$, $R^2 = 0.886$); monochalcogenides − S, Se, Te (triangles: fitted equation: $\beta = 0.325V_{pr}$, $R^2 = 0.878$); monopnictides − N, P, As, Sb (crosses: fitted equation: $\beta = 0.288V_{pr}$, $R^2 = 0.976$); I−III chalcopyrites (stars: fitted equation: $\beta = 0.314V_{pr}$, $R^2 = 0.894$); II−IV chalcopyrites (circles: fitted equation: $\beta = 0.331V_{pr}$, $R^2 = 0.707$).

with a slope near one in their log−log plot, implying this result. The dihalides exhibit smaller compressibilities with a reduced volume dependence. The slope of the line for the set of other 1:1 solids (MX) together with the chalcopyrites (whose formula volumes have been normalized to a pair of atoms, by multiplication by $2/n$) is still smaller at 0.317 GPa^{-1} V_{pr}^{-1} ($R^2 = 0.914$), with even smaller compressibilities.

The impressive observation that the compressibilities of the chalcopyrites, with four atoms per formula unit, can be brought as atom-pairs into concordance with those of a wide range of 1:1 MX solids confirms that the normalization to binary may be extended more widely, as was also done by Anderson and Nafe.[7]

It has earlier been noted[8] that the compressibilities of the cubic spinel oxides are confined within a narrow range around 0.005 GPa^{-1}. This observation can now be extended to cover a whole range of complex oxides, with small volume dependence, as may be seen in Figure 2.

Data Sources and Choices

Only data labeled as experimental has been used to produce these correlations. The following are the principal sources of the data used (and listed in the accompanying Supporting Information, where the information sources are

indicated). For bulk moduli and compressibilities: alkali halides and dihalides;[3,10] monoxides;[3,11] monochalcogenides;[9,12] monopnictides;[9,13] chalcopyrites;[13−16] spinels (AB_2O_4), garnets ($A_3B_5O_{12}$) and other oxides.[3] For molar volumes: NIMS.[17] Compressibility data from various sources differ to some extent, as discussed. The only data deliberately excluded from the correlations are those for BN and for the silicas, for the reasons explained below.

Kumar et al.[14] report several bulk moduli for each I−III chalcopyrite listed; in each case, the largest value (that is, smallest compressibility) has here been selected for use and, as can be seen from Figure 1 and 2, these compare reasonably well with data for the 1:1 MX materials considered, whereas the smaller values are discordant. It is suggested that the largest bulk moduli (corresponding to most strongly resisted compression) relate to the least defective or purest experimental material and so may be best representative of the true bulk material.[18]

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Neumann[19] suggests experimental errors in compressibility values for the rock-salt alkali halides of at least 3%. On the basis of the range of compressibility values reported by Kumar et al.[14] for I−III chalcopyrites, we would not be surprised to find experimental ranges of 10%, or even more for the general run of materials,[18] as represented by the error bars in Supporting Information, Figure S1.

Example

The following is used as an example as to how these data and correlations may be used for predictive purposes. La_3S_4 has a density, ρ, of 5.0 g cm^{-3}, a molar mass of 545.0 g, and so a volume per atom pair

$$V_{pr} = (2/n)(M/[602.2\rho]) = (2/7)[545.0/(602.2 \times 5.0)]$$

$$= 0.0517 nm^3$$

where the factor 602.2 cm^3 mol^{-1} nm^{-3} converts molar volume, in cm^3 mol^{-1}, to nm^3 per formula unit.

As a convenient reference material, we select LaS, which has an atom-pair volume of 0.0501 nm^3, and a compressibility $\beta = 0.0120$ GPa^{-1}. The monochalcogenide correlation is $\beta = 0.325 V_{pr}$. Hence

$$\beta/GPa^{-1} = 0.0120 + 0325(0.0517 - 0.0501) = 0.0125$$

For comparison, Every and McCurdy[3] list a compressibilty of 0.0136 GPa^{-1} for La_3S_4, corresponding to a difference from this prediction of 8%.

Discussion

We have here plotted compressibility versus formula volume per ion-pair for different classes of materials and show that the data are well represented by linear correlations, with differing slopes according to the class of material, although all the 1:1 non-alkali halide compounds behave very similarly. By contrast, Anderson and Nafe[7] plotted the logarithms of the reciprocals of these quantities and found slopes of −1 (corresponding to the linear correlations that we report for 1:1 compounds), but very much steeper slopes (between −3 and −4) for their set of "oxide" compounds, implying a strongly nonlinear, V_{pr}^3 to V_{pr}^4, relation to compressibility. It appears that this discrepancy follows from their combining different classes of "oxides" together. By separating the materials into some obvious classes, we have removed some of the complexity of the relations and the necessity for log−log plots.

Neumann[19] has divided the NaCl-structured alkali halides into separate cation classes by introducing an ionicity factor, but it seems that there is little need for this since they fit well within a single compressibility versus atom-pair volume correlation. The Cs halides have lower compressibilities, whether in NaCl or CsCl structures.

Four of the monochalcogenides (triangles - ErS, YS, LaS, LaTe) fall rather below their correlation line, but no obvious cause for this difference has been found.

Among the oxides with chemical formulas other than 1:1 (such as rutile: TiO_2), we note that the 4-coordinate open-structured silicas, SiO_2 (quartz, α- and β-cristobalite, coesite,

α- and β-tridymite) have large compressibilities and do not fit the oxide correlation at all. Thus, these open silica structures, being more compressible than the closer-packed oxides, have been omitted from this analysis. Stishovite, the high-pressure 6-coordinate silica polymorph, has a rutile structure and does approximately fit into the correlation (but with a compressibility which is rather too small to be included for an adequate fit). Materials which may be considered to be oxide sums (such as spinel itself: $MgAl_2O_4 = MgO \cdot Al_2O_3$ and other spinels, garnets ($A_3B_4O_{12}$) and ferrites such as ilmenite: $FeTiO_3 = FeO \cdot TiO_2$) fit reasonably into this close-packed oxide correlation.

Thermodynamic quantities correlated with volume[6] have proven to be largely independent of structure. Similarly, the thermoelastic properties of simple cubic structures are basically volume dependent, but we see here that the influence of structure does obtrude as the complexities of the materials increase.

We note an interesting progression of compressibilities, with the alkali halides being most compressible, then the dihalides, followed by a large group of 1:1 binary materials (including many which may be regarded as sums of 1:1 binaries), finally succeeded by the close-packed (dense[11]) oxides, which are poorly compressible. It would be of considerable interest to establish reasons for the ion interactions which lead to these groupings of materials; this will require detailed computational analysis.

The incompressible oxides include many minerals of considerable geophysical concern. This justifies further consideration, which is presently being undertaken.

The correlations here provided permit estimation of the compressibility of materials within each class, without elaborate calculation. Furthermore, we suggest that selective classification is likely to lead to improved correlations over a wide range of materials.

Note Added in Proof. Zhang et al.[20] list tables of values of molar volumes and experimental bulk moduli for A(N)B(8-N) materials, classified by structure and coordination, but do not explore their correlation. From their data, we find slopes of β versus V_{pr} as follows: alkali halides (6:6 coord.) 0.990; Cs and Tl halides (8:8 coord.) 0.972; II−VI chalcogenides (6:6 coord.) 0.381; II−VI chalcogenides (4:4 coord.) 0.329; III−VI pnictides (4:4 coord.) 0.296. These values accord well with those reported herein.

Supporting Information Available: Two supplementary Tables are provided: Table S1 lists experimental volumes per atom pair and compressibilities of 20 alkali halides, 7 dihalides, 11 monoxides, 18 monochalcogenides, 13 pnictides, 13 I−III chalcopyrites and 10 II−IV chalcopyrites; Table S2 lists values for 25 close-packed oxides. Figure S1 duplicates Figure 2, with 10% compressibility error bars. This material is available free of charge via the Internet at http://pubs.acs.org.

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