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Anharmonicity in the equations of state of Cu, Ag, and Au and related uncertainties in the realization of a practical pressure scale

Wilfried B Holzapfel

FB Physik, Universität Paderborn, D-33095 Paderborn, Germany

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Abstract

For the realization of a practical pressure scale based on equation of state (EOS) data for selected calibrants, a detailed modelling of the thermal contributions is required. While 'parametric EOS' forms with their temperature-dependent parameters $V_0(T)$, $K_0(T)$, and $K_0'(T)$ are useful for limited ranges in pressure and temperature, the separate modelling of the zero-temperature and thermal contributions is more appropriate especially for wide temperature ranges under high pressures (Holzapfel W B, Hartwig M and Sievers W 2001 *J. Phys. Chem. Ref. Data* **30**). The remaining uncertainties due to explicit anharmonic contributions beyond the implicit contributions of the quasiharmonic approximation are therefore discussed here in more detail.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

A detailed analysis of the thermal and thermo-elastic properties for Cu, Ag, and Au at ambient pressure over a wide range in temperature has shown recently [1] that explicit anharmonic contributions beyond the implicit contributions already included in the quasiharmonic phonon approximation must be taken into account in an accurate modelling of these properties, especially if this modelling is to give a precise description of equation of state (EOS) data for extended regions in temperature and pressure. On the basis of a Mie–Grüneisen (MG) model, which separates the thermal contributions from the zero-temperature EOS, explicit anharmonic contributions have been worked out [1–5]. However, the variations of these explicit anharmonic contributions under pressure have not yet been studied in detail. The remaining uncertainties in these pressure dependences are analysed here with the intention of giving more accurate estimates for the uncertainties in the present practical pressure scales based on EOS data for pressure markers such as Cu, Ag, and Au [1].

2. The model

Within the MG approach the total pressure

$$p(V,T) = p_c(V) + p_{th}(V,T) \tag{1}$$

is divided at first into the cold (zero-temperature) contribution $p_c(V)$ and the thermal contribution $p_{th}(V,T)$, whereby the rigorous MG approach assumes that the temperature T enters only as 'scaled temperature' $\tau = T/\theta(V)$ into

$$p_{th}(V,T) = \frac{\gamma_\theta(V)}{V} 3Nk\theta(V)u(\tau) \tag{2}$$

and into the thermal internal energy

$$U_{th}(V,T) = 3Nk\theta(V)u(\tau). \tag{3}$$

The 'characteristic temperature' $\theta(V)$ and the Grüneisen parameter

$$\gamma_\theta(V) = \mathrm{d}\ln\theta(V)/\mathrm{d}\ln V \tag{4}$$

depend both only on the volume V. With the heat capacity at constant volume

$$C_V(V,T) = 3Nku'(\tau) \tag{5}$$

with the derivative $u'(\tau) = \mathrm{d}u(\tau)/\mathrm{d}\tau$, and with the isothermal bulk modulus $K_T(V,T)$, one finds that the 'thermal' Grüneisen parameter

$$\gamma_{th}(V,T) = \alpha(V,T)VK_T(V,T)/C_V(V,T) \tag{6}$$

becomes independent of T and equal to γ_θ within this rigorous MG approximation.

If one at first identifies θ with the low-temperature value of the commonly used Debye temperature, one can then introduce explicit anharmonic corrections by the replacement of θ in the previous (quasiharmonic) relations by a temperature-dependent anharmonic form:

$$\theta_a(V,T) = \theta(V)(1 - A(V)u(\tau)). \tag{7}$$

To first order in A one obtains then for the thermal internal energy

$$U_{th}(V,T) = 3Nk\theta u(1 + A(2\tau u' - u'), \tag{8}$$

for the heat capacity

$$C_V(V,T) = 3Nku'(1 + 2A\tau(u' + uu''/u')), \tag{9}$$

for the thermal Grüneisen parameter

$$\gamma_{th}(V,T) = \gamma_\theta - 2\delta_A u, \tag{10}$$

and for the (different) thermobaric Grüneisen parameter

$$\gamma_{tb}(V,T) = Vp_{th}/U_{th} = \gamma_\theta - \delta_A u \tag{11}$$

where the volume dependences of $\theta(V)$, $A(V)$, and $\delta_A(V) = \mathrm{d}A/\mathrm{d}\ln V$, as well as the τ-dependence of u, u', and u'' are not indicated explicitly in the forms (8)–(11) just for convenience.

The quasiharmonic phonon contribution in $u(\tau)$ has been described [1] by a modified pseudo-Debye–Einstein model (MoDE2) with a 10% pseudo-Debye contribution [2] for the low-frequency acoustic phonons and two Einstein terms with adjusted frequency factors f_1 and f_2 with 45% contributions, respectively. Furthermore, a small conduction electron contribution is taken into account by $\Delta u_e = 2A_{el}\tau$ with the dimensionless parameter $A_{el} = (\pi^2/12)(\theta/T_F)$; if the small correction $A_{el} \approx 0.01$ is considered as constant, this implies a scaling of the effective Fermi temperature T_F like $\theta(V)$. Typical fits of this model to the ambient pressure data for Cu are represented in figure 1.

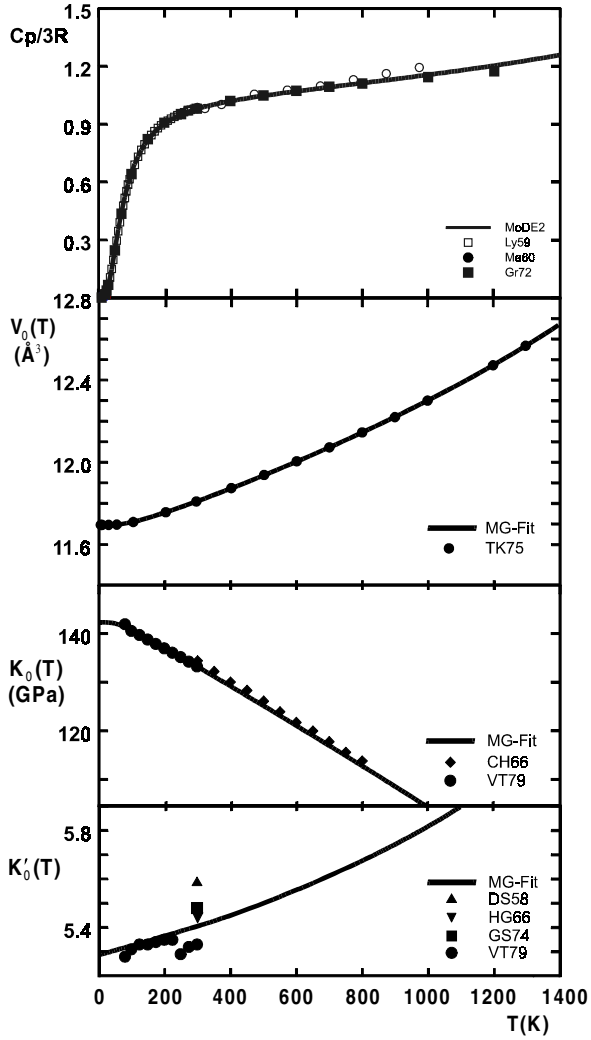

Figure 1. MoDE2 fits [1] of experimental data [6–18] for $C_{V0}(T)$, $V_0(T)$, $K_0(T)$, and $K_0'(T)$.

3. Results

With this type of fit the anharmonicity parameters A and δ_A were determined previously [1] for Cu, Ag, and Au at ambient pressure with A ranging from 0.005(2) to 0.001(2) and δ_A from 0.0030(5) to 0.032(3). The corresponding fit of $\gamma_{th0}(T)$ for Cu is illustrated here in figure 2.

While δ_A effects the fit of $V_0(T)$ only marginally, it makes a significant contribution to $\gamma_{th0}(T)$ as shown in figure 2. Dispersion in the mode Grüneisen parameters $\gamma_{Ei} \neq \gamma_\theta$ allows for a better fit of $\gamma_{th0}(T)$ at lower temperatures ($T < \theta$) but this variation of $\gamma_{th0}(T)$ is not significant for the calculation of the thermal pressure due to the fact that the thermal pressure at lower temperatures ($T < \theta$), is very small anyway. The contribution of the δ_A-term to the thermal pressure, on the other hand, increases like T^2 at higher temperatures and therefore the possible variation of δ_A itself with pressure is certainly of interest. However, so

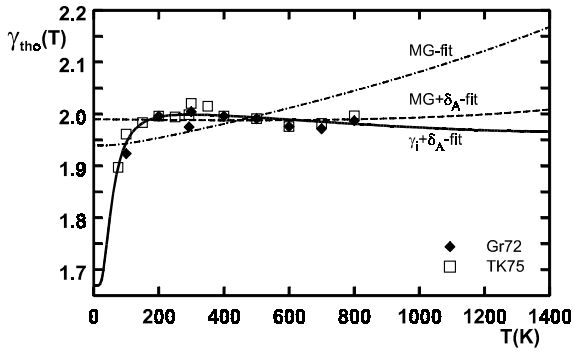

Figure 2. The MoDE2 fit [1] of experimental data for $\gamma_{th0}(T)$. The dominant uncertainty in the experimental data for $\alpha_0(T)$ is illustrated by different sets of data points [8, 10]. The effect of $\delta_A = 0$ and $\delta_A \neq 0$ is represented by the dashed–dotted and dashed curves marked 'MG-fit' and 'MG + δ_A-fit', respectively. Small deviations of this fit for $\gamma_{th0}(T)$ at lower temperatures ($T < \theta_0 = 342$ K) result from volume-independent frequency factors f_1 and f_2, corresponding to equal mode Grüneisen parameters $\gamma_D = \gamma_{E1} = \gamma_{E2} = \gamma_\theta$. Adjusted values of $\gamma_{Ei} \neq \gamma_\theta$ result in the solid curve marked '$\gamma_i + \delta_A$-fit'.

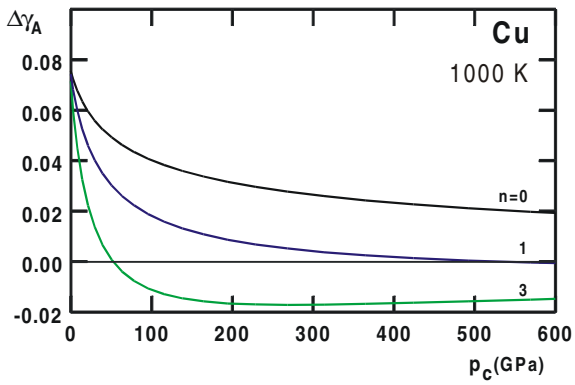

Figure 3. Decreases of the anharmonic contributions $\Delta\gamma_A = \delta_A u = \gamma_\theta - \gamma_{tb}$ under pressure for constant δ_A, for a moderate decrease and for a strong decrease of δ_A with $n = 0$, 1, and 3 in equation (12) respectively.

far nothing is known about this variation and therefore we assume at first $\delta_A =$ constant and, as other alternatives, a decrease of δ_A with a crossover to negative values at a finite compression $v_1 = V_1/V_0 = 0.5$, as the more likely case, and at $v_3 = V_3/V_0 = 0.8$ as an alternative with an earlier crossover to negative values. The corresponding crossover pressures would be 540 and 54 GPa, respectively, and the actual form would be

$$\delta_{An}(x) = \delta_A x^n (x^n - x_n^n)/(1 - x_n^n) \tag{12}$$

(with $n = 0, 1, 3$), where $\delta_A = 0.030$, $x_0 = 0$, $x_1 = \sqrt[3]{v_1} = 0.794$, and $x_3 = \sqrt[3]{v_3} = 0.938$, since x_0 drops out anyway. This crossover to negative values of $\delta_A(x)$ appears to be most likely because a positive value of δ_A implies a continuous increase in the anharmonic contribution under pressure, but, ultimately, a decrease should be expected.

Figure 3 illustrates for the Grüneisen parameters of Cu at 1000 K that the contribution of the δ_A-term in equation (11) decreases in any case strongly with increasing pressure partly due to the decrease of $u(\tau)$. The resulting effect on the thermal pressure of Cu at 1000 K is illustrated

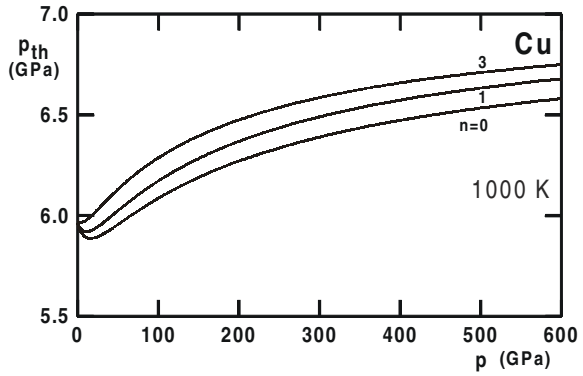

Figure 4. The effect of anharmonic corrections $\delta_A \neq 0$ on the thermal pressure $p_{th}(T, v)$ of Cu at 1000 K with respect to the cold pressure $p_c(v)$ at the same volume V.

in figure 4, which shows that the total uncertainty of the thermal pressure of Cu at 1000 K due to the uncertainty in the δ_A-term is about ± 0.1 GPa. However, this uncertainty increases with temperature quadratically. At room temperature, it can be completely neglected! More serious errors are usually made by the representation of EOS data at elevated temperatures with the use of a parametric EOS form, for instance of the type AP2 [1–5]:

$$p_{AP2} = 3K_0 \frac{1-x}{x^5} \mathrm{e}^{c_0(1-x)}(1 + c_2 x(1-x)). \tag{13}$$

Thereby, the volume V_0, the bulk modulus K_0, and its pressure derivative K_0' at zero pressure enter as temperature-dependent parameters, for instance in

$$x = (V/V_0)^{1/3}, \qquad c_0 = -\ln(3K_0/p_{FG0}), \qquad c_2 = \tfrac{3}{2}(K_0' - 3) - c_0$$

with the Fermi gas pressure $p_{FG0} = a_{FG}(Z/V_0)^{5/3}$, where $a_{FG} = 0.023\,37$ GPa nm^{-5} is a universal constant and Z/V_0 represents the total (average) electron density at ambient pressure. The corresponding relative error $\Delta p/p$ of the parametric pressure $p_{AP2}(V, T)$ with respect to the MG pressure $p_{MG}(V, T)$ is illustrated in figure 5, where p_{MG} is based on the form AP2 for the cold pressure p_c in equation (1) with the thermal pressure p_{th} in equation (1) using the average anharmonic corrections according to δ_{A1} of equation (12). Since the values for $K_0(T)$ are usually well known, the parametric form uses these same values for $K_0(T)$, which are reproduced also by the MG form as illustrated before in figure 1. Due to the larger uncertainty in the value for K_0', the value K_{0eff}' for the parametric form must be slightly readjusted to minimize the deviation in the given pressure range. When the parametric form uses also a different readjusted 'effective' value for K_0, a positive deviation in $\Delta P/P$ would be produced at zero pressure, but the average deviation could be reduced. Two curves for this $\Delta P/P$, one for 300 K and one for 1000 K, are shown in figure 5 to illustrate that this difference depends strongly on the temperature of these isotherms. The dotted and dash–dotted curves in figure 5 represent the uncertainties from δ_A in the thermal pressure of Cu at 1000 K discussed in figure 4. First of all, the relative error of this contribution amounts at most to 0.4% with its maximum at low pressures! This uncertainty is almost an order of magnitude smaller than the error introduced by the use of the parametric EOS form.

Finally, figure 6 illustrates that the relative deviations of various literature data [19–27] for the 300 K isotherm of Cu are even larger than the differences discussed so far. Obviously, these differences result from the limited accuracy of theoretical models on the one hand, and from the problems in the thermal corrections of the shock wave data on the other hand. The

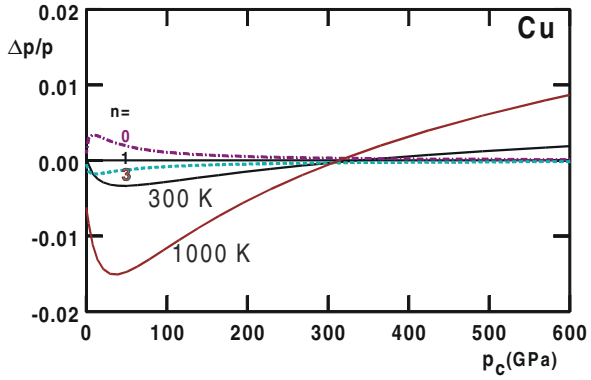

Figure 5. Relative deviations $\Delta p/p$ from the present 'best' MG isotherm represented by the use of the 'average' anharmonic correction ($n = 1$). The deviation obtained by the use of a constant $\delta_A = 0.030$ ($n = 0$) and the strongly decreasing form equation (12) with $n = 3$ are illustrated by the dash–dotted and the dashed curve, respectively, for the 1000 K isotherm of Cu. Deviations of the parametric EOS forms for 300 and 1000 K are represented by solid curves labelled with these temperatures.

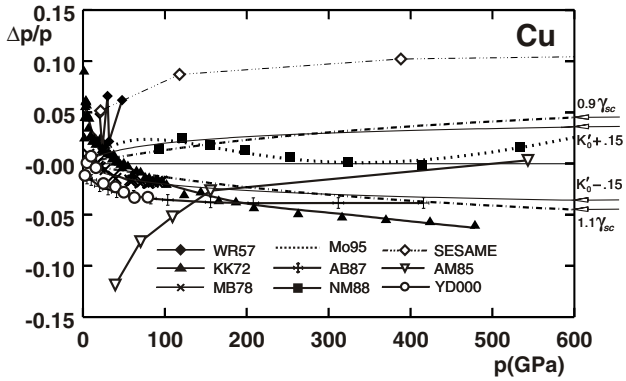

Figure 6. Relative deviations $\Delta p/p$ of literature data from the present 'best' MG isotherm of Cu at 300 K.

estimated uncertainties of the present MG EOSs are represented in figure 6 on the one hand by the dash–dotted curve, illustrating a 10% uncertainty in the values for γ_θ, and on the other hand by continuous thin lines, showing the effect of a ± 0.15 uncertainty in the value of K_0'.

4. Conclusions

The present MG approach with an AP2 form for the cold pressure p_c and anharmonic contributions added to the thermal pressure of the normal MG approach results in reliable isotherms for normal solids such as Cu, Ag, and Au. These isotherms are based on ambient pressure data for V_0, K_0, K_0', and C_{V0}, and on the use of a reasonable interpolation to the ultimate Fermi gas behaviour by the use of the AP2 form for the cold pressure p_c.

The total uncertainty in the present pressure scale based on these calibrants is estimated to be smaller than 5% even at very strong compression. The anharmonic effects discussed in this paper have not been studied in detail experimentally for any of these markers; however,

the present considerations do illustrate that comparative x-ray diffraction measurements on these markers at high temperature under high pressure are urgently needed to understand the high-pressure–high-temperature EOS behaviour of these 'simple' marker materials.

References

[1] Holzapfel W B, Hartwig M and Sievers W 2001 *J. Phys. Chem. Ref. Data* **30**
[2] Holzapfel W B 1994 *Phys. Chem.* **55** 711
[3] Holzapfel W B 1998 *High Pressure Res.* **16** 81
[4] Holzapfel W B 2001 *J. Low. Temp. Phys.* **122** 401
[5] Holzapfel W B 2001 *Z. Kristallogr.* **216**
[6] Lyusternik V E 1959 *Prib. Tekh. Eksp.* **4** 127
[7] Martin D L 1960 *Can. J. Phys.* **38** 17
[8] Gray D E (ed) 1972 *AIP Handbook* 3rd edn (New York: McGraw-Hill)
[9] Touloukian Y S and Buyco E H 1970 *Thermophysical Properties of Matter, Specific Heat, Metallic Elements and Alloys* vol 4 (New York: Plenum)
[10] Touloukian Y S, Kirby R K, Taylor R E and Desai P D 1975 *Thermophysical Properties of Matter, Thermal Expansion, Metallic Elements and Alloys* vol 12 (New York: Plenum)
[11] Chang Y A and Himmel L 1966 *J. Appl. Phys.* **37** 3567
[12] Van't Klooster P, Trappeniers N J and Biswas S N 1979 *Physica* B **97** 65
[13] Daniels W B and Smith C S 1958 *Phys. Rev.* **111** 713
[14] Hiki Y and Granato A 1966 *Phys. Rev.* **144** 411
[15] Guinan M W and Steinberg D J 1974 *Phys. Chem. Solids* **35** 1501
[16] Leksina I E and Novikova S I 1963 *Sov. Phys.–Solid State* **5** 798
[17] Simmon G and Wang H 1971 *Single Crystal Elastic Constants and Calculated Aggregate Properties: a Handbook* (Cambridge, MA: MIT Press)
[18] Barsch G R and Chang Z P 1967 *Phys. Status Solidi* **19** 139
[19] Walsh J M, Rice M H, McQueen R G and Yarger F L 1957 *Phys. Rev.* **108** 196
[20] Keeler R N and Kennedy G C 1972 *American Institute of Physics Handbook* ed D E Gray (New York: McGraw-Hill) p 4938
[21] Mao H K, Bell P M, Shaner J W and Steinberg D J 1978 *J. Appl. Phys.* **49** 3276
[22] Albers R C, McMahan A K and Muller J E 1985 *Phys. Rev.* B **31** 3435
[23] Al'tshuler L V, Brusnikin S E and Kuz'menkov E A 1987 *J. Appl. Mech. Tech. Phys.* **28** 129
[24] Nellis W J, Moriarty J A, Mitchell A C, Ross M, Dandrea R G, Ashcroft N W, Holmes N C and Gathers G R 1988 *Phys. Rev. Lett.* **60** 1414
[25] Moriarty J A 1995 *High Pressure Res.* **13** 343
[26] Wang Y, Chen D and Zhang X 2000 *Phys. Rev. Lett.* **84** 3220
[27] SESAME (provided by D Young with permission)