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Thermal Expansion, Heat of Fusion, and Electron Density of Monovalent Metals

By

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The enthalpy of monovalent metals is calculated as a function of electron density according to the model of nearly free electrons. The coefficient of thermal expansion of solid and liquid monovalent metals is given by heat capacity and Fermi energy, $\alpha_P(T) = 2.5 \times C_P(T)/\varepsilon_F(T)$. The heat of fusion is determined by Fermi energy and relative change in volume at the melting point, $L_m = 0.4\varepsilon_F(T_m) \times (V_L - V_S)/V_L$. The agreement with experimental data is quite satisfactory for all alkali and noble metals.

Die Enthalpie einwertiger Metalle wird als Funktion der Elektronendichte nach dem Modell der fast freien Elektronen berechnet. Der Koeffizient der thermischen Ausdehnung fester und flüssiger einwertiger Metalle wird durch die Wärmekapazität und Fermienergie gegeben, $\alpha_P(T) = 2{,}5 \times C_P(T)/\varepsilon_F(T)$. Die Schmelzwärme wird durch die Fermienergie und die relative Volumenänderung am Schmelzpunkt bestimmt, $L_m = 0{,}4\varepsilon_F(T_m) \times (V_L - V_S)/V_L$. Die Übereinstimmung mit experimentellen Werten für Alkali- und Edelmetalle ist recht zufriedenstellend.

1. Introduction

Thermal expansion and fusion are generally attributed to anharmonic phonon–phonon interactions in condensed matter. In a first approach thermal expansion may be linked to the anharmonic ionic potential. This will lead to a coefficient of thermal expansion, which is proportional to the anharmonic coefficient of the potential [1]. However, the model neither reflects the temperature dependence of α_P similar to specific heat at low temperatures, nor does it show a close relation to fusion, which makes it unsuitable for a more detailed discussion of these effects.

Most calculations of thermal expansion are based on the Grüneisen relation, which connects the coefficient of volume expansion α_P to heat capacity at constant volume C_V [1],

$$\alpha_P = \frac{GC_V}{B_T V} . \tag{1}$$

In alkali metals the bulk moduli B_T have been calculated quite accurately from pseudo potential calculations. Thermal expansion may then be reduced to the discussion of the Grüneisen parameter G [2 to 6] according to (1). However, the discussion proves to be complex, as all phonon branches as well as the electrons will have a specific Grüneisen parameter. Thus little is revealed about the mechanism of thermal expansion.

The heat of fusion of alkali metals has been obtained from pseudo potential calculations [7]. Again a mechanism of anharmonic interactions or fusion and its relation to thermal expansion has not been obtained from these calculations.

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In the present paper thermal expansion will be discussed by the electron density concept. The enthalpy of the free electron gas or an alkali metal will depend on the electron density. Due to thermal expansion or melting electron density and enthalpy will change according to

$$\mathrm{d}H = \left(\frac{\mathrm{d}H}{\mathrm{d}V}\right)_T \mathrm{d}V + \left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_V \mathrm{d}T\,. \tag{2}$$

Differentiating at constant pressure with respect to temperature we obtain

$$C_P = V\left(\frac{\mathrm{d}H}{\mathrm{d}V}\right)_T \alpha_P + C_V\,, \tag{3}$$

$\alpha_P = (\mathrm{d}V/\mathrm{d}T)_P/V$ is the coefficient of volume expansion. Integrating (2) at constant melting temperature T_m leads to the heat of fusion L_m,

$$L_\mathrm{m} = \left(\frac{\mathrm{d}H}{\mathrm{d}V}\right)_{T_\mathrm{m}} (V_\mathrm{L} - V_\mathrm{S})\,, \tag{4}$$

with V_L and V_S being the volume of the liquid and the solid at the melting point, respectively. In order to apply (3) and (4) to alkali metals, the enthalpy of the free electron gas will be calculated in the next section.

2. Enthalpy of Alkali Metals at Constant Pressure $P = 0$

The mean kinetic energy of N free electrons at constant pressure as a function of temperature T is given by

$$\langle E_\mathrm{kin}\rangle = \frac{3}{5} N\varepsilon_\mathrm{F}\left\{\left[\frac{V(0)}{V(T)}\right]^{2/3} + \frac{5}{3}\left[\frac{\pi k_\mathrm{B}T}{2\varepsilon_\mathrm{F}}\right]^2\right\}. \tag{5}$$

ε_F is the Fermi energy at $T = 0$, ε_F is proportional to the 2/3rd power of the electron density n. Equation (5) agrees with the calculations for constant volume [8], and includes thermal expansion. The kinetic energy is determined by the electron density of the first term in (5), the second term is a second-order correction, and will affect a few electrons at the Fermi surface, only. This is due to the high energy of the Fermi system at $T = 0$, changing the temperature will only have a relatively small effect on the energy of the electronic system.

According to Slater [9] the total energy $E(T)$ of an electron system may be derived from the virial theorem. For $P = 0$ the virial theorem for any Coulomb type interaction yields

$$E(T) = -\langle E_\mathrm{kin}\rangle\,, \tag{6}$$

$E(T)$ is the total energy at equilibrium, it is equal to the negative kinetic energy (5) due to the bound state of the electrons. The total energy $E(T)$ contains the volume $V(T)$ as a function of temperature. For the free electron gas the volume will be given as a constant boundary condition, which is generally unaffected by temperature. In real systems like alkali metals, however, the volume of the free electron gas is defined by the volume of the ions, which will change with temperature due to the movement of the ions.

So far the energy of the ions has not been mentioned. The Coulomb potential of the ions confines the free electron gas within the volume of a metal. It is responsible for the bound state of the electrons, which has been calculated by the virial theorem in (6). This implies that the enthalpy of the ions is implicitly incorporated in (6).

For $P = 0$ enthalpy $H = E + PV$ and energy E will be equal and we obtain the enthalpy of the free electron gas,

$$H(T) = -\frac{3}{5} N\varepsilon_F \left\{\left[\frac{V(0)}{V(T)}\right]^{2/3} + \frac{5}{3}\left[\frac{\pi k_B T}{2\varepsilon_F}\right]^2\right\}. \tag{7}$$

We may now proceed to calculate thermal expansion and heat of fusion according to (3) and (4).

3. Thermal Expansion

Heat capacity C_P is the derivative of enthalpy H (7) with respect to temperature T at constant pressure P. According to (2) and (3), we now obtain

$$\left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_P = \frac{2}{5} N\varepsilon_F \left[\frac{V(0)}{V(T)}\right]^{2/3} \alpha_P - N\,[\pi k_B]^2 \frac{T}{2\varepsilon_F}. \tag{8}$$

Dividing (8) by the number of electrons N we find the heat capacity per (monovalent) atom at $P = 0$,

$$C_P + [\pi k_B]^2 \frac{T}{2\varepsilon_F} = 0.4\,\varepsilon_F \left[\frac{V(0)}{V(T)}\right]^{2/3} \alpha_P\,. \tag{9}$$

The first term may be considered as heat capacity of the phonons, which are incorporated in the present model. The second term in (9) is the electronic contribution to specific heat. The total heat capacity is a function of the density of electronic states or Fermi energy ε_F and the coefficient of thermal expansion α_P.

We may now solve (9) for α_P. Introducing the temperature dependent Fermi energy

$$E_F(T) = \varepsilon_F \left[\frac{V(T)}{V(0)}\right]^{2/3}, \tag{10}$$

we obtain the coefficient of volume expansion as a function of temperature T,

$$\alpha_P(T) = 2.5\,\frac{C_P(T)}{E_F(T)}. \tag{11}$$

Equation (11) is equivalent to the Grüneisen relation (1), which relates thermal expansion to heat capacity. In contrast to (1) all functions in (11) are well known, the Grüneisen constant G does not appear. In the present model thermal expansion is a function of heat capacity and electron density or Fermi energy.

3.1 Thermal expansion of solid Li from 0 to 453 K

In order to calculate the thermal expansion of lithium as a function of temperature, we will approximate $C_P(T)$ by $C_V(T)$, which may be calculated as a function of temperature by the Debye function $D(T/T_D)$ and the Debye temperature T_D [10],

$$C_V = \left(\frac{125}{T_D}\right)^3 D\left(\frac{T}{T_D}\right). \tag{12}$$

In addition we may replace the hardly temperature dependent Fermi energy $E_F(T)$ in (11) by the constant ε_F. The coefficient of thermal expansion between 0 K and T_m will now depend on the two parameters Fermi energy and Debye temperature, only,

$$\alpha_P = 2.5\left(\frac{125}{T_D}\right)^3 \frac{D\left(\frac{T}{T_D}\right)}{\varepsilon_F}. \tag{13}$$

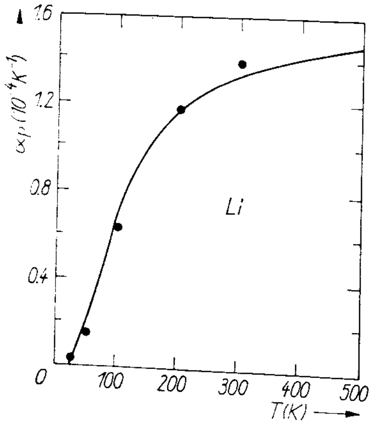

Fig. 1. Volume expansion of Li according to (13). Experimental data according to [11], T_D and ε_F from [8]

Fig. 1 shows the coefficient of volume expansion of Li as a function of temperature T in the temperature range from 0 to 453 K. The calculated solid line in Fig. 1 correspond to (13) with $\varepsilon_F = 4.74$ eV and $T_D = 400$ K [8], and agrees well with data points of Li from literature [11].

3.2 Thermal expansion of alkali metals at 300 K

For other alkali metals sufficient data are given only near room temperature. Table 1 shows the volume expansion coefficient of solid alkali metals at 300 K calculated according to (11), experimental data [10] are given in the second column. The ratio of experimental and calculated values is given in the third column.

3.3 Thermal expansion of liquid alkali metals at T_m

The model of free electrons is also applicable to liquid metals [13], and the above calculations of thermal expansion should be valid for liquid alkali metals as well. Table 2 shows the coefficients of thermal expansion α_P calculated according to (11) for liquid alkali metals at the melting point T_m. Values for specific heat and Fermi energy at the melting point are taken from the literature [13]. Experimental values [14] are given in the second column. The ratio of experimental and calculated values is given in the third column.

Table 1

Coefficients of thermal expansion α_P of solid alkali metals at $T = 300$ K. Calculations according to (11), experimental data from the literature [10]. The ratio of experimental and calculated values is given in the third column

metal	$\alpha_P(300\text{ K})\ (10^{-4}\text{ K}^{-1})$		
	calc.	exp.	exp./calc.
Li	1.3	1.35	1.0
Na	2.2	2.13	1.0
K	3.6	2.49	0.7
Rb	4.3	2.70	0.6
Cs	5.1	2.91	0.6

Table 2

Coefficients of thermal expansion α_P of liquid alkali metals at the melting point T_m. Calculations according to (11), experimental data from Webber and Stephens [14]. The ratio of experimental and calculated data is given in the third column

metal	$\alpha_P(T_m)$ (10^{-4} K^{-1})		
	calc.	exp.	exp./calc.
Li	1.8	1.6	0.9
Na	2.7	2.42	0.9
K	4.1	2.90	0.7
Rb	4.7	3.38	0.7
Cs	5.5	3.95	0.7

3.4 Heat of fusion of alkali metals

The heat of fusion of alkali metals may be obtained from the enthalpy of the free electron gas (7) and (4),

$$L_m = 0.4 E_F(T_m) \frac{V_L - V_S}{V_L}. \tag{14}$$

The heat of fusion L_m according to (14) is proportional to the relative change in volume $(V_L - V_S)/V_L$ and the Fermi energy at the melting temperature T_m. Melting of alkali metals is accompanied by a change in volume of 1.5% for Li, 2.5% for Na and other alkali metals [15].

Table 3 shows the heat of fusion L_m of alkali metals. The first column gives the calculation according to (14). The Fermi energy at the melting point according to (10) may be calculated from the volume of the liquid and has been taken from the literature [13]. The relative change in volume has been given by Wray [15].

Experimental values of the heat of fusion [13] are given in the second column. The ratio of experimental and calculated values in the third column is nearly unity for Li and Na and about 0.7 for other alkali metals.

3.5 Discussion of alkali metals

The calculation of thermal expansion and heat of fusion according to the concept of electron density leads to satisfying results. The agreement of experimental and

Table 3

Heat of fusion L_m of alkali metals. Calculations according to (14), experimental data from [13]. The ratio of calculated and experimental data is given in the third column

metal	L_m (meV)		
	calc.	exp.	calc./exp.
Li	27	31	0.9
Na	31	27	1.1
K	19	24	0.8
Rb	17	23	0.7
Cs	16	23	0.7

calculated values for solid and liquid expansion as well as for heat of fusion of alkali metals in Tables 1, 2, and 3 is 10% for Li and Na and within 30% for other alkali metals. The ratio of experimental and calculated values in the third column of all three tables is about 1.0 for Li and Na and about 0.7 for K, Rb, and Cs. This ratio may be interpreted as an effective mass ratio of the nearly free electrons in alkali metals. Similar effective mass ratios for alkali metals have been calculated in the literature [12]. The good agreement of the simple free electron model with experimental data of alkali metals is due to the s-type band structure of the alkali metals. If an application to other metals should be possible, it will at least require modifications according to additional p- or d-bands of the crystals.

4. Solid Noble Metals

For solid noble metals the volume expansion coefficient α_P calculated according to (11) will be too large by a factor of about 2, if the Fermi energy of the literature [10] is applied. This is due to the fact that in (5) only the kinetic energy of s-electrons has been taken into account. In solid noble metals, however, d-electrons will have to be considered, as well. The kinetic energy of a d-electron may be approximated by a Taylor series in wave number k,

$$E_{\text{kin}} = \varepsilon_0 + \varepsilon_2 k^2 + \varepsilon_4 k^4 + \dots \tag{15}$$

Retaining only the first two terms we may calculate the mean kinetic energy of all five d-bands by taking the sum of all states k_n from $n = 0$ to $n = n_\text{F}$. Due to the parabolic approximation the kinetic energy of d-electrons will be similar to that of the s-electrons,

$$\langle E_{\text{kin}} \rangle_\text{d} = E_0 + \frac{3}{5} N \varepsilon_\text{d} \left[\frac{V_0}{V(T)} \right]^{2/3} . \tag{16}$$

The first term in (16) is a constant, and will drop out of the calculations after differentiating with respect to volume V. The second terms contains the contribution of d-electrons to kinetic energy. ε_d corresponds to the width of all d-bands similar to ε_F, which indicates the width of the filled s-band. The total kinetic energy of s- and d-electrons in solid noble metals will be the sum of (5) and (16). The Fermi energy ε_F is replaced by the sum of ε_F and ε_d. The effective Fermi energy $\varepsilon_\text{F}^* = \varepsilon_\text{F} + \varepsilon_\text{d}$ takes into account s- and d-electrons.

According to band calculations by Burdick [8, 16] the width of the d-bands of Cu is about 80% of the width of the filled s-band. This leads to $\varepsilon_\text{F}^* = 1.8\varepsilon_\text{F}$ for Cu. This result corresponds to the calculation of thermal expansion for Cu, which deviates by a factor of 2 from experimental data, if only the Fermi energy ε_F is employed. Lacking similar band structure calculations for Ag and Au we will determine the effective Fermi energy for Ag and Au by fitting thermal expansion at 300 K to experimental data. This way we obtain $\varepsilon_\text{F}^* = 2.1\varepsilon_\text{F}$ for Ag and $\varepsilon_\text{F}^* = 2.8\varepsilon_\text{F}$ for Au.

4.1 Noble metals at low temperatures

At low temperatures the molar specific heat of noble metals is represented by the linear electronic contribution and the Debye cubic term. This leads to a thermal volume expansion coefficient [1]

$$\alpha_P = a_1 T + a_3 T^3 . \tag{17}$$

Table 4
Calculated coefficients of thermal expansion a_1 and a_3 of solid noble metals at low temperatures according to (18), experimental data from the literature [11]

metal	a_1 (10^{-10} K^{-2})		a_3 (10^{-10} K^{-4})	
	calc.	exp.	calc.	exp.
Cu	5.8	7	0.98	0.83
Ag	7.1	7	3.9	3.6
Au	3.9	6	7.3	6.0

With (9) and (12) we find

$$\begin{aligned} a_1 &= 5\left[\frac{\pi k_{\mathrm{B}}}{2E_{\mathrm{F}}^*}\right]^2, \\ a_3 &= \frac{5}{2}\left(\frac{125}{T_{\mathrm{D}}}\right)^3 \frac{1}{E_{\mathrm{F}}^*}\,. \end{aligned} \tag{18}$$

Table 4 shows the calculated values of a_1 and a_3 according to (18) for copper, silver, and gold. The same effective Fermi energy has been employed as in Fig. 2a to c. Experimental values [11] are shown in the second column. Again the agreement is quite satisfactory, only gold shows a deviation of calculation and experiment that exceeds 20%.

4.2 *Thermal expansion of solid noble metals from 0 K to $2T_D$*

In the calculation of thermal expansion of noble metals as a function of temperature T we have to replace ε_{P} in (18) by $\varepsilon_{\mathrm{F}}^*$,

$$\alpha_P = 2.5\left(\frac{125}{T_{\mathrm{D}}}\right)^3 D\left(\frac{T}{T_{\mathrm{D}}}\right)\frac{1}{\varepsilon_{\mathrm{F}}^*}\,. \tag{19}$$

Fig. 2a shows the volume expansion coefficient of Cu as a function of temperature in the range from 0 to 600 K. The parameters are $T_{\mathrm{D}} = 315$ K and $\varepsilon_{\mathrm{F}} = 7.0$ eV [10], and $\varepsilon_{\mathrm{F}}^* = 1.8\varepsilon_{\mathrm{F}}$. The solid line represents (19) and agrees well with the data points given by [11].

The same holds for silver and gold. Fig. 2b shows the calculation of α_P according to (19) for silver with the literature values $T_{\mathrm{D}} = 215$ K and $\varepsilon_{\mathrm{F}} = 5.49$ eV [10]. The effective energy is again $\varepsilon_{\mathrm{F}}^* = 2.1\varepsilon_{\mathrm{F}}$. In Fig. 2c α_P is given for gold with literature values $T_{\mathrm{D}} = 170$ K, $\varepsilon_{\mathrm{F}} = 5.53$ eV [10], and $\varepsilon_{\mathrm{F}}^* = 2.8\varepsilon_{\mathrm{F}}$. The solid line calculated according to (19) agrees rather well with the data points given in the literature [11].

4.3 *Liquid noble metals*

The calculations of thermal expansion may be applied again to liquid noble metals. Table 5 shows the coefficients of thermal expansion α_P calculated according to (11) for liquid noble metals at the melting point T_{m}. Values for specific heat and Fermi energy at the melting point are taken from the literature [13]. Experimental values [14] are given in the second column. The ratio of experimental and calculated values is given in the third column.

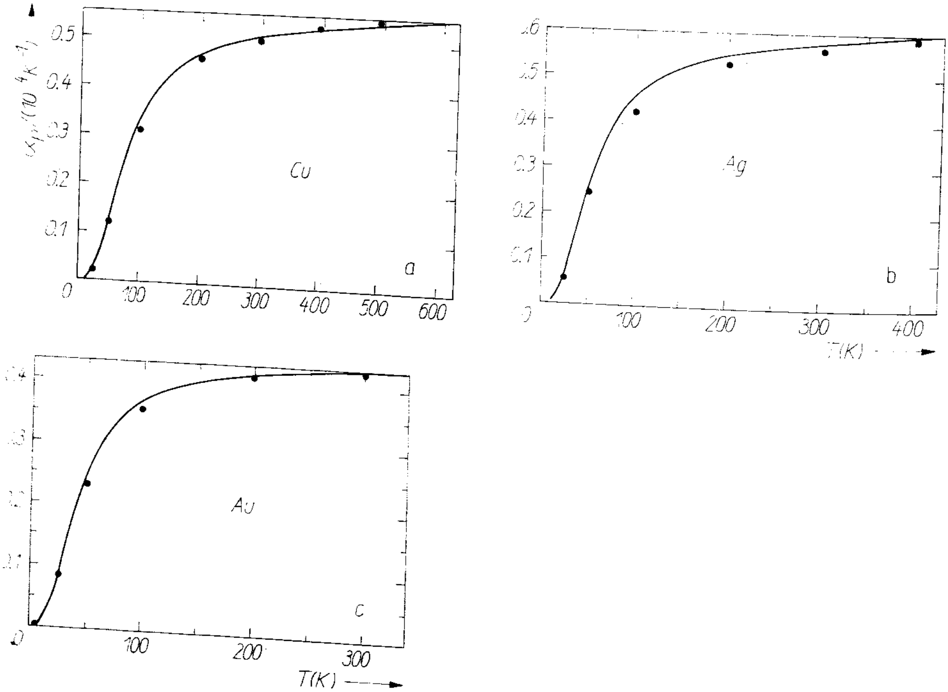

Fig. 2. Thermal volume expansion according to (19), experimental data according to [11], T_D and ε_F from [8]; a) Cu, $\varepsilon_F^* = 1.8\varepsilon_F$, b) Ag, $\varepsilon_F^* = 2.1\varepsilon_F$, c) Au, $\varepsilon_F^* = 2.8\varepsilon_F$

In the calculation of thermal expansion of liquid noble metals the Fermi energy of the literature has been employed without any correction for the d-electrons. For Cu the value of α_P agrees well with the data. The Ag calculation deviates by 30%, however, data for the bulk modulus [13] indicate an experimental value of α_P that agrees within 10% with the calculation above. These results indicate that thermal properties of liquid noble metals seem to depend on s-electrons only.

Table 5

Coefficients of thermal expansion α_P of liquid noble metals at the melting point T_m. Calculations according to (11), experimental data from Webber and Stephens [14]. The ratio of experimental and calculated data is given in the third column

metal	$\alpha_P(T_m)$ (10^{-4} K^{-1})		
	calc.	exp.	exp./calc.
Cu	1.2	1.17	1.0
Ag	1.6	(1.19)	(0.75)
Au	1.5	—	—

Table 6

Heat of fusion L_m of noble metals. Calculations according to (14), experimental data from [13]. The ratio of calculated and experimental data is given in the third column

metal	L_m (meV)		
	calc.	exp.	calc./exp.
Cu	139	134	1.0
Ag	110	116	1.0
Au	120	132	0.9

4.4 Fusion of noble metals

The heat of fusion L_m according to (14) is proportional to the relative change in volume and the Fermi energy at the melting temperature T_m.

Table 6 shows the heat of fusion L_m of noble metals. The first column gives the calculation according to (13). The Fermi energy at the melting point according to (10) may be calculated from the volume of the liquid and has been taken from the literature [13]. The relative change in volume has been taken from Wray [15].

In the calculation of heat of fusion of liquid noble metals no correction due to d-electrons has been used. This may again indicate that d-electrons do not take part in the bonding of liquid noble metals as much as they do in the solid.

4.5 Discussion of noble metals

The calculations for thermal expansion and heat of fusion of noble metals indicate that the electron density concept may indeed be applicable for monovalent metals. The results for thermal expansion of all liquid and solid monovalent metals as well as for the heat of fusion is, in spite of the simplicity of the nearly free electron model, quite satisfactory. The effective Fermi energy shows to represent the cohesive energy: the larger the cohesive energy, the smaller thermal expansion.

Moreover, we have found an indication to differences in the electronic state of solid and liquid noble metals. In liquid noble metals the d-bands seem to contribute little to cohesion and thus to thermal expansion and fusion. However, before discussing these results in more detail, additional calculations have to be carried out for other f.c.c. metals.

Acknowledgements

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