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Thermophysical properties of cubic elements [☆]

J. Mimkes *, M. Lübbers, H.H. Thomas

FB Physik, University of Paderborn, 33098 Paderborn, Germany

Abstract

The Grüneisen-Debye equation of state (EOS) is presented for cubic solids. The Helmholtz free energy $F(T,V)$ is obtained from the second integral of the Grüneisen relation. $F(T,V)$ is determined by six constants: molar volume V_0, cohesive energy ε_c, Debye temperature Θ_0, Grüneisen parameter Γ, exponent δ and constant of electronic contribution to specific heat γ'.

Thermophysical and high pressure properties, such as functions of temperature T, volume V or pressure p, have been calculated for cubic elements. Volume $V(T)$, $V(p)$, heat capacity $C_p(T)$, volume expansivity $\alpha_p(T)$, bulk modulus $K_T(T)$, $K_T(p)$ and the pressure coefficient $K_0' = \Gamma + \delta + 2$ show excellent agreement for the alkali metals Li, Na and K, the transition metals Cu, Ag, Au, Ni and Fe, the main group metals Al and Pb, and solid rare gas crystals Ne, Ar, Kr and Xe.

Keywords: Alkali metal; Cubic element; Kinetics; Pressure; Rare gas; Thermodynamics; Transition metal

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1. Introduction

In 1912 Grüneisen [1] and Debye [2] published their equations of state (EOS) in the same issue of Annalen der Physik. These EOS [1-10] are presently of interest in the calculation of high pressure data such as the pressure coefficient K_0' of bulk modulus for cubic elements. We shall show that the pressure coefficient K_0' of the

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* Corresponding author.

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bulk modulus for cubic elements may be derived from a modified Grüneisen EOS in good agreement with experimental data for alkali metals, transition metals and rare gas solids.

The basic idea of the present paper is to expand the modified Grüneisen EOS [1,11] for simple cubic elements by the Debye model [2] and restrict the validity of the model to the temperature range in which the Debye temperature is nearly constant. In the first section we shall calculate the Helmholtz free energy $F(T,V)$ and its derivatives for the Grüneisen–Debye model. In the following section we shall compare the results with experimental data and finally we shall discuss the Grüneisen function $G(V)$ in more detail.

2. Calculation of thermophysical properties

The Grüneisen–Debye EOS of cubic elements may be obtained by a twofold integration of the Grüneisen relation

$$-\partial^2 F/\partial V\,\partial T = \alpha_p K_T = \Gamma C_v/V \qquad (1)$$

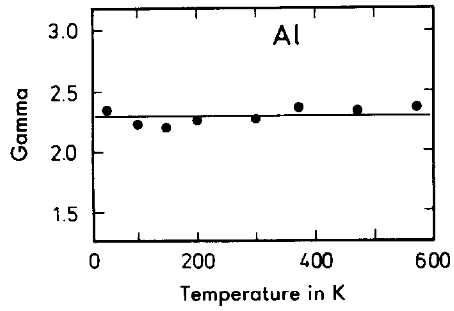
$F(V,T)$ is the Helmholtz free energy, α_p the volume expansivity, K_T the isothermal bulk modulus, V the molar volume, C_v the molar heat capacity at constant volume and Γ the mean Grüneisen parameter for the three acoustic branches of cubic elements.

2.1. The first integral of the Grüneisen relation

If the first integral is carried out with respect to T at constant V, the mean Grüneisen parameter Γ has to be known as function of temperature T. The function

$$\Gamma(T) = \alpha_p(T)K_T(T)V(T)/C_v(T) \qquad (2)$$

may be obtained from data in the literature [14–17]. Fig. 1 shows for aluminum that Γ is constant in the temperature range 0–600 K. For solid xenon Γ is constant



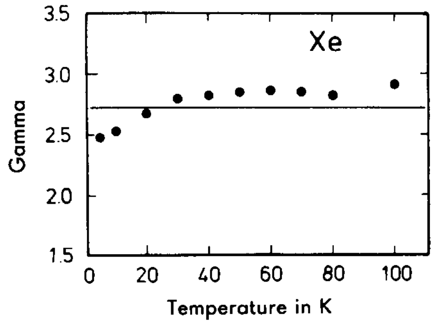


Fig. 1 (left). Γ values for Al. Solid line according to Eq. (2); data from authors of Figs. 7, 9, 11 and 13.

Fig. 2 (right). Γ values for Xe. Solid line according to Eq. (2); data from authors of Figs. 8, 10, 12 and 14.

in the temperature range 30–100 K, and drops by 10% below 30 K, as shown in Fig. 2.

Accordingly, for Al and Xe the Grüneisen relation (1) may be integrated with respect to T at constant V.

$$p(T,V)V = \Gamma[E(T,V) + G(V)] \tag{3}$$

Eq. (3) is the EOS by Grüneisen [1]; $G(V)$ is an integration constant.

In first order the Grüneisen function $G(V)$ has been represented by a simple power function [11], as will be discussed later.

$$G(V) = \varepsilon_c(V_0/V)^{\delta} \tag{4}$$

The exponent δ may be calculated as follows: for $p = 0$ the Grüneisen relation (3) implies $E(T) = -G(V(T))$. The molar heat capacity C_p at $p = 0$

$$\begin{aligned} C_p(T) &= -(\partial G/\partial V)(\partial V/\partial T)_{p=0} \\ &= \delta\varepsilon_c(V_0/V(T))^{\delta}\alpha_p \end{aligned} \tag{5}$$

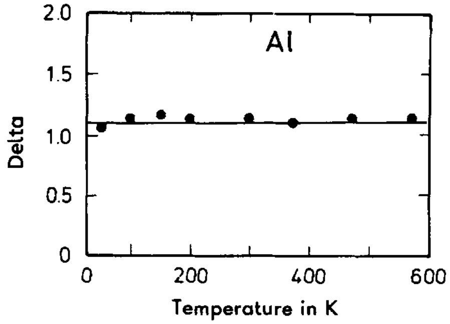
leads to an implicit function for the exponent δ. We may solve for δ as a function of molar heat capacity C_p at constant pressure, volume expansion coefficient α_p and cohesive energy ε_c

$$\delta(T) = [C_p/\alpha_p]/[\varepsilon_c - C_pT] \tag{6}$$

Fig. 3 shows for aluminum that δ calculated according to Eq. (6) from the literature [12–17] is indeed constant in the temperature range 0–600 K. The same holds for Xe in Fig. 4 in the range 30–100 K; below 30 K the value of δ increases by 10%.

2.2. The second integral of the Grüneisen relation

The second integral of the Grüneisen relation (1) has to be carried out with respect to volume at constant temperature. At $T = 0$, with $F(V) = E(V)$ the



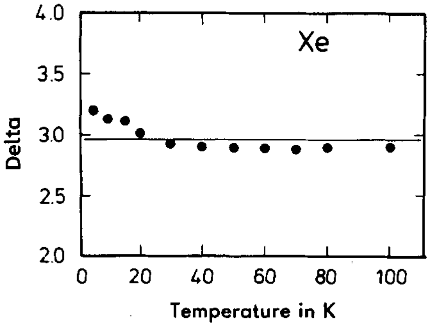


Fig. 3 (left). δ values for Al. Solid line according to Eq. (6); data from authors of Figs. 9 and 11.

Fig. 4 (right). δ values for Xe. Solid line according to Eq. (6); data from authors of Figs. 10 and 12.

Grüneisen EOS (3) equals [11]

$$-(\partial F(V)/\partial V)_T V = \Gamma[F(V) + G(V)] \tag{7}$$

This is an inhomogeneous differential equation for the Helmholtz free energy $F(V)$. It is solved by variation of the constant of the homogeneous solution. The result is given by the homogeneous solution and a particular solution depending on $G(V)$ [11]

$$F(V) = \varepsilon_c[\delta(V_0/V)^\Gamma - \Gamma(V_0/V)^\delta]/(\Gamma - \delta) \tag{8}$$

At $T = 0$ the Helmholtz free energy is given by the $\Gamma - \delta$ potential similar to the $m - n$ potential proposed by Grüneisen [1]. At $T = p = 0$ the free Helmholtz energy is equal to the (negative) cohesive energy ε_c.

2.3. *Helmholtz free energy* F(T,V)

We may now calculate the Helmholtz free energy $F(T,V)$ and all thermophysical properties of cubic elements by taking into account the specific heat of phonons (and of electrons in metals).

With the models of Grüneisen, Debye and Sommerfeld [1,2,10] we obtain the Helmholtz free energy $F(T,V)$ of cubic elements

$$\begin{aligned} F(T,V) &= 3RT \ln[1 - \exp(-\Theta/T)] - RTD_1(\Theta/T) \\ &\quad + \varepsilon_c[\delta(V_0/V)^\Gamma - \Gamma(V_0/V)^\delta]/(\Gamma - \delta) - 0.5\gamma'(V/V_0)^\Gamma T^2 \end{aligned} \tag{9}$$

where

$$D_1 = \frac{3}{(\Theta/T)^3} \int_0^{\Theta/T} \frac{x^3\, \mathrm{d}x}{\mathrm{e}^x - 1} \tag{10}$$

and

$$\gamma' = 0.5R^2\pi^2/\varepsilon_F \tag{11}$$

$\Theta = \Theta_0(V_0/V)^\Gamma$ is the Debye temperature and ε_F is the Fermi energy. Six constants are necessary to calculate the Helmholtz free energy as a function of temperature T and volume V: (1) zero pressure volume $V_0 = V(T = p = 0)$; (2) cohesive energy $\varepsilon_c = E(T = V = 0)$; (3) Debye constant Θ_0; (4) electronic specific heat constant $\gamma' = 0.5R^2\pi^2/\varepsilon_F$; (5) Grüneisen constant $\Gamma = \alpha_p K_T V/C_v$; (6) exponent $\delta = [C_p/\alpha_p]/[\varepsilon_c - C_p T]$.

For each cubic element a set of six constants will be sufficient to calculate all thermophysical properties as functions of temperature T, volume V, or pressure p.

2.4. *Energy* E(T,V)

The energy $E(T,V)$ of this Grüneisen–Debye model is given by

$$E(T,V) = 3RTD_1(\Theta/T) + 0.5\gamma'(V/V_0)^{\Gamma}T^2 + \varepsilon_c[\delta(V_0/V)^{\Gamma} - \Gamma(V_0/V)^{\delta}]/(\Gamma - \delta) \qquad (12)$$

At constant volume we obtain the energy according to Debye and Sommerfeld [2,10].

2.5. *Entropy* S(T,V)

The entropy of the Grüneisen–Debye model is $S(T,V) = -(\partial F/\partial T)_V$

$$S(T,V) = -3R\ \ln[1 - \exp(-\Theta/T)] + 4RD_1(\Theta/T) + \gamma'(V/V_0)^{\Gamma}T \qquad (13)$$

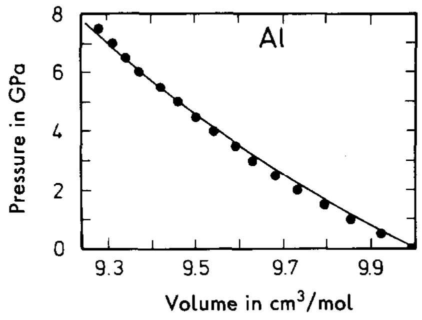
The functions for D_1 and γ' are given in Eqs. (10) and (11).

2.6. *Pressure* p(T,V)

The pressure is obtained from $p(T,V) = -(\partial F/\partial V)_T$. Calculated results according to

$$p(T,V) = \{3RTD_1(\Theta/T) + 0.5\gamma'(V/V_0)^{\Gamma}T^2 + \varepsilon_c\delta[(V_0/V)^{\Gamma} - (V_0/V)^{\delta}]/(\Gamma - \delta)\}\Gamma/V \qquad (14)$$

and experimental data [15,16] for aluminum and xenon are given in Figs. 5 and 6.



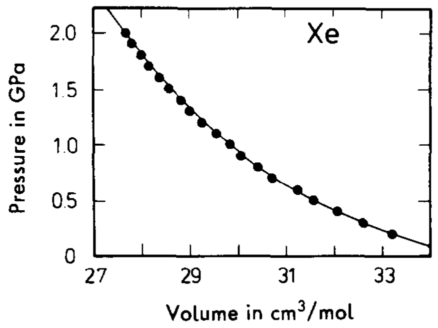
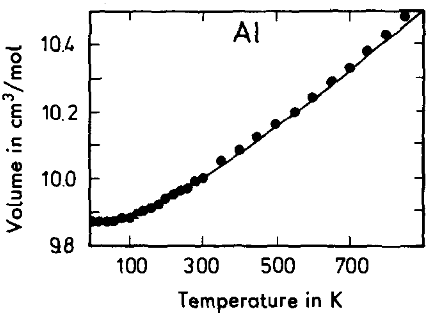


Fig. 5 (left). $p(V)$ for Al. Solid line according to Eq. (14); data from P.W. Bridgman (1948) in Ref. 16.

Fig. 6 (right). $p(V)$ for Xe. Solid line according to Eq. (14); data from M.S. Anderson and C.A. Swenson (1975) in Ref. 15.

2.7. *Volume* V(T,p)

Eq. (14) may also be regarded as an implicit function for $V(T,p)$. For application to cubic elements we will use Eq. (14) especially for constant temperature ($T = 0$) in order to calculate $V(p)$, or at constant pressure ($p = 0$) for the calculation of $V(T)$. Results of the calculations and experimental data [15,17] are given for Al and Xe in Figs. 7 and 8.



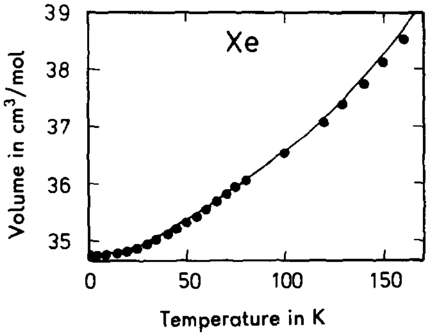
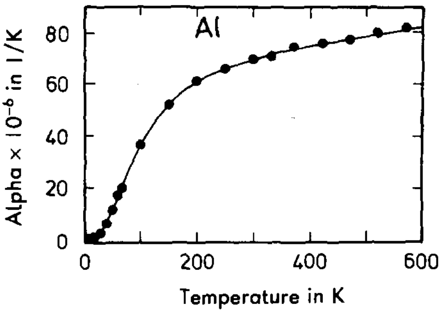


Fig. 7 (left). $V(T)$ for Al. Solid line according to Eqs. (14)-(16) at $p = 0$; data from G.N. Kamm and G.A. Alers (1964) in Ref. 17, p. 6, and D. Gerlich and E.S. Fisher (1969) in Ref. 17, p. 7.

Fig. 8 (right). $V(T)$ for Xe. Solid line according to Eqs. (15) and (16) at $p = 0$; data from D.R. Sears and H.P. Klug (1962) in Ref. 15.

2.8. *Volume expansivity* $\alpha_p(T)$

The relations for heat capacity [12] $C_p = C_v + \alpha_p{}^2 K_T T V = C_v(1 + \Gamma\alpha_p T)$ and $C_p = \delta\varepsilon_c(V_0/V(T))^\delta\alpha_p$ (Eq. (5)) may be solved for the coefficient of volume expan-



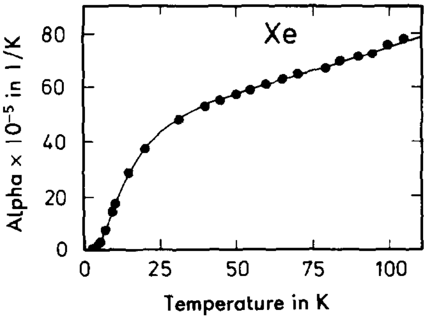


Fig. 9 (left). $\alpha_p(T)$ for Al. Solid line according to Eqs. (15) and (16); data from F.G. Awad and D. Gugan (1971) in Ref. 14, Vol. (12)1, p. 12, D.B. Fraser and A.C. Hollis-Hallett (1961) in Ref. 14, Vol. (12)1, p. 12, and K. Honda and Y. Okubo (1924) in Ref. 14, Vol. (12)1, p. 12.

Fig. 10 (right). $\alpha_p(T)$ for Xe. Solid line according to Eqs. (15) and (16); data from C.R. Tilford and C.A. Swenson (1972) in Ref. 14, Vol. 13(1), p. 174.

sivity α_p. With $V(T) = V_0(1 + \alpha_p T)$, we obtain

$$\alpha_p(T) = \frac{(3RD_0(\Theta/T) + \gamma' T)}{[\delta\varepsilon_c - (\Gamma + \delta)(3RD_0(\Theta/T) + \gamma' T)T]} \tag{15}$$

$$D_0 = \frac{3}{(\Theta/T)^3} \int_0^{\Theta/T} \frac{x^4 e^x \, dx}{(e^x - 1)^2} \tag{16}$$

In Eqs. (15) and (16) we have used the relation for Debye functions $4D_1(x) = D_0(x) + 3x/(e^x - 1)$, which may be obtained by partial integration. The results of calculations for Al and Xe with the same parameters (see Table 1) as in the figures above are compared with experimental data [14] in Figs. 9 and 10.

2.9. *Molar heat capacity* $C_p(T)$

Molar heat capacity C_p may be calculated from $C_p = C_v(1 + \Gamma\alpha_p T)$

$$C_p(T) = [3RD_0(\Theta/T) + \gamma' T][1 + \Gamma\alpha_p(T)T] \tag{17}$$

with α_p and D_0 given by Eqs. (15) and (16), respectively. The calculated values for Al and Xe are compared with experimental data [14,15] in Figs. 11 and 12.

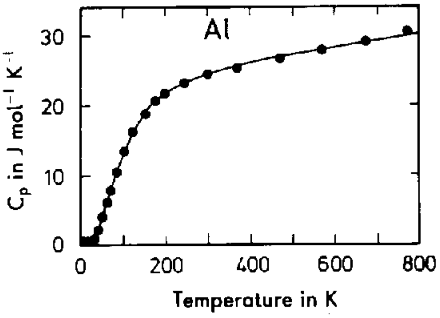


Fig. 11 (left). $C_p(T)$ for Al. Solid line according to Eq. (17); data from J.A. Kok and W.H. Keesom (1937) in Ref. 14, Vol. 4, p. 3, W.F. Giaugue and P.F. Meads (1941) in Ref. 14, Vol. 4, p. 3, H. Mäder (1951) in Ref. 14, Vol. 4, p. 3 and T.E. Pochapsky (1953) in Ref. 14, Vol. 4, p. 3.

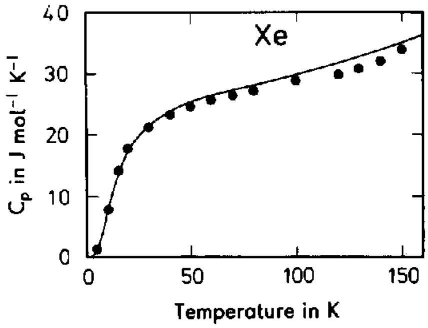


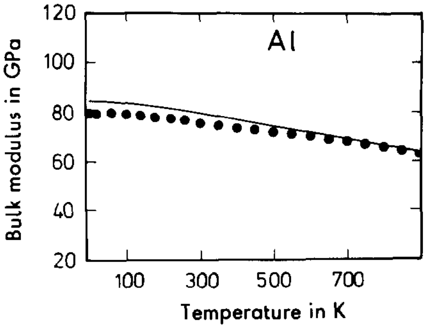
Fig. 12 (right). $C_p(T)$ for Xe. Solid line according to Eq. (17); data from H. Fenichel and B. Serin (1966) in Ref. 15, p. 783 and J.U. Trefny and B. Serin (1969) in Ref. 15, p. 783.

2.10. *Bulk modulus* $K_T(T)$

The bulk modulus $K_T(T)$ is determined by the Grüneisen relation (1) as

$$K_T(T) = \Gamma C_v(T)/(\alpha_p(T)V) \tag{18}$$

Calculated results and experimental data [15,17] are given in Figs. 13 and 14.



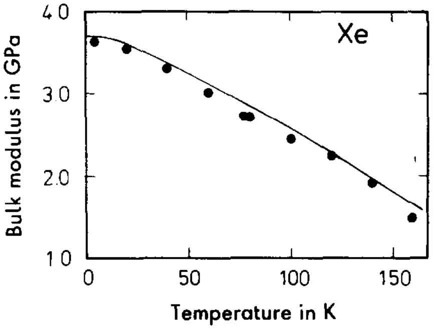


Fig. 13 (left). $K_T(T)$ for Al. Solid line according to Eq. (18); data from G.N. Kamm and G.A. Alers (1964) in Ref. 17, p. 6 and D. Gerlich and E.S. Fisher (1969) in Ref. 17, p. 7.

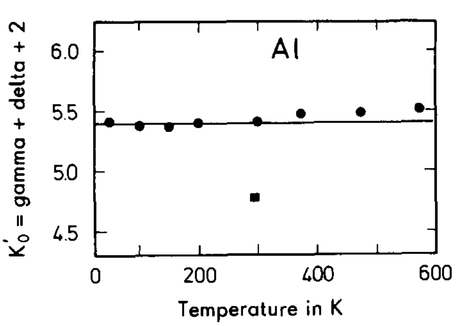
Fig. 14 (right). $K_T(T)$ for Xe. Solid line according to Eq. (18); data from M.S. Anderson and C.A. Swenson (1975) in Ref. 15, p. 813.

2.11. *Pressure coefficient* K'_0 *of bulk modulus*

With compressibility $\beta = \beta(T,p)$ and $K_T = 1/\beta$, the bulk modulus $K_T(T,V)$ may also be regarded as a function of pressure, $K_T(p) = K_T(V(p)) = -V(\delta p/\delta V)_T$. We obtain $K'_T = (\delta K/\delta p)_{p=0} = (\delta K/\delta V)_T(\delta V/\delta p)_T = -\{\delta[V(\delta p/\delta V)_T]/\delta V\}_T/(\delta p/\delta V)_T$. With $p(V)$ at $T = 0$ according to Eq. (14) we find for the limit of zero pressure

$$K'_0 = \Gamma + \delta + 2 \tag{19}$$

Calculated values and experimental data [12–17] are given in Figs. 15 and 16.



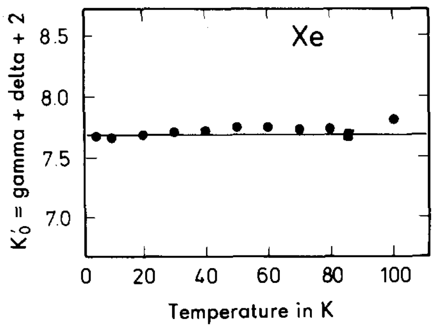


Fig. 15 (left). $\Gamma + \delta + 2$ of Al. Solid line according to Eq. (19); solid circles are thermophysical data from authors of Figs. 7, 9, 11 and 13; solid square for high pressure data from Ref. 18.

Fig. 16 (right). $\Gamma + \delta + 2$ of Xe. Solid line according to Eq. (19); solid circles are thermophysical data from authors of Figs. 8, 10, 12 and 14; solid square for high pressure data from Ref. 19.

Table 1

The six constants of the Grüneisen–Debye EOS for 18 elements, volume [12,17], cohesive energy [12], constant of electronic contribution to specific heat [12], Debye temperature [12,13], exponents Γ and δ optimized according to Figs. 1–40 for literature data [14–17]; the sum of exponents $\Gamma+\delta+2$ is compared to the pressure coefficient of bulk modulus K_0' from the literature [17–19]

Group	Crystal structure	Element	V_0/cm^3 mol^{-1}	ε_c/kJ mol^{-1}	γ'/mJ mol^{-1} K^{-1}	Θ_0/K	Γ	δ	$\Gamma+\delta+2$ [a]	K_0'
Alkali	b.c.c.	Li	12.71	158	1.63	344	0.86	1.20	4.06	3.52
		Na	22.60	107	1.38	158	1.16	1.36	4.52	4.2
Metals		K	43.28	90	2.08	91	1.38	1.38	4.10	4.21
Metals	f.c.c.	Cu	7.04	336	0.695	343	2.03	1.49	5.52	5.48
Monovalent		Ag	10.145	284	0.646	225	2.48	1.61	6.09	6.12
		Au	10.105	368	0.729	165	3.05	1.66	6.71	6.43
Bivalent	f.c.c.	Ni	6.55	428	7.02	450	1.82	1.60	5.42	5.5
		Pd	8.82	376	9.42	274	(2.33)	(1.93)	(6.26)	5.42
		Pt	9.02	564	6.8	240	(2.58)	(1.80)	(6.38)	5.2
	b.c.c.	Fe	7.05	413	4.98	470	1.69	1.74	5.43	5.29
		Nb	10.811	730	7.79	275	1.61	1.61	4.23	4.06
		Ta	10.827	782	5.9	240	1.64	1.64	4.25	3.79
Trivalent	f.c.c.	Al	9.87	327	1.35	428	2.30	1.10	5.40	4.85
Quadrivalent	f.c.c.	Pb	17.88	196	2.98	105	2.70	1.67	6.37	5.53
Noble gas	f.c.c.	Ne	13.39	1.92	0	75	2.71	2.92	7.63	9.2
		Ar	22.56	7.74	0	92	2.86	3.07	7.93	7.2
		Kr	27.10	11.2	0	72	2.75	3.00	7.75	5.9
		Xe	34.73	15.9	0	64	2.72	2.96	7.68	7.69

[a] When $\Gamma=\delta$ the K_0' value is given by $K_0'=(\Gamma+1)^2/\Gamma$.

3. Thermophysical data for cubic elements

The good results for Al and Xe show that calculations of thermophysical and high pressure properties are in good agreement with experimental data. Further calculations of volume $V(T)$, $V(p)$, heat capacity $C_p(T)$, volume expansivity $\alpha_p(T)$, bulk modulus $K_T(T)$, $K_T(p)$, pressure coefficient $K'_0(T)$, $\Gamma(T)$ and $\delta(T)$ have been compared to experimental data for 18 cubic elements: the alkali metals Li, Na, K, Rb and Cs, the transition metals Cu, Ag, Au, Ni, Fe, Nb and Ta, the main group metals Al and Pb, and solid rare gas crystals Ne, Ar, Kr and Xe.

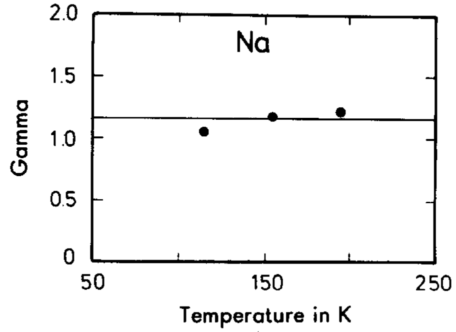
Table 1 shows for 18 cubic elements the set of six parameters which have been used to calculate all thermophysical properties as functions of temperature T, volume V of pressure p, zero pressure volume V_0 [12,17], cohesive energy ε_c [12], Debye constant Θ_0 [12,13] and electronic specific heat constant γ' [12].

The mean Grüneisen constant Γ and the exponent δ have been recalculated in a wide temperature range according to $\Gamma = \alpha_p K_T V / C_v$ and $\delta = [C_p/\alpha_p]/[\varepsilon_c - C_p T]$ and may differ from the literature values given in Ref. 11.

The range of validity according to Figs. 17, 18, 25, 26, 33 and 34 below is given by the range of temperature in which Γ and δ are constant.

3.1. Alkali metals

For sodium the calculations and data [14,16–18] of Γ and δ as a function of temperature, pressure $p(V)$, volume $V(T)$, volume expansivity $\alpha_p(T)$, heat capacity $C_p(T)$, bulk modulus $K_T(T)$, pressure coefficient K'_0 and $\Gamma + \delta + 2$ are shown in Figs. 17–24. The data [14,16–18] fit well except for $\alpha_p(T)$ at low temperatures. However, a change in constants for Na, e.g. in Θ_0 would alter the plot for $C_p(T)$, where more data are available.



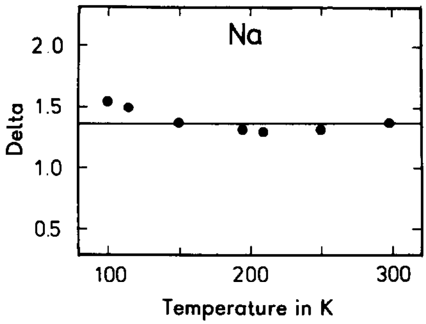
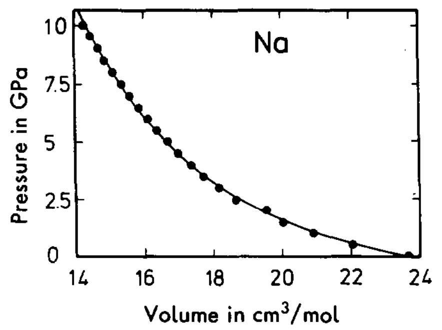


Fig. 17 (left). Γ values for Na. Solid line according to Eq. (2); solid circles are thermophysical data from authors of Figs. 20–23.

Fig. 18 (right). δ values for Na. Solid line according to Eq. (6); solid circles are thermophysical data from authors of Figs. 21 and 22.



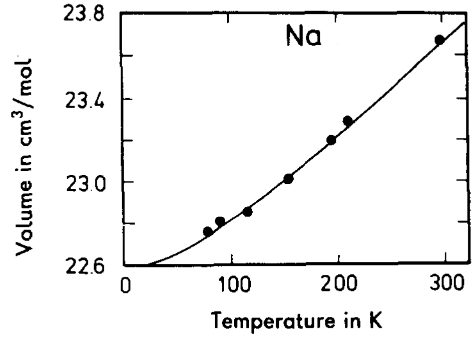
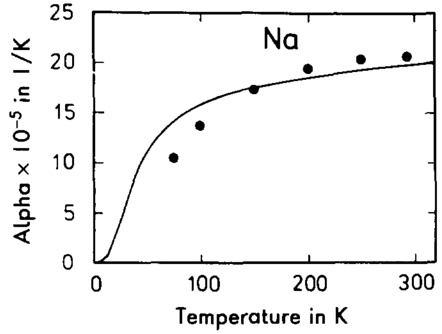


Fig. 19 (left). $p(V)$ for Na. Solid line according to Eq. (14); data from P.W. Bridgman (1948) in Ref. 16, p. 4-42.

Fig. 20 (right). $V(T)$ for Na. Solid line according to Eqs. (14)–(16) at $p = 0$; data from M.E. Diederich and J. Trivisonno (1966) in Ref, 17, p. 90, K.S. Alexandrow and T.V. Ryshova (1961) in Ref. 17, p. 90 and R.F.S. Hearmon (1946) in Ref. 17, p. 91.



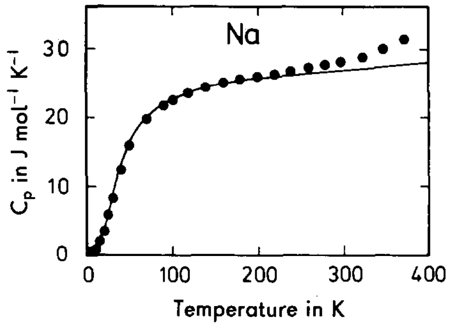


Fig. 21 (left). $\alpha_p(T)$ for Na. Solid line according to Eqs. (15) and (16); data from R.K. Kirby, Th.A. Hahn and B.D. Rothrock in Ref. 16, p. 4-130.

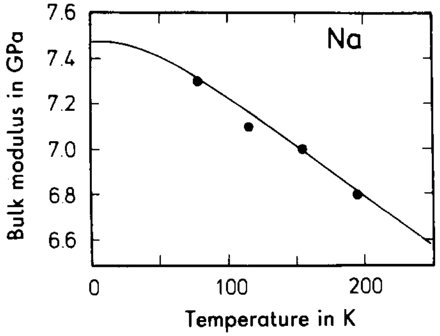
Fig. 22 (right). $C_p(T)$ for Na. Solid line according to Eq. (17); data from L.M. Roberts (1957) in Ref. 14, Vol. 4, p. 216, D.L. Martin (1960) in Ref. 14, Vol. 4, p. 216 and D.C. Ginnings, T.B. Douglas and A.F. Ball (1950) in Ref. 14, Vol. 4, p. 216.

Similar results have been obtained for lithium and potassium with good agreement between calculations and data [14,16–18]. For rubidium and cesium the experimental data were not sufficient for a reliable calculation of Γ and δ.

In alkali metals we find $\delta > \Gamma$. We have to consider δ as the exponent of the repulsive potential and Γ the exponent of the attractive potential.

The value of Γ is 0.86 for Li, 1.16 for Na and 1.38 for K; for δ we have obtained 1.20, 1.36 and 1.38, respectively. The sums of $\Gamma + \delta + 2$ agree well with data for the pressure coefficient of bulk modulus K_0' from high pressure experiments, as given in Table 1.

Comparing the EOS of the literature [1–10] only the Birch equation [9], which is generally used for metals, agrees with the data of alkali metals: $m/3 = 5/3$ is somewhat larger than the observed values of $\Gamma = 0.86$ to 1.38, the second exponent



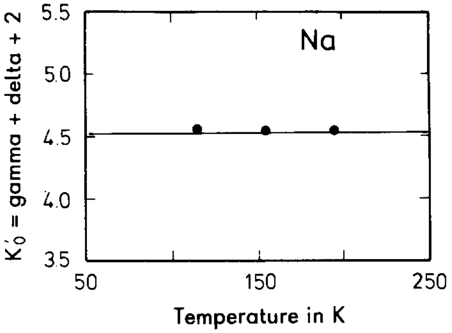


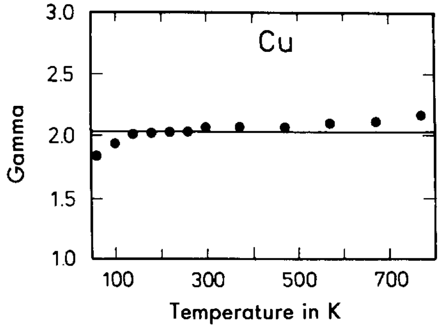
Fig. 23 (left). $K_T(T)$ for Na. Solid line according to Eq. (18); data from M.E. Diederich and J. Trivisonno (1966) in Ref. 17, p. 90 and R.F.S. Hearmon (1946) in Ref. 17, p. 91..

Fig. 24 (right). $\Gamma + \delta + 2$ of Na. Solid line according to Eq. (19); solid circles are thermophysical data from authors of Figs. 20–23.

$n/3 = 4/3$ is close to $\delta = 1.35$ of the present model. The sum $m/3 + n/3 + 2 = 4$ agrees well with the observed values of K_0' between 3.5 and 4.2. Other models (e.g. those of Slater [4] and Bardeen [6]) lead to much smaller values for K_0'; but that of Lennard-Jones and Ingham [3] leads to larger values for K_0'.

3.2. Transition metals

Figs. 25–32 show the calculations and data [14,16,17] for copper: Γ and δ as a function of temperature, pressure $p(V)$, volume $V(T)$, volume expansivity $\alpha_p(T)$, heat capacity $C_p(T)$ and bulk modulus $K_T(T)$. The agreement is good with data in all plots. Similar results have been obtained [14,16–19] for silver, gold and nickel. For palladium, platinum, iron, niobium and tantalum the calculations do not always agree with the data [14,16–18].



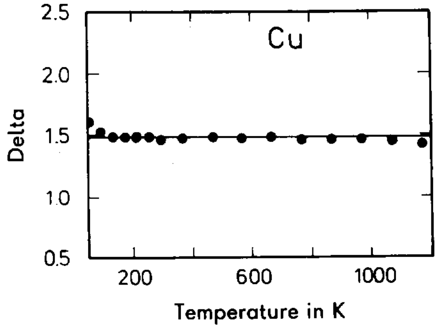
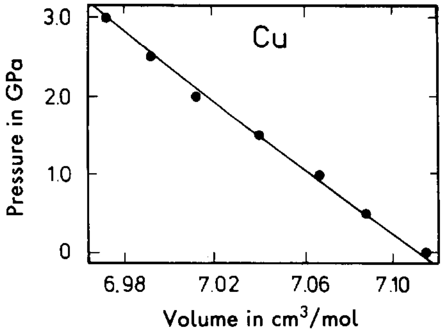


Fig. 25 (left). Γ values for Cu. Solid line according to Eq. (2); solid circles for thermophysical data from authors of Figs. 29–31.

Fig. 26 (right). δ values of Cu. Solid line according to Eq. (6); solid circles for thermophysical data from authors of Figs. 29 and 30.



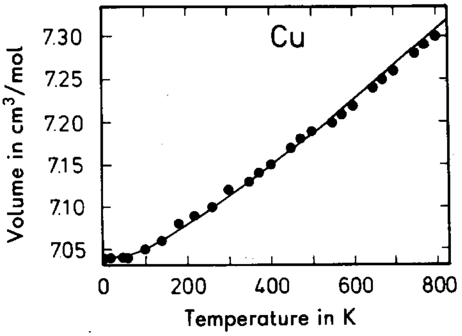


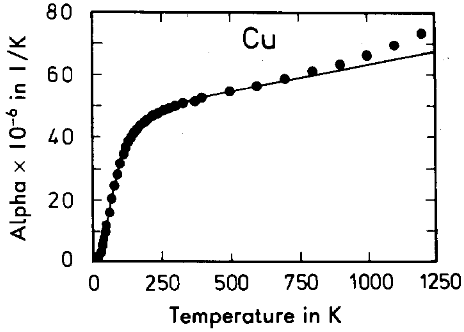
Fig. 27 (left). $p(V)$ for Cu. Solid line according to Eq. (14); data from P.W. Bridgman (1949) in Ref. 16, p. 4-41.

Fig. 28 (right). $V(T)$ for Cu. Solid line according to Eqs. (14)–(16) at $p = 0$; data from W.C. Overton and J. Gaffney (1955) in Ref. 17, p. 23 and Y.A. Chang and L. Himmel (1966) in Ref. 17, p. 24.

Figs. 33–40 show the calculations and data [14,16–18] for iron: Γ and δ as a function of temperature, volume $V(T)$, volume expansivity $\alpha_p(T)$, heat capacity $C_p(T)$, bulk modulus $K_T(T)$ and $K_T(p)$.

The data of $\delta(T)$, $\alpha_p(T)$ and $C_p(T)$ in Figs. 34, 36 and 37 reflect the b.c.c. to f.c.c. phase transition at 1158 K, which is not incorporated into the calculations. Similar results are found for Ni, where a magnetic phase transition is observed.

For niobium and tantalum the calculated values of Γ and δ have about the same value. This leads to a logarithmic potential in Eq. (8), and the pressure coefficient of bulk modulus given by $K'_0 = (\Gamma + 1)^2/\Gamma$ agrees with the data. However, the specific heat plots do not agree very well with the experimental data [14] for Nb and Ta.



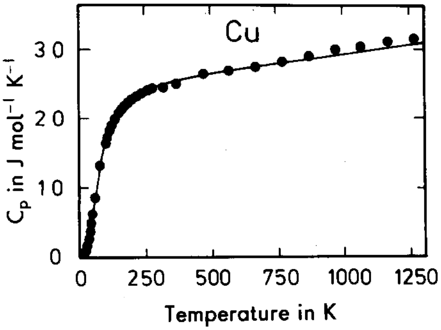
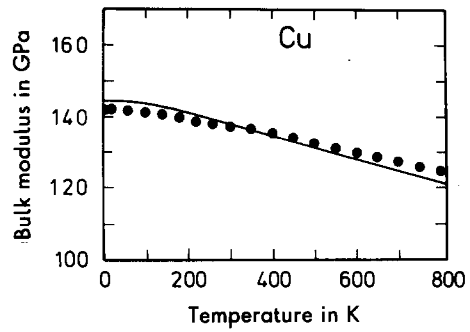


Fig. 29 (left). $\alpha_p(T)$ for Cu. Solid line according to Eqs. (15) and (16); data from K.O. McLean, C.A. Swenson and C.R. Case (1972) in Ref. 14, Vol. 12(1), p. 90, F.C. Awad and D. Gugan (1971) in Ref. 14, Vol. 12(1), p. 91, G.V. Bunton and S. Weintraub (1968) in Ref. 14, Vol. 12(1), p. 89, J.E. Leksina and S.J. Novikova (1963) in Ref. 14, Vol. 12(1), p. 90 and P.D. Pathak and N.G. Vasavada (1970) in Ref. 14, Vol. 12(1), p. 89.

Fig. 30 (right). $C_p(T)$ for Cu. Solid line according to Eq. (17); data from J.P. Franck, F.D. Manchester and D.L. Martin (1961) in Ref. 14, Vol. 4, p. 55, T.A. Sandenaw (1959) in Ref. 14, Vol. 4, p. 55, D.L. Martin (1960) in Ref. 14, Vol. 4, p. 55 and V.E. Lyusternik (1959) in Ref. 14, Vol. 4, p. 55.



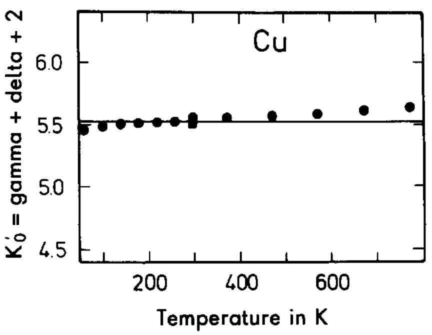
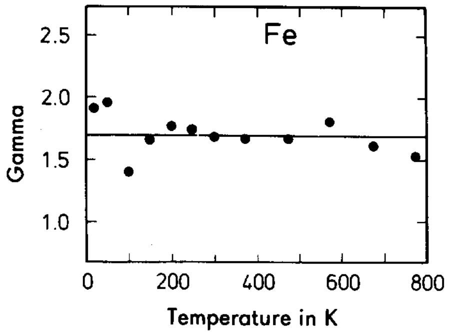


Fig. 31 (left). $K_T(T)$ for Cu. Solid line according to Eq. (18); data from W.C. Overton and J. Gaffney (1955) in Ref. 17, p. 23 and Y.A. Chang and L. Himmel (1966) in Ref. 17, p. 24.

Fig. 32 (right). $\Gamma + \delta + 2$ for Cu. Solid line according to Eq. (19); solid circles for thermophysical data from authors of Figs. 28-31; solid square for high pressure data from Ref. 18.



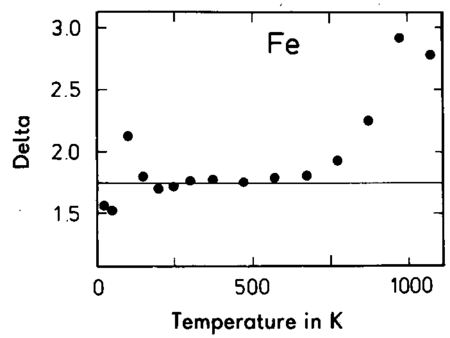
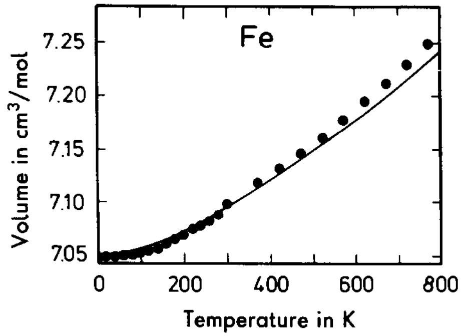


Fig. 33 (left). Γ values for Fe. Solid line according to Eq. (2); solid circles for thermophysical data from authors of Figs. 35-38.

Fig. 34 (right). δ values for Fe. Solid line according to Eq. (6); solid circles for thermophysical data from authors of Figs. 36 and 37.

For transition metals we find $\Gamma > \delta$. The value of the exponent δ of the attractive part of the potential is nearly equal to 5/3 for all transition metals. The value of Γ of the repulsive potential varies between 2 and 3 for the f.c.c. transition metals, and is close to 5/3 for the b.c.c. transition metals. The sums $\Gamma + \delta + 2$ agree well with K'_0 for high pressure data [18] in Table 1.

The Birch model [9] with $m/3 + n/3 + 2 = 4$ is again suited to the b.c.c. transition metals with K'_0 close to 4, but it cannot be applied to f.c.c. transition metals where the predicted values for Γ, δ and K'_0 are much smaller than the experimental values. No other EOS [1-8] can be applied to transition metals.



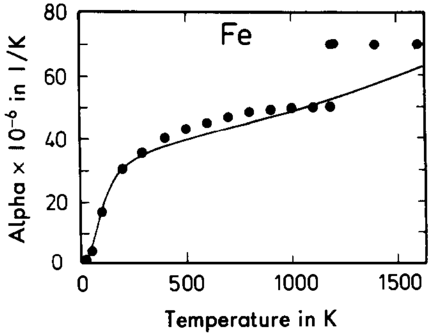
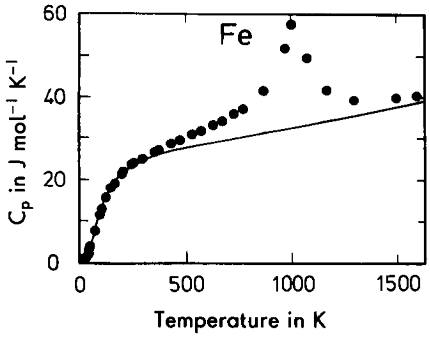


Fig. 35 (left). $V(T)$ for Fe. Solid line according to Eqs. (14)-(16) at $p = 0$; data from J.A. Rayne (1961) in Ref. 17, p. 34, M.W. Guinan and D.N. Beshers (1968) in Ref. 17, p. 35 and J. Leese and A.E. Lord, Jr. (1968) in Ref. 17, p. 35.

Fig. 36 (right). $\alpha_p(T)$ for Fe. Solid line according to Eqs. (15) and (16); recommended data from Ref. 14, Vol. 12(1), p. 157.



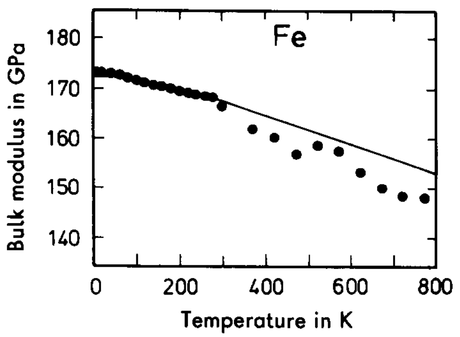


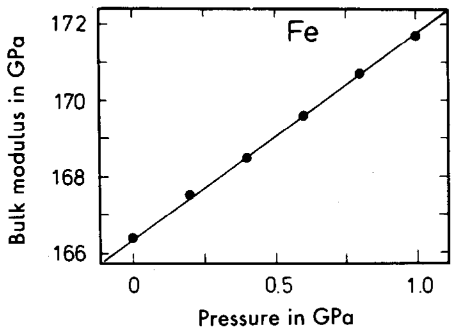
Fig. 37 (left). $C_p(T)$ for Fe. Solid line according to Eq. (17); data from G. Duyckaerts (1939) in Ref. 14, Vol. 4, p. 106, A. v. Eucken and H. Werth (1930) in Ref. 14, Vol. 4, p. 106, K.K. Kelley (1943) in Ref. 14, Vol. 4, p. 105, D.L. McElroy (1957) in Ref. 14, Vol. 4, p. 105 and P.D. Anderson and R. Hultgren (1962) in Ref. 14, Vol. 4, p. 106.

Fig. 38 (right). $K(T)$ for Fe. Solid line according to Eq. (19); data from J.A. Rayne (1961) in Ref. 17, M.W. Guinan and D.N. Beshers (1968) in Ref. 17 and J. Leese and A.E. Lord, Jr. (1968) in Ref. 17.

3.3. *Main group metals: Al and Pb*

The results for aluminum have been presented in Figs. 3, 5, 7, 9, 11, 13 and 15. Similar results have been found for lead. The constants for lead are listed in Table 1.

Aluminum and lead are f.c.c. metals and have $\Gamma > \delta$. The values of Γ are between 2 and 3 and larger than predicted by the Birch model [9]; the value of δ for lead is equal to 5/3, as for f.c.c. transition metals. Only δ for Al is as small as in alkali metals ($\delta = 4/3$). Again the sums of $\Gamma + \delta + 2$ agree with high pressure data for the pressure coefficient of bulk modulus K_0' in Table 1, and are closer to the value of $K_0' = 4$, as predicted by Birch.



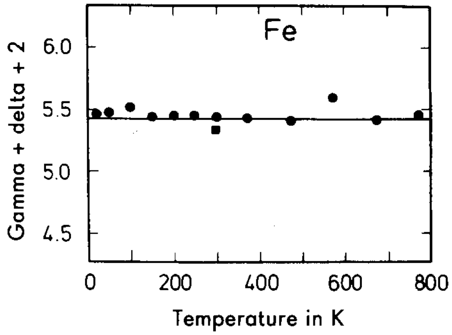


Fig. 39 (left). $K_T(p)$ for Fe. Solid line according to Eqs. (18) and (19); data from M.W. Guinan and D.N. Beshers (1968) in Ref. 17, p. 35.

Fig. 40 (right). $\Gamma + \delta + 2$ for Fe. Solid line according to Eq. (19); solid circles for thermophysical data from authors of Figs. 35–38; solid square for high pressure data from Ref. 18.

3.4. *Rare gas crystals*

The calculations for xenon have been presented in Figs. 2, 4, 6, 8, 10, 12, 14 and 16. Similar results [14,15] have been found for neon, argon and krypton. The constants of the calculations are listed in Table 1.

All rare gas crystals show about the same values for Γ and for δ. For alkali metals we find $\delta > \Gamma$, where δ is the exponent of the repulsive part and Γ is the exponent of the attractive potential. We find $\delta = 9/3$ and $\Gamma = 8/3$. The sums of $\Gamma + \delta + 2$ are constant and agree well with the high pressure data for the pressure coefficient of bulk modulus K_0' in Table 1 for Ar and Xe, which are in the same range. For Ne and Kr the calculated results and experimental [5] high pressure data for K_0' differ by only 20%.

The Lennard-Jones and Ingham [3] potential with $m/3 = 12/3 = 4$ and $n/3 = 6/3 = 2$ due to dipole–dipole interactions and $m/3 + n/3 + 2 = 8$ is very close to the observed values for Γ, δ and K_0' in rare gas crystals. No other equations, including the Birch EOS, can be applied.

4. Discussion

The results for the calculations of thermophysical properties show that the first order Grüneisen function $G(V)$ (Eq. (4)) leads to a self-consistent model with good agreement for most of the data for the 18 cubic elements. We now have to discuss the Grüneisen function $G(V)$ and the exponents Γ and δ in terms of the experimental results in Table 1 in more detail.

Table 1 shows the crystal structure, the exponents Γ and δ, with the sum $\Gamma + \delta + 2$ compared to K_0' for 18 elements.

4.1. Exponent of repulsive potential

For each element in Table 1 the larger exponent (Γ or δ) belongs to the repulsive part of the potential. We find the exponent of the repulsive potential to depend on the crystal structure. For f.c.c. crystals this exponent is about 9/3 to 6/3. For b.c.c. crystals the value is between 4/3 and 5/3. This result seems plausible, since the f.c.c. lattice is packed more densely than the b.c.c. lattice, and the repulsive exponent should be higher the closer the lattice is packed.

4.2. Exponent of attractive potential

The exponent of the attractive part of the potential is given by the smaller value of Γ and δ in Table 1. This exponent does not depend on crystal structure, but on the group to which the element belongs. For alkali metals we find 0.86 to 1.38, but for Al 1.1. For all transition metals and for lead the smaller exponent is about 5/3. Rare gas crystals with $\delta > \Gamma$ show uniquely 8/3 for the smaller exponent.

4.3. Pressure coefficient of bulk modulus K_0'

In contrast to the models of the literature [1–10] the present model is able to determine the exponents δ and Γ for all cubic elements. By $m/3 = \Gamma$ and $n/3 = \delta$ the exponents are related to experimental data which, unlike in the Birch EOS [9], may change with the elements. In addition we obtain a reasonable value for the pressure coefficient of the bulk modulus K_0', which compares well with the data.

4.4. The Grüneisen function

In order to discuss the exponent of the attractive potential we have to look back at the Grüneisen function.

(a) At equilibrium or $p = 0$ the Grüneisen EOS (3) yields $G(V) = -E$. The Grüneisen function $G(V)$ is equal to the (negative) total energy E or the cohesive energy of the crystal. This leads to $G(V) = \varepsilon_c$ at $T = 0$.

(b) However, at equilibrium the total energy according to the virial theorem [1,2,4] is equal to the negative kinetic energy, $E = -E_{\mathrm{kin}}$, or $G = -E = E_{\mathrm{kin}}$. If we assume the virial law to be valid for metals, the Grüneisen function $G(V)$ will be given by the kinetic energy $E(k)$ of electrons, which is the sum of even powers of momentum k

$$G(V) = E_{\mathrm{kin}}(k) = \sum a_{2n} k^{2n} \qquad n = 1, 2, \ldots \tag{20}$$

The maximum of momentum $k_{\max}$ of electrons is proportional [12] to $(1/V)^{1/3}$. In normalizing Eq. (20) by the energy of cohesion ε_c we obtain

$$G(V) = \varepsilon_c \sum c_{2n} (V_0/V)^{2n/3} \qquad n = 1, 2, \ldots \tag{21}$$

with $V = V(T)$. In general Eq. (21) will replace Eq. (4).

The exponent δ may be calculated from molar heat by differentiating the total energy with respect to T, $C_p(T) = (\partial E/\partial V)(\partial V/\partial T)$. With $E = -G(V(T))$ in Eq. (21) we find

$$C_p(T) = \alpha_p(T)\varepsilon_c \sum (2n/3)c_{2n}(V_0/V)^{2n/3} \tag{22}$$

and similarly to Eqs. (5)–(7)

$$\delta = \sum (2n/3)c_{2n}(V_0/V)^{2n/3} \qquad n = 1, 2, \ldots \tag{23}$$

with $\Sigma c_{2n} = 1$. The exponent δ is the mean value of a sum of exponents $2n/3$ with a weight factor c_{2n}.

For $n = 1$ we obtain the free electron band structure and $\delta = 2/3$. This exponent has been used for a free electron EOS by Slater [4] and Bardeen [6], and turns out too small in the calculation of thermal properties.

For $n = 2$ we have a non-quadratic band structure. In alkali metals and aluminum we have $\Gamma < \delta$ as the attractive exponent; the experimental results with $\Gamma = 0.86$ to 1.38 indicate a summation up to $n = 2$.

For $n = 3$ we obtain terms with the sixth power of k in the band structure. Transition metals and lead almost uniquely show $\delta = 5/3$, which is equivalent to a summation up to $n = 3$.

In order to compare these results with band structure calculations for metals [20] we have to look for the curvature of the energy band $E(k)$ at the Fermi surface. This energy level is mainly affected by a change in temperature and pressure. Calculations of $E(k)$ for alkali, noble and other f.c.c. transition metals [20] indicate a value higher than $n = 1$ of the free electron solution. However, it is difficult to extract the exact exponent from the tabulation of Slater–Koster parameters [20].

Calculations of $E(k)$ for b.c.c. transition metals [20] show that generally more than one branch of $E(k)$ crosses the Fermi level. This may explain why b.c.c. transition metals are not so well represented by the first order Grüneisen function $G(V)$ in Eq. (7).

Rare gas crystals show $\delta > \Gamma$; the exponent of the attractive potential is close to 8/3. This corresponds to a summation up to $n = 4$ or 5. However, in contrast to metals we have to assume dipole–dipole interactions for the insulating rare gas crystals to account for the high exponent in these solids.

We may conclude that the Grüneisen EOS (Eq. (3)) and the first order Grüneisen approximation (Eq. (7)) may well be applied to most calculations of thermophysical properties of cubic elements. The Grüneisen function $G(V)$ appears to represent the cohesive energy of the crystal.

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