Integrated form of the Anderson-Grüneisen equation of state for $p$-$V$-$T$ data fit: Application to the compounds of boron, carbon, silicon and some metals.

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Abstract. The pressure-volume-temperature equations of state have been constructed by combining experimental data and semiempirical estimations for a number of compounds recently synthesized under extreme pressure-temperature conditions. The solids with various bonding types were considered: covalent hard and superhard boron-rich and diamond-like compounds ($\text{B}_6\text{O}$, $\text{B}_{13}\text{N}_2$, BP, $\text{cBC}_5$, and nano-cBN), ionic semiconductors ($\text{Mg}_2\text{C}$ and $\text{Mg}_2\text{C}_3$), as well as intercalation compounds (clathrates $\text{Na}_4\text{Si}_{24}$ and $\text{Na}_{24+x}\text{Si}_{136}$), and simple substances ($\gamma$-$\text{B}_{28}$ and $\text{t}'$-$\text{B}_{52}$ boron allotropes, Na and Mg metals, and open-framework silicon allotrope $\text{o-Si}_{24}$). We also showed how the reliable $p$-$V$-$T$ equations of state may be constructed using different types of available data.

1. Introduction

Recent studies of phase transformations and chemical interactions in various systems under high pressure and high temperature (HPHT) conditions have led to the discovery of a number of novel materials [1-4]. We need to explore the HPHT thermodynamics for understanding the syntheses of these new materials for new challenging applications as superhard [5,6], advanced electronic [7] and photovoltaic [8], superconductors [9] as well as clathrate thermoelectric materials [10,11]: (1) boron allotropes [12] (orthorhombic $\gamma$-$\text{B}_{28}$ [13-16], pseudo-cubic $\text{t}'$-$\text{B}_{52}$ [17]) and boron-rich compounds (subnitride $\text{B}_{13}\text{N}_2$ [18,19]), (2) superhard compounds with diamond structure (nanostructured cBN [20] and $\text{c-BC}_5$ [21,22]); (3) covalent clathrates of new stoichiometries ($\text{Na}_4\text{Si}_{24}$ [8,10] & $\text{Na}_{24+x}\text{Si}_{136}$ [10,11]) and even (4) new unexpected semiconductors, like antifluorite $\text{Mg}_2\text{C}$ [23,24], dense $\text{Mg}_2\text{C}_3$ [25] and pure silicon allotrope with quasi-direct bandgap, $\text{Si}_{24}$ [8]. Although a part of the lacking data can be replaced by fitted parameters of common models [26-28] or with $ab$ $initio$ calculations [24], the reliable $p$-$V$-$T$ equations of state (EOS) data are crucial for that.

In the present paper we describe the method of construction of such equations of state using integrated form of the Anderson-Grüneisen equation [29,30]. The method is efficient even in the case of small number of experimental data [31] and may be easily combined with $ab$ $initio$, semiempirical and even empirical modeling [32].
2. Theoretical background

In our previous works [31,33] we have shown that the Anderson-Grüneisen equation [29,30], which takes into account the pressure dependence of thermal expansion through the volume change, i.e.

\[ \alpha(p,T) = \alpha(0,T) \left( \frac{V(p,T)}{V(0,T)} \right)^{\delta_T}, \]  

(1)

can be integrated (under the assumption that \( \delta_T \) is constant) to

\[ V(p,T) = \left[ V(0,T)^{-\delta_T} + V(0,300)^{-\delta_T} - V(p,300)^{-\delta_T} \right]^{1/\delta_T}, \]  

(2)

where thermal expansion (i.e. \( V(0,T) \) at 0.1 MPa) and isothermal compression (i.e. \( V(p,300) \) at 300 K) can be presented in any analytical form, e.g. polynomial

\[ V(0,T) = V(0,300) \left[ 1 + a(T-300) + b(T-300)^2 \right] \]  

(3)

and Murnaghan (or any other) equation of state

\[ V(p,300) = V(0,300)(1 + B_a \rho / B_b)^{1/B_b}. \]  

(4)

Finally, a set of parameters is needed to describe an EOS using equations (2-4) is \( V_0 \equiv V(0,300) = M / \rho_0, B_0, B_0', a, b \) and \( \delta_T \) (usually \(-4\) to \(-6\)). Such form of the EOS, (2), allows one easily approximate the \( V(p,T) \) in the vicinity of a new compound formation, which is often the principal domain of interest in the terms of HPHT thermodynamics. Here the unit cell volume can be estimated \textit{in situ} using X-ray diffraction (300-K EOS may be measured on decompression and recovery).

In some other cases, the knowledge of phase equilibrium curves may allow evaluating the HPHT EOS of unknown phase through the known one. For example, we succeeded to fit the experimental melting curves (\( p-T \) coordinates) of \( \alpha- \) and \( \beta-B_2O_3 \) and to find the parameters determining the \( p-V-T \) EOS for liquid \( B_2O_3 \) [34]. The melting was observed experimentally, while the bulk modulus and thermal expansion parameters were adjusted so that the experimental curve fits the theoretical one.

3. Boron-rich solids.

In the case of boron-rich solids the only unknown bulk modulus, that of pseudo-cubic \( t'-B_{52} \) phase was estimated using the density data by the method described elsewhere for various elastic characteristics of covalent and ionic materials [5,32,35,36] and previously justified for boron allotropes [37,38]. At the same time, the thermal expansion parameters are known just for \( B_6O \) [39,40] and \( \beta-B_{106} \) [41]. For both dense allotropes, \( \gamma-B_{28} \) and \( t'-B_{52} \), we propose to take, in the first approximation, values of \( \beta-B_{106} \) [41], while for boron subnitride \( B_{13}N_2 \) one can take a value of suboxide \( B_6O \) having similar crystal structure. Except for \( B_6O \), the \( \delta_T \) parameter – linking 300-K \( p-V \) data with 0.1-MPa thermal expansion data – was fixed to 5.5. Figure shows that the parameters well agree with \textit{in situ} experimental observations for \( B_{13}N_2 \). Better fit may be obtained with \( \delta_T = B_0' = 4 \) (just like in the case of \( B_6O \), \( \delta_T = B_0' = 6 \)) or by adjusting the \( a \) and \( b \) thermal expansion parameters, or even by suggestion of a pressure drop from 5 to 4 GPa. So, the lack of experimental data does not allow making a choice, and so far we suggest a value of \( \delta_T = 5.5 \).

4. Diamond-like solids.

For diamond-like phases – nano-cBN, cBC5 and BP – all bulk moduli were established experimentally. Only for BP the thermal expansion data at 0.1 MPa have been available in literature. The \( a \) and \( b \) parameters were established from the literature data (for nano-cBN – its conventional
counterpart [42], for c-BC$_5$ – the linear combination of diamond and boron). $\delta_T$ parameter was chosen as 5.5 for all compounds. Figure shows that the parameters well agree with experimental in situ observations for cBC$_5$. Just like in the case of B$_{13}$N$_2$ discussed above, the “ideal” match of an experimental point to the theoretical curve may be achieved, but it is not clear which parameter should be used for such adjustment (e.g. $a$ or pressure drop during the transformation).

![Figure 1. $p$-$V$-$T$ equation of state of B$_{13}$N$_2$. Experimental points [27] were obtained at HASYLAB (multianvil press MAX80, resistive heating).](image1)

![Figure 2. $p$-$V$-$T$ equation of state of c-BC$_5$. Experimental points [22] were obtained at ESRF (diamond anvil cell, laser heating).](image2)

5. Na-Si system.
The equations of state for sodium and silicon have been previously measured. Our special interest to Na is due to the fact that Na is highly compressible solid (i.e. the reliable $p$-$V$-$T$ data can be obtained in the region where pressure and temperatures can be easily measured). The data down to $V/V_0 \sim 0.85$ [43] can be perfectly fitted with proposed equation (2) (Figure 3). The value of $\delta_T = 6.1$.

In the case of clathrate compounds of the Na-Si system the situation with the data is the most complicated. High-temperature data, especially, at low pressure can hardly be obtained, since the compounds easily decompose. From another side, at high pressure these compounds often have only narrow domains of stability. However, it has been established that elastic properties mainly depend on the rigid silicon framework and are close to those of diamond silicon [44,45]. For Na$_{24+x}$Si$_{136}$ and Na$_4$Si$_{24}$ the values of bulk moduli were fixed to that of Na$_{24}$Si$_{136}$, while for open framework “high-pressure” clathrate silicon, to the values of Si$_{136}$ [44,46]. The experimental results on these compounds will be published elsewhere.

6. Mg-C system.
The equation of state of magnesium has been previously studied in ref. [47]. Figure 4 shows the results of the fit to equation (2). One can see that thermal expansion at ambient pressure and 300-K EOS data allowed us to predict the $p$-$V$-$T$ data quite reasonably by adjusting only one parameter, i.e. $\delta_T = 3.8$.

Magnesium and carbon, both of which form numerous compounds with other elements, have remarkably low affinity for one another. At ambient pressure, only the reaction of Mg or MgO with hydrocarbons leads to the formation of metastable carbides with reasonable yields, and pure Mg and carbon do not react to form stable compounds at any temperature. After exploring pressure as
additional dimension for chemistry of the Mg–C system, four magnesium carbides are now known: (1) tetragonal MgC₂, (2) orthorhombic α-Mg₂C₃, (3) monoclinic β-Mg₂C₃, and (4) cubic Mg₂C.

For Mg-C compounds stable at HP (Mg₂C [23,24] and β-Mg₂C₃ [25]), bulk moduli were established experimentally. In the case of Mg₂C the a and b parameters for thermal expansion were established by fitting the p-V data at high temperature (~1500 K) [24], while in other cases they were estimated from the literature data. δₚ parameter was chosen as 5.5 for all compounds except Mg₂C. Figure 5 shows that the parameters well agree with experimental *in situ* observations for Mg₂C.

**Figure 3.** p-V-T equation of state of Na. Experimental points from ref. [43].

**Figure 4.** p-V-T equation of state of Mg. Experimental points from ref. [47].

**Figure 5.** p-V-T equation of state of Mg₂C. Experimental points [24] were obtained at ESRF (multianvil press, resistive heating).

**Figure 6.** Bulk moduli of crystalline and liquid forms of boron oxide B₂O₃ [34].
7. Crystalline and liquid boron oxide B$_2$O$_3$.

Equations of state of α-, β-, and liquid boron oxide were obtained by fitting our experimental $p$-$V$-$T$ data, while for self-consistency some parameters were adjusted to be compatible with experimental equilibria at high pressure, in the $p$-$T$ domain where the kinetic effects become negligible [34]. In this way we have estimated both the 300-K equation of state ($p$-$V$ coordinates) and coefficient $\delta_T$ describing the $p$-$T$ evolution of thermal expansion and compressibility through the volume dependence. Only thermal expansion of liquid phase has been known from experimental measurements [48]. It is interesting to note that for a given composition the bulk modulus vs density show the power dependence.

Table 1. $p$-$V$-$T$ equation of state data for compounds synthesized at high pressure.

| Phase            | Parameters of EOS                                                                 |
|------------------|-----------------------------------------------------------------------------------|
| Boron-rich solids| $\gamma$-B$_{28}$; $\rho_0 = 2.544, B_0 = 237, B_0' = 2.7,$                       |
| [37,38]          | $a = 6$, $b = 0$ and $\delta_T = 5.5,$                                           |
|                  | t'-B$_{32}$; $\rho_0 = 2.493, B_0 = 232$, $B_0' = 2.7$                         |
| [17]             | $a = 6$, $b = 0$ and $\delta_T = 5.5,$                                           |
| B$_2$O           | $\rho_0 = 2.601, B_0 = 180$, $B_0' = 6,$                                          |
| [31,33,49]       | $a = 14$, $b = 5$ and $\delta_T = 6,$                                           |
| B$_{10}$N$_2$    | $\rho_0 = 2.666$, $B_0 = 200$, $B_0' = 4$,                                     |
| [19,27,50]       | $a = 14$, $b = 5$ and $\delta_T = 5.5,$                                           |
| Diamond-like     | Nano-cBN; $\rho_0 = 3.615$, $B_0 = 375$, $B_0' = 2.3$,                        |
| phases           | $a = 15$, $b = 0$ and $\delta_T = 5.5,$                                           |
|                  | c-BC$_3$; $\rho_0 = 3.267$, $B_0 = 335$, $B_0' = 4.5$,                          |
| [22]             | $a = 13$, $b = 0$ and $\delta_T = 5.5,$                                           |
| BP               | $\rho_0 = 2.966$, $B_0 = 174$, $B_0' = 3.2$,                             |
| [52-54]          | $a = 16.5$, $b = 0$ and $\delta_T = 5.5,$                                           |
| Mg-C system      | Mg$_2$C; $\rho_0 = 2.503$, $B_0 = 87$, $B_0' = 5.1$,                           |
| [23,24]          | $a = 48$, $b = 7.1$ and $\delta_T = 4.3,$                                      |
|                  | $\beta$-Mg$_2$C$_3$; $\rho_0 = 2.580$, $B_0 = 103$, $B_0' = 4.0$,                  |
| [25]             | $a = 48$, $b = 7.1$ and $\delta_T = 5.5,$                                           |
| Na-Si system     | Na$_{20}$Si$_{36}$; $\rho_0 = 2.318$, $B_0 = 90$, $B_0' = 4$,                   |
|                  | $\alpha = 17$, $b = 0$ and $\delta_T = 5.5,$                                      |
|                  | Si$_{24}$; $\rho_0 = 2.395$, $B_0 = 90$, $B_0' = 4$,                           |
| [10]             | $\alpha = 17$, $b = 0$ and $\delta_T = 5.5,$                                      |
|                  | Si$_{24}$; $\rho_0 = 2.163$, $B_0 = 90$, $B_0' = 4$,                           |
| [8]              | $\alpha = 12$, $b = 0$ and $\delta_T = 5.5,$                                      |

Units: $\rho_0$ in g/cm$^3$; $B_0$ in GPa; $B_0$ is dimensionless; $a$ in 10$^6$ K$^{-1}$; $b$ in 10$^9$ K$^{-2}$; $\delta_T$ is dimensionless.

8. Conclusion

Finally, we have illustrated the applicability of a simple integrated form of Anderson-Grüneisen equation for description of the $p$-$V$-$T$ data for a wide range of substances. A number of methods to construct the equations of state with limited number of available data has been shown and applied to the recently discovered high-pressure materials.

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10. References

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