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Pressure coefficient K_0' of bulk modulus for cubic elements

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Abstract. The Grüneisen relation $\Gamma = a_p K_T V/C_v$ has been integrated with respect to T at constant volume. This leads to a potential $E(V)$ with the two exponents $\Gamma = m/3$ and $\delta = n/3$. The Grüneisen constant Γ is the exponent of the repulsive term. The exponent δ of the attractive term may be determined from heat capacity, thermal expansion and cohesive energy, $\delta = C_p/a_p/\varepsilon_c$.

The pressure coefficient of the bulk modulus of an m-n potential $E(V)$ is given by $K_0' = m/3 + n/3 + 2$. According to the calculations above we obtain K_0' from thermophysical data by $K_0' = \Gamma + \delta + 2 = a_p K_T V/C_v + C_p/a_p/\varepsilon_c + 2$, with $K_0' = 4-5$ for alkali metals, $K_0' = 5.2-6.2$ for transition metals and $K_0' = 7-8$ for solid rare gas crystals. This is in good agreement with high pressure data.

Keywords: Pressure coefficient; Bulk modulus; Equation of state.

1 Introduction

Thermophysical properties as well as high pressure data of solids may be calculated from Helmholtz or Gibbs free energy. Several equations of state (EOS) have been proposed for solids [1 – 10]. In first order the potentials $E(V)$ have generally been chosen

$$E(V) = C[(V_0/V)^{m/3} - (V_0/V)^{n/3}] . \tag{1}$$

The choice of C, m and n depends on the proposed EOS.

The pressure coefficient of bulk modulus at $p = 0$ is given [10] by

$$K_0' = (\partial K_T/\partial P)_{p=0} = m/3 + n/3 + 2 . \tag{2}$$

Experimental values of K_0' [11] are of the order of 4 for alkali metals, near 6 for transition metals [11] and about 8 for rare gas crystals [12].

The calculations of K_0' vary with the models, some EOS give $K_0' = 3$ [3, 10], the Birch EOS [7, 8] leads to $K_0' = 4$, Lennard-Jones [2] with $m = 12$, $n = 6$ yields $K_0' = 8$, other models [1, 4, 6] leave only undefined values for m and n. A recent discussion of EOS [10] revealed that none of the reviewed EOS can predict the correct values of K_0' for all types of materials.

This deficiency in the calculation of K_0' has been the motivation for the present paper to propose a model that may be applied to all cubic materials.

2 The Grüneisen EOS

The present model is based on the Grüneisen relation [1]: volume expansion a_p, bulk modulus K_T and molar volume V are proportional to molar heat capacity C_v,

$$a_p K_T V = \Gamma C_v , \tag{3}$$

Γ is the Grüneisen constant. The Grüneisen relation (3) is equivalent to

$$(\partial P/\partial T)_v V = \Gamma (\partial E/\partial T)_v , \tag{4}$$

and may be integrated with respect to T at constant V. This leads to the Grüneisen EOS [1] for cubic solids,

$$P(T, V) V = \Gamma [E(T, V) + G(V)] , \tag{5}$$

$\Gamma = -(\mathrm{dlog}\, \Theta/\mathrm{dlog}\, V)$ and Θ is the Debye temperature. The integration constant $G(V)$ is an arbitrary function of volume. Grüneisen [1] suggested for this function

$$G(V) = -C[(V_0/V)^{m/3} - (V_0/V)^{n/3}] .$$

However, in the present calculations we will not follow Grüneisen's suggestion for $G(V)$. Instead, we will integrate the Grüneisen EOS (5) according to Slater [3] and look for a proper Grüneisen function $G(V)$, later on.

3 Integral fo the Grüneisen EOS

At $T = 0$ we have $P = -\partial(E\text{-}TS)/\partial V = -\partial E/\partial V$, and the Grüneisen EOS (5) may be written as

$$-\partial E/\partial V\, V = \Gamma[E + G(V)] . \tag{6}$$

This is an inhomogeneous differential equation in $E(V)$. It is solved by the sum of the solutions of the homogeneous equation and a particular solution that depends on $G(V)$:

$$E(V) = AV^{-\Gamma} - V^{-\Gamma}\Gamma \int G(V)\, V^{\Gamma-1}\, dV . \tag{7}$$

A is the integration constant of the homogeneous solution. In contrast to Eq. (1) the Slater idea [3] leads to a potential $E(V)$ with the Grüneisen constant Γ being the exponent of the first (repulsive) term.

4 The modified Grüneisen function $G(V)$

For further integration of Eq. (7) we need to find an appropriate Grüneisen function $G(V)$. With $G(V) = 0$ we only get the repulsive term of the potential $E(V)$ in Eq. (7). This indicates that $G(V)$ may be connected to the attractive term of the potential $E(V)$. As the repulsive term is a power function in V, we may also assume $G(V)$ in first order to be a power function in V with a real exponent δ, $G(V) = B\,V^{-\delta}$, with B being a constant.

The constant B on the other hand may be obtained by looking at the Grüneisen EOS (5) for $p = 0$. With $V(p = 0, T) = V(T)$ we find

$$E(T) = -G[V(T)]\,, \tag{8}$$

the Grüneisen function $G[V(T)]$ is equivalent to the negative energy $E(T)$ at $p = 0$. Moreover, for $P = T = 0$ the potential energy E is equivalent to the negative cohesive energy ε_c and we get $E = -G(V_0) = -\varepsilon_c$. This defines the constant B and leads to the modified Grüneisen function

$$G(V) = \varepsilon_c(V_0/V)^{\delta}\,. \tag{9}$$

In contrast to $G(V)$ [1] the modified Grüneisen function $G(V)$ is a simple power function in V with one exponent δ.

The exponent δ again may be calculated from molar heat capacity C_p at constant pressure by differentiating the energy in Eq. (8) with respect to T,

$$C_p = (\partial E/\partial T)_p = (\partial E/\partial V)(\partial V/\partial T)_p = \delta\varepsilon_c\,(V_0/V[T])^{\delta}\,a_p\,. \tag{10}$$

At low temperatures the ratio $V_0/V(T) \approx 1$, and we obtain

$$\delta = (C_p/a_p)/\varepsilon_c\,. \tag{11}$$

The exponent δ of the (repulsive) potential is given by the ratio of molar heat capacity C_p, volume expansion coefficient a_p and cohesive energy ε_c at low temperatures.

5 The potential $E(V)$ at $T = 0$

With $G(V)$ of Eq. (9) it will be possible to continue integration of the potential energy $E(V)$ in Eq. (7). The integration constant A is determined by the condition $V = V_0$ and $\partial E/\partial V = 0$ for $P = 0$. This leads finally to the potential energy

$$E(V) = \varepsilon_c[\delta(V_0/V)^{\Gamma} - \Gamma(V_0/V)^{\delta}]/(\Gamma - \delta)\,. \tag{12}$$

At $T = 0$ $E(V)$ is given by the cohesive energy ε_c and the zero pressure volume V_0. The exponent of the repulsive term is given by the Grüneisen constant Γ, and δ is the exponent of the attractive term, if $\Gamma > \delta$. This new interpretation of Γ is independent of the choice of $G(V)$.

The calculation of $E(V)$ according to the modified Grüneisen function $G(V)$ leads again to an *m-n* potential. Comparing Eq. (1) and (12) we find $\Gamma = m/3$ and $\delta = n/3$. However, in contrast to Eq. (1) the exponents Γ and δ of Eq. (12) are experimentally defined by $\Gamma = a_p\,K_T\,V/C_v$ and $\delta = (C_p/a_p)/\varepsilon_c$.

6 The pressure coefficient K_0' of bulk modulus

The pressure coefficient of bulk modulus K_0' at $T = P = 0$ according to Eq. (2) is now equal to

$$K_0' = (\partial K_T/\partial P)_{p=0} = \Gamma + \delta + 2 = a_p K_T V/C_v + (C_p/a_p)/\varepsilon_c + 2 \tag{2'}$$

With the modified Grüneisen function $G(V)$ the high pressure value of K_0' is now related to thermo-physical data like thermal expansion a_p bulk modulus K_T and cohesive energy ε_c.

7 Experimental data for cubic elements

For a large number of cubic elements the Grüneisen parameter Γ [13] and the cohesive energy ε_c [13, 14] as well as the ratio of heat capacity C_p and volume expansion coefficient a_p [14, 15] have been tabulated and we will now compare literature data for Γ and δ to high pressure data for K_0' [11, 12].

In Fig. 1 the ratio of C_p/a_p vs. ε_c is drawn for the 5 alkali metals [14, 15]. The slope is equal to $\delta = 1.1$ for all five metals:

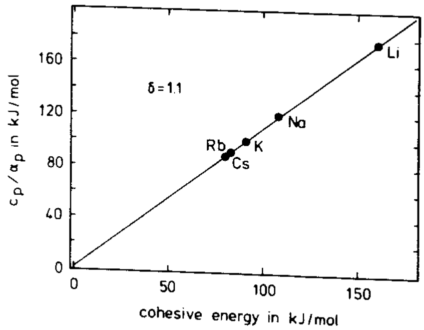

Fig. 1 Ratio of heat capacity C_p to expansivity a_p vs. heat of sublimation ε_c [14, 15] for alkali metals. The slope of the line is $\delta = 1.1$.

In Fig. 2 the ratio of C_p/a_p vs. ε_c is given for 9 transition metals and lead [14]. The slope is given by $\delta = 1.7 \approx 5/3$ [14], and is nearly the same for all ten metals:

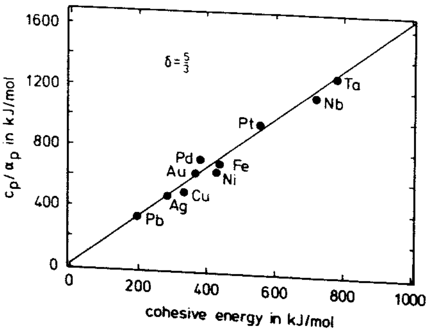

Fig. 2 Ratio of heat capacity C_p to expansivity a_p vs. heat of sublimation ε_c [14] for transition metals. The slope of the line is $\delta = 5/3$.

Fig. 3 shows the ratio of C_p/a_p vs. ε_c for three noble gas crystals [12, 13], the slope is given by $\delta = 2.7 \approx 8/3$:

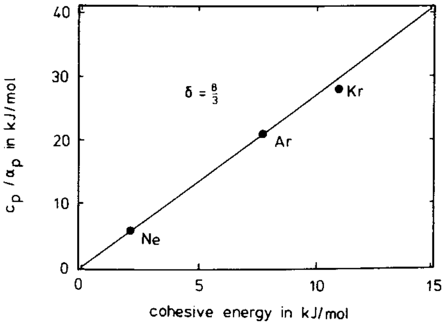

Fig. 3 Ratio of heat capacity C_p to expansivity a_p vs. heat of sublimation ε_c [12, 13, 15] for noble gas crystals. The slope of the line is $\delta = 8/3$.

Table 1 shows data from the literature for the ratio of heat capacity C_p to expansivity a_p [14, 15], heat of sublimation ε_c [13], ratio δ of C_p/a_p and ε_c, Grüneisen constant Γ [13], pressure coefficient of bulk modulus K_0' [11, 12] from high pressure experiments and sum of $\Gamma + \delta + 2$ for 19 cubic elements.

Table 1 Ratio of heat capacity C_p to expansivity a_p [14, 15], heat of sublimation ε_c [13], ratio of δ of C_p/a_p and ε_c [14], Grüneisen constant Γ [13], pressure coefficient of bulk modulus K_0' [11, 12] and sum of $\Gamma + \delta + 2$ for cubic elements.

Element	C_p/a_p [kJ/mol]	ε_c [kJ/mol]	δ	Γ	K_0'	$\Gamma + \delta + 2$
Ag	470	284	1.7	2.40	6.2	6.1
Al	374	312	1.2	2.2	4.8	5.4
Au	632	367	1.7	2.7	6.4	6.4
Cu	500	338	1.5	2.0	5.5	5.5
Cs	88	80	1.1	1.8	4.5	4.9
Fe	700	436	1.6	1.6	5.2	5.2
Li	177	160	1.1	0.9	3.5	4.0
K	100	91	1.1	1.3	4.2	4.4
Na	120	108	1.1	1.3	4.2	4.3
Nb	1 150	722	1.6	1.6	4.2	5.2
Ni	642	428	1.5	1.9	5.2	5.4
Pb	332	197	1.7	2.2	5.5	5.9
Pd	725	382	1.9	2.2	5.4	6.1
Pt	964	555	1.7	2.5	6.0	6.2
Rb	91	83	1.1	1.6	4.2	4.9
Ta	1 280	780	1.6	1.7	3.9	5.3
Ne	5.7	2.1	2.7	2.8	8.5	7.5
Ar	21	7.7	2.7	2.8	7.2	7.5
Kr	28	11	2.5	3.0	5.9	7.5

8 Discussion

The experimental data for Γ, δ and K_0' allow for a discussion of the present calculations as well as different model EOS of the literature [1–10]. The data suggest a discussion by groups of elements:

8.1 *Alkali metals*

The value of δ according to Fig. 1 is $\delta = 1.1$ for all alkali metals. The Grüneisen constant for alkali metals according to Table 1 is $\Gamma \approx 1.3-1.8$. The calculated sum $\Gamma + \delta + 2$ of the present model will be between 4 and 5, and agrees within 20% with the observed values of the pressure coefficient of bulk modulus $K_0' \approx 3.5-4.5$.

Comparing the models of EOS of the literature [1–10] the Birch model agrees well with the data for alkali metals. According to Birch [7, 8], $m/3 = 5/3$ is close to the observed value of $\Gamma \approx 1.3-1.8$. The second exponent in the Birch equation [7, 8] $n/3 = 4/3$ compares well with $\delta = 1.1$ of the present model. The sum in the Birch model [7, 8] gives $m/3 + n/3 + 2 = 4$, which is also very close to the pressure coefficient of bulk modulus $K_0' \approx 3.5-4.5$. For alkali metals the Birch model [7, 8] is also well suited. Other models, e.g. Lennard-Jones [2], Slater [3], Bardeen [5] lead to insufficient values of K_0'.

8.2 *Transition metals*

The value of δ according to Fig. 2 is $\delta = 5/3$ for all transition metals. The Grüneisen constant for transition metals according to Table 1 is $\Gamma = 1.6-2.5$. The calculated sum $\Gamma + \delta + 2 = 5.3-6.2$ of the present model is within 20% of the observed values of the pressure coefficient of bulk modulus $K_0' = 5-6$.

The Birch model [7, 8] gives $m/3 = 5/3$ and $n/3 = 2/3$ again, both values are smaller than the literature data for Γ and δ. The sum $m/3 + n/3 = 4$ is much smaller than the literature value of K_0'. This indicates, that the Birch model [7, 8] is not sufficient for transition metals. The values of m and n should rather be $m = 6-7$, and $n = 5$.

8.3 *Rare gas crystals*

The value of δ according to Fig. 3 is $\delta = 8/3$ for all rare gas crystals. The Grüneisen constant for rare gas crystals according to Table 1 is $\Gamma = 2.5-3$. The calculated sum $\Gamma + \delta + 2 = 7-7.5$ of the present model agrees again within 20% with the observed values of the pressure coefficient of bulk modulus $K_0' = 6-8.5$.

The Lennard-Jones potential [2], which cannot be applied to metals, also is quite suitable to characterize rare gas crystals. The exponent $m/3 = 12/3 = 4$ is somewhat larger than the literature values of $\Gamma = 2.5-3$, and $n/3 = 6/3 = 2$ slightly smaller than the data for $\delta = 2.5-3$. The sum of the exponents $m/3 + n/3 = 8$ is within the range of the observed value of $K_0' = 6-8.5$.

The Birch [7, 8] model as well as other EOS lead to smaller values for Γ, δ and K_0'.

So far the difference $\Gamma - \delta$ has not been considered. The exponents of the repulsive and attractive potential in all model equations of state [1–10] give $m/3 - n/3 = 0.6-2$, and we should expect $\Gamma > \delta$. According to Table 1 this condition is not observed for the transition metals Fe, Nb, Ta and the rare gas crystals, where $\Gamma \approx \delta$ has been observed. This would lead to a logarithmic term in the calculations. However, so far the high pressure data are accurate only within 20–30%, and it is not yet possible to discuss, which model should apply to these elements.

9 Conclusions

The pressure coefficient K_0' of the bulk modulus has been calculated from the Grüneisen equation of state (5) for 19 different cubic elements. The agreement of the high pressure data for K_0' and the sum of the thermophysical ratios $\Gamma + \delta + 2 = a_p K_T V/C_v + C_p/a_p/\varepsilon_c + 2$ is within 20% for all three material groups. In contrast to the models of Birch [7, 8] or Lennard-Jones [2] the present model applies to all groups of materials equally well and gives specific exponents Γ and δ for each element.

In addition, the modified Grüneisen model should predict thermophysical and high pressure data like volume, specific heat, thermal expansion, bulk modulus and pressure coefficient as functions of temperature, volume or pressure for all cubic elements, if e.g. the model of Debye is applied. These calculations are presently in preparation.

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