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LETTER TO THE EDITOR

An accurate analytic approximation to the non-linear change in volume of solids with applied pressure

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Abstract. An accurate analytic expression for the non-linear change of the volume, $\Delta V/V_0$, of a solid as a function of applied pressure, P, is of great interest in high-pressure experimentation. We have found that the two-parameter analytic expression, $(\Delta V/V_0) = (1/\alpha)\ln(1+\beta P)$, fits the experimental $\Delta V/V_0$ data, to within a few per cent over the entire experimentally attainable pressure range. Results are presented for 24 different materials including metals, ceramic semiconductors, polymers, ionic and rare-gas solids.

In high-pressure experiments one generally determines the volume or density of the sample as a function of the applied pressure. The measured volume is a non-linear function of pressure, particularly at high compressions. On the other hand, most of the frequently used equations of states (EOS) express the pressure as a function of volume in a not simply invertible form. Thus, it would be useful to have a simple analytic expression that accurately fits the experimentally measured $\Delta V/V_0$ values as a function of the applied pressure. In addition, an accurate analytic expression for the density change with pressure would be of great value in certain applications; i.e. in the characterisation of liquids under pressure as in tribology.

More than twenty years ago, Gschneidner fitted the then available experimental $(\Delta V/V_0)$ data for monatomic solids by series expansions in powers of P, and tabulated the resultant expansion coefficients [1]. Since then many additional experimental results up to ultra-high pressures have appeared in the literature, and extensive tabulations of volume versus pressure data are available. Indeed, ultra-high pressures up to several megabars are now being routinely attained with shock tube techniques and in diamond anvil presses. Thus, the ability to represent accurately the voluminous tabulated experimental data with a simple analytic form would be a result of great utility. In addition, the tabulated power series expansion coefficients [1] are now no longer capable of accurately fitting the extremely non-linear $\Delta V/V_0$ data over the extended pressure ranges achieved in the newer experiments. These observations have motivated our search for an analytic expression capable of accurately representing the experimental $\Delta V/V_0$ data over the entire attainable pressure range. In pursuit of this goal we have analysed the data for 24 different materials, including metals [2, 3], ceramic semi-

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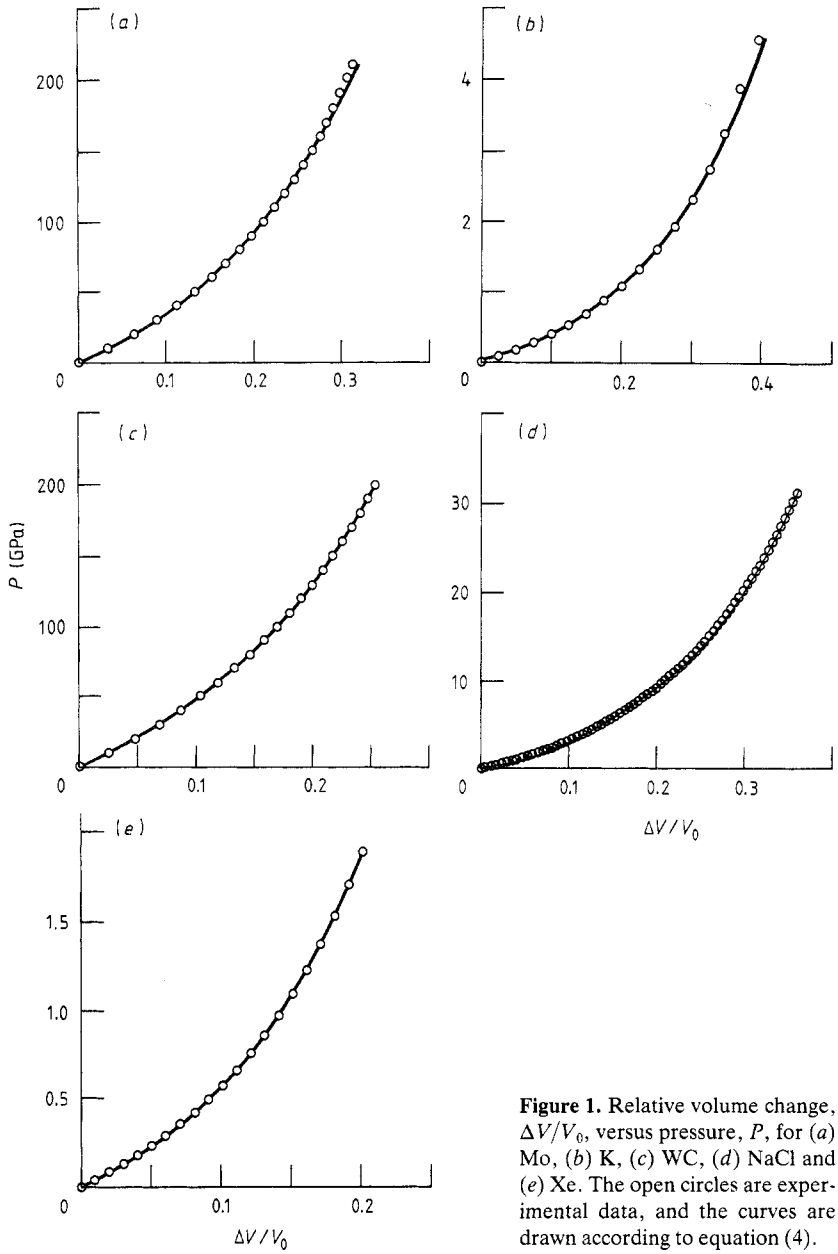

Figure 1. Relative volume change, $\Delta V/V_0$, versus pressure, P, for (*a*) Mo, (*b*) K, (*c*) WC, (*d*) NaCl and (*e*) Xe. The open circles are experimental data, and the curves are drawn according to equation (4).

conductors [2, 4], polymers [2], ionic [5] and rare-gas [6] solids. We find that the two parameter analytic expression

$$(\Delta V/V_0) = (1/\alpha)\ln(1 + \beta P) \tag{1}$$

fits the experimental data to within a few per cent over the entire range of attainable pressures; $\Delta V = V_0 - V$ and V_0 is the volume at zero pressure.

The starting point for the derivation of an analytic expression for $\Delta V/V_0$ is the simply invertible Tait EOS [7, 8]

Table 1. Analytic fit for $(\Delta V/V_0)$.

Material	α	100β (GPa^{-1})	P_{max} (GPa)	Maximum error (%)	Reference
Be	4.4782	3.7903	90	1.97	[2]
Cr	6.4224	3.4382	140	1.08	[2]
Cu	6.6860	5.2064	240	1.89	[2]
Fe	7.8857	8.1602	270	0.49	[2]
Hf	4.4933	3.9859	60	1.08	[2]
Ir	6.1463	1.8328	300	0.87	[2]
Mg	5.7413	18.1802	80	2.43	[2]
Mo	4.9719	1.8510	210	0.93	[2]
Nb	4.9062	2.9272	180	1.78	[2]
Pd	6.9340	3.9133	210	1.75	[2]
Pt	6.4653	2.4012	270	1.16	[2]
Re	5.3554	1.4670	280	0.40	[2]
Rh	5.6089	1.9739	190	0.58	[2]
V	4.9444	3.1978	130	1.30	[2]
W	5.0558	1.6445	270	1.13	[2]
K[a]	5.6580	193.330	4.57	1.00	[3]
Na[a]	5.8060	98.0379	4.86	2.68	[3]
Rb[a]	5.5980	246.771	4.83	1.55	[3]
MgO	5.7920	3.8311	110	2.15	[4]
SiC	3.5820	1.7812	110	1.85	[2]
WC	5.5496	1.5459	200	0.79	[2]
NaCl	6.1484	26.1634	31.15	0.83	[5]
Xe[b]	8.8688	245.5400	1.89	0.53	[6]
Neoprene	6.9118	74.5473	18	2.26	[2]

[a] $T = 295$ K
[b] $T = 4$ K

$$P = B_0 \left(\exp(\alpha \Delta V/V_0) - 1\right)/\alpha \tag{2}$$

which approximates the more accurate non-analytically invertible EOS of Vinet and co-workers [9, 10], and which yields the following isothermal bulk modulus expression:

$$B = B_0(V/V_0)\exp(\alpha \Delta V/V_0). \tag{3}$$

Taking the logarithm of both sides of equation (2) and solving for $(\Delta V/V_0)$ one obtains

$$(\Delta V/V_0) = (1/\alpha)\ln(1 + \beta P). \tag{4}$$

The density variation with pressure is then given by

$$(\rho/\rho_0) = [1 - (1/\alpha)\ln(1 + \beta P)]^{-1}. \tag{5}$$

In equations (4) and (5) the parameters α and β equal $1 + B_0'$ and α/B_0 respectively, where B_0 and B_0' are the isothermal bulk modulus and its pressure derivative at zero pressure. This choice of α and β ensures that equation (3) agrees with the expression in [9] for the isothermal bulk modulus to first order in $1 - (V/V_0)^{1/3}$.

Thus, one can predict the non-linear change in volume of a solid as a function of pressure solely from the zero-pressure values of B and B'. The necessary values of B_0 and B_0' may be obtained independently of the high-pressure experiments from ultrasonic measurements.

To demonstrate the quality of analytic fit to the data, the experimental data and the analytic fit for several different classes of materials are plotted in figure 1. In addition the results of the fits to $(\Delta V/V_0)$ with equation (4) for 24 different solids including metals, semiconductors, polymers, ionic and rare-gas solids are given in table 1. Note that the simple two-parameter analytic expression fits the experimental $(\Delta V/V_0)$ data with a maximum deviation of a few per cent over the entire pressure range investigated in the various experiments.

In summary, we have given analytic expressions for $\Delta V/V_0$ or ρ/ρ_0 as a function of pressure. The analytic expression for $(\Delta V/V_0)$ is valid over a considerably greater pressure range than the series approximations presented by Gschneidner [1], and fits the experimental $(\Delta V/V_0)$ data for a wide class of materials to within a few per cent over the entire experimentally attainable pressure range.

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