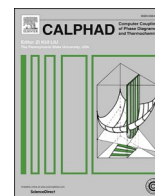




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Description of the thermodynamic properties of pure gold in the solid and liquid states from 0 K

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ABSTRACT

Thermodynamic data for pure gold were critically assessed using an extended Einstein model from 0 K for the crystalline FCC_A1 phase and a two state model for the liquid phase. During the assessment, careful critical evaluation of the experimental data on thermodynamic properties of solid (FCC_A1) and liquid phases was carried out. Due to the fact that there is a large scatter in the experimental data for crystalline gold in the temperature range between 200 K and the melting point, we carried out additional *ab initio* calculations of the thermodynamic properties. In order to fulfil the need for a precise evaluation of $S_{298.15}^0$ we needed to use an additional technique using multiple Einstein functions, which allows the experimental heat capacity and enthalpy data for the solid phase to be approximated accurately from 0 K up to the melting point. It was found during the data analysis that there is a large scatter in experimental data for the enthalpy of fusion and the liquid phase.

1. Introduction

This paper, dedicated to the description of the data for pure gold from zero K, is a part of collaborative project to develop a self-consistent set of data for the thermodynamic properties of the pure elements. The basis underlying the thermodynamic models originates from the developments carried out at the Ringberg workshop in 1995 which were later published in the proceedings [1]. The models were first tested and applied successfully to the most intriguing iron [2] and then modified during the evaluation of other elements as a result of collaboration within SGTE [3–10]. The aim of these models is to adopt a universal approach which incorporates multiple physical contributions to the thermodynamic properties [11] for the solid phases and uses a two state model [12–13] to describe the thermodynamic properties of the liquid phase.

As was discussed earlier in our assessment of the data for Pb and Sn [3–4], the decision to use the Einstein model rather than the Debye model was taken because of the complexities in the derivation of the thermodynamic functions such as the enthalpy, entropy and Gibbs

energy using the Debye model. Furthermore, in practice, calculations are generally useful for temperatures only above 100 K.

With the Einstein model approximating the vibrational energy, other parameters were introduced to take into account anharmonicity, electronic effects and the correction from constant volume to constant pressure. In order to answer the need for an accurate re-evaluation of the value of $S_{298.15}^0$, a careful evaluation of the C_p data from 0 K to 298.15 K needs to be carried out. In order to do this we used a technique and software developed at MSU [14–15] which allows a detailed analysis of the experimental heat capacity and enthalpy data for the solid phase and their accurate approximation from 0 K up to the melting. Due to the fact that the data for heat capacity of gold at low temperatures is more precise while there is a large uncertainty in the data at high temperatures we used the Voronin-Kutsenok [14–15] approach also to constrain the fit to the high temperature data. Moreover, the SGTE modelling with 2 Einstein temperatures was also carried out for the same purposes and comparison. Finally the model for the solid phase with just 1 Einstein temperature could then be obtained by refitting the obtained values for the high temperature interval.

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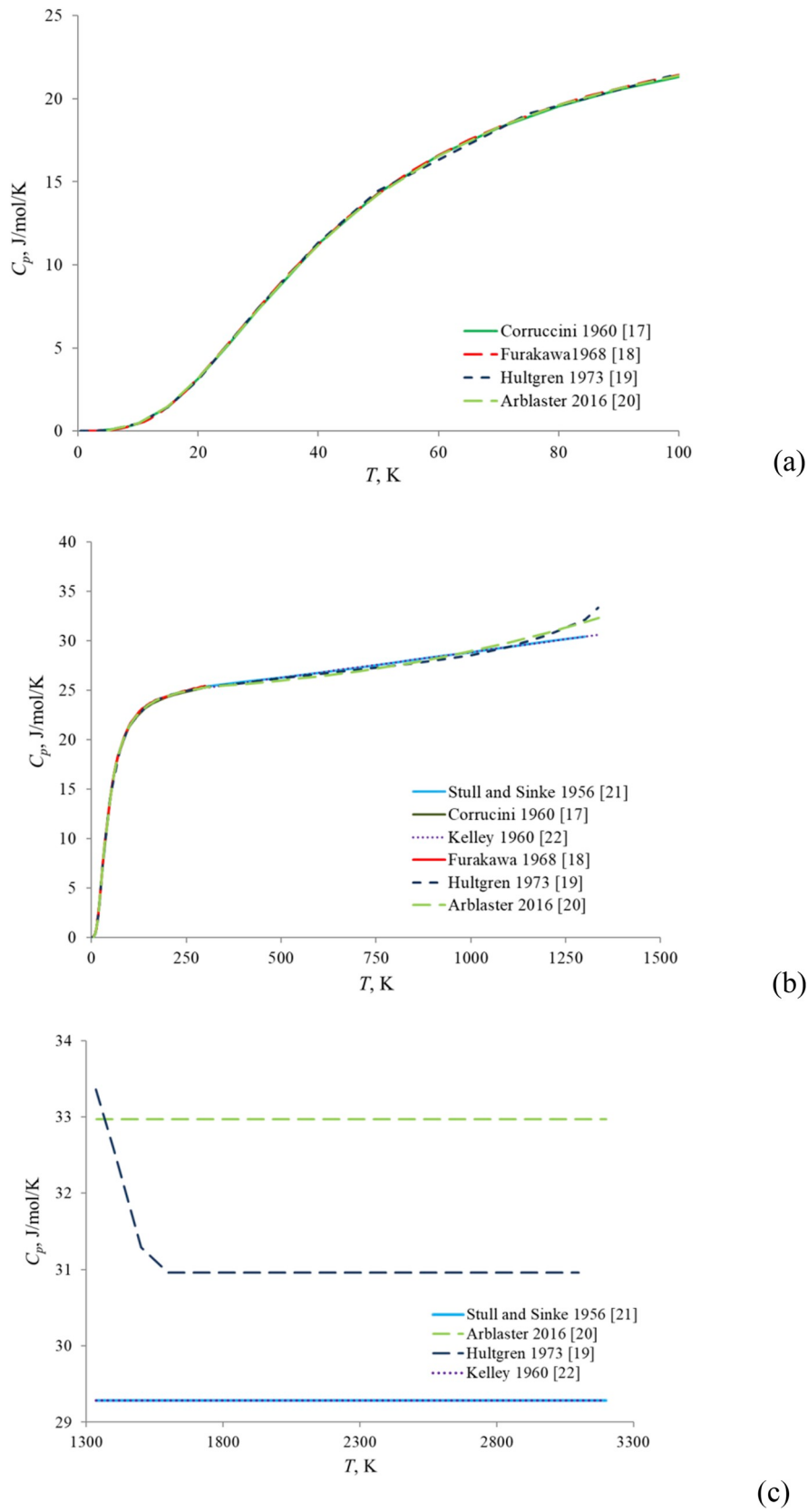


Fig. 1. Comparison of the heat capacity calculated from the assessed datasets: solid gold a) 0–100 K, b) 0–1400 K, c) liquid gold. Please note that the curves are drawn from the values tabulated by the assessors and are therefore smooth. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1

Experimental determinations of the heat capacity.

Temperature interval, K	Relative uncertainty, %	Method	Purity as reported in the original publications, %	Weight	Reference
14.96–212.5	n/a in the paper	Adiabatic calorimetry	n/a	0	Clusius and Hartek [23]
15.81–309.02	3%	Low temperature adiabatic Giauque and Egan GoldIII calorimeter	99.99%	0	Geballe and Giauque [24]
1.19–4.17	n/a	Vacuum adiabatic calorimetry	99.999%	1	Corak [25]
1.412–4.163	n/a	Vacuum adiabatic calorimetry	99.97%	0	Ramanathan and Srinivasan [26]
1.81–4.83	5%	Adiabatic low temperature calorimetry	99.99%	1	Zimmerman and Crane [27]
1.4–5	5%	Adiabatic low temperature calorimetry	n/a	0	Crane [28]
12.71–272.92	0.5%	Adiabatic low temperature calorimetry	99.99%	1	Franzosini and Clusius [29]
1.63–3.92	2%	n/a	99.9999%	1	Issacs [30]
1.33–4.9	n/a	Vacuum adiabatic calorimetry	99.999%	1	du Chatenier et al. [31]
2–4	0.1%	Adiabatic calorimetry	99.9999%	1	Will and Green [32]
0.43–1.5	0.4%	Adiabatic calorimetry	99.9999%	0.5	Martin [33]
0.4–1.4	0.4%	Adiabatic calorimetry	99.9999%	1	Martin [34]
1–30	0.24%	Adiabatic calorimetry	99.9999%	1	Boerstael et al. [35]
2.5–30	0.5	Quasi-adiabatic discrete-heating calorimeter	99.9999%	1	Martin [36]
80.91–1000	1.5%	Laser-Flash calorimeter	99.9%	0.5	Takahashi and Akiyama [37]
1.9–3.6	3%	Thermal relaxation calorimeter	99.999%	1	Lashley et al. [38]
20–320	0.3%	Adiabatic calorimetry	99.9999%	1	Martin [39]
400–1164	5%	Radiometric method	n/a	0	Butler and Inn [41]
340–510	1%	DSC	n/a	1	O'Neill [42]
678–1309	2.5%	Electric resistance method with potentiometric compensation scheme	99.99%	1	Kraftmakher and Strelkov [43]
300–1336	1%	Quasi-adiabatic calorimetry	99.96%	0	Vollmer and Kohlhaas [40] Also reported by Braun et al. [50]
451–1207	5%	Joule heating method	99.99%	0	Skelskey and van den Sype [44]
323–1194	1%	Continuous adiabatic calorimetry	99.9998%	1	Cordoba and Brooks [45]
451–1216		Adiabatic calorimetry	99.999%	1	Ferrier [46]
365–645		DSC		0	Jiang et al. [47]
373–1600	5%	DSC	99.9999%	0	Wilde et al. [48]
350–750	2%	DSC	99.99%	0	Elhert [49]

The extrapolation of data for the solid phase above the melting point was carried out in a similar way to previous work [2] towards the definition of data for the elements in the SGTE database [16] by merging the heat capacity function of the solid phase above the melting point to that of the liquid phase at high temperatures while ensuring that the heat capacity and its derivative are continuous at the melting point.

2. Literature data analysis

2.1. Reviews

The thermodynamic properties of pure gold have been reviewed several times [17–22]. The low temperature data were reviewed in papers [17–20] and their recommended values are in almost exact agreement with each other (Fig. 1a), as seen by rather small scatter in the assessed results. This will be discussed later in the present paper. Earlier reports gave an almost linear behavior of the heat capacity data for the solid phase between 200 K and the melting temperature [17,21–22] (Fig. 1b). More recent reviews show some curvature towards lower values in the temperature interval between 400 and 1100 K [19–20], while at higher temperatures the values are higher than those in the earlier works. However it should be noticed that the values from Arblaster [20] are lower than those of Hultgren et al. [19] at the melting point. It should be mentioned that the SGTE pure elements database [16] accepted the evaluated data of Hultgren et al. [19], which means that the data published after 1973 had not been considered.

An examination of the recommended data for the liquid phase does not show any agreement between the different authors (Fig. 1c). The earlier works give a constant C_p equal to 29.288 J/(mol·K) [21–22].

Hultgren et al. [19] reported a decrease in the C_p just after the melting point reaching constant values equal to 30.962 J/(mol·K) at 1600 K. The most recent work of Arblaster [20] gives a constant C_p for the liquid phase equal to 32.97 J/(mol·K).

2.2. Experimental heat capacity of crystalline Au

The low temperature C_p was measured in numerous works [23–38] (Table 1). The earliest measurements, performed by Clusius and Hartek [23], published in 1928, gave slightly higher values than other measurements in the temperature interval between 45 and 65 K. The measurements were repeated by the same group in 1963 [29]. The values from Ramanathan and Srinivasan [26] are slightly higher than those from other papers in the temperature interval between 1.5 and 4 K, which is possibly explained by the lower purity of the sample. Martin, in 1968 [34], reported that the small difference in the obtained values compared to those from their earlier work [33] is because “the slight radiofrequency heating of the thermometer had invalidated the extrapolation below 0.7 K of the calibration of the carbon thermometer used.” More recent investigations of Boerstael et al. [35] confirmed the values obtained by Martin [34]. Later Martin carried out measurements between 2 and 30 K [36], which are in agreement with his previous work [34] and with the results of Boerstael et al. [35]. The most recent measurements in the temperature range between 1.9 and 3.6 K were carried out by Lashley et al. [38]. The obtained results are in a good agreement with the values from previous works. In general all works after 1952 show very good agreement with each other in the temperature interval between 0 and 100 K (Fig. 2a). In the temperature range between 100 K and 300 K the scatter in the experimental values

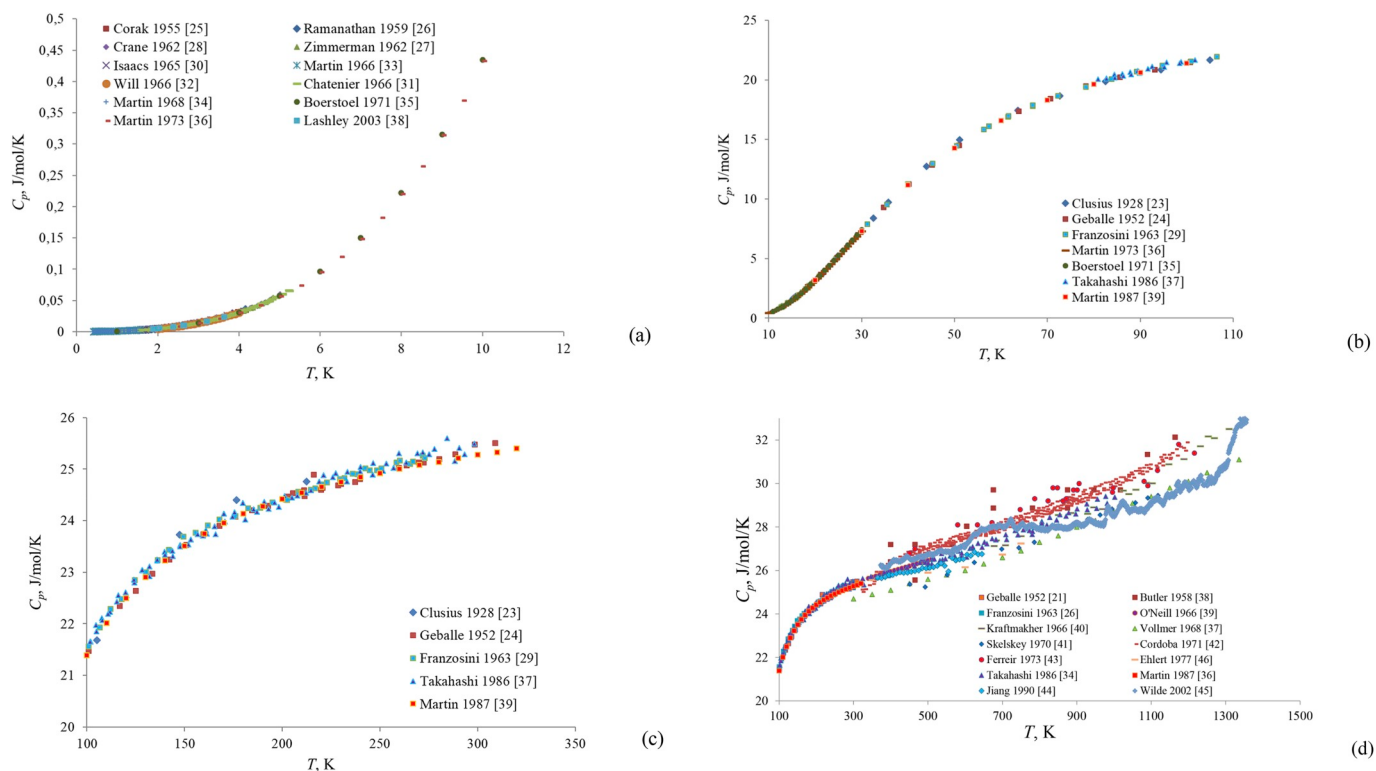


Fig. 2. Experimental heat capacity data for gold: a) 0–10 K; b) 10–100 K; c) 100–300 K and d) 300 K to the melting point. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Experimental values of the enthalpy increments for solid gold.

Temperature interval, K	Relative uncertainty, %	Method	Purity as reported in the original publications %	Units to be used for transfer into J	Measured value	Reference
83.15–373.15	1%	n/a	n/a	15 °C calorie	$H^0(T)$ - $H^0(290.15)$	Schimpff [59]
373.15–1337.15	5%	Drop calorimetry	n/a	15 °C calorie	$H^0(T)$ - $H^0(273.15)$	Wüst et al. [55]
654.7–1124.2	n/a	Drop calorimetry	n/a	20 °C	$H^0(T)$ - $H^0(293.15)$	Schlapfer and Debrunner [56]
373.15–1273.15	1%,	Drop calorimetry	n/a	15 °C calorie	$H^0(T)$ - $H^0(273.15)$	Umino [57]
404.15–1331.25	3%	Bunsen drop calorimetry	99.999	Thermo-chemical calorie	$H^0(T)$ - $H^0(298.15)$	Plaza [58]
692.04–1272.91	1.5%	Ice calorimeter	n/a	15 °C calorie	$H^0(T)$ - $H^0(273.15)$	Jaeger et al. [60]

increases not only between experimental data from different works but also within the same work. The work of Franzosini and Clusius [29] shows slightly higher values than Martin [39] and Geballe and Giauque [24] but within the scatter of the experimental values from the measurements of Takahashi and Akiyama [37].

Experimental investigations of the heat capacity of gold between 300 K and the melting point were measured in several works [37, 40–48]. Butler and Inn's [41] investigations of the possibility of using radiometric methods for the determination of the high temperature heat capacity of metals showed rather higher values in comparison to the other investigations. At the same time the results reported by Vollmer and Kohlhaas [40], Skelskey and van den Syne [44] and Ehlert [49] are lower than the other measurements. The data from Vollmer and Kohlhaas [40] and Skelskey and van den Syne [44] were given higher weight by Hultgren [19] and by Arblaster [20]. At the same time it is obvious from the Fig. 2 that at 300 K the results from Vollmer and Kohlhaas [40] are far too low when compared with the results from the lower temperature measurements. However it must be pointed out that Vollmer

and Kohlhaas [40] did not report raw experimental results, only interpolated smoothed values, which do not allow us to see the real experimental scatter and the overlap between different sets of values from different authors. It should also be mentioned that the same results were also reported by the same authors in another paper [50]. Skelskey and van den Syne [44] used a modulation method, which does not directly measure the heat capacity, but determines the ratio of the heat capacity to the resistivity coefficient. For this reason a lower weight should be given to these results.

Ehlert [49] and Wilde et al. [48] applied DSC (Differential Scanning Calorimetry) measurements for the determination of the heat capacity of gold; as it is known this method does not apply to high-precision one. However both sets of results give rather low values. It should be also noted that there is big experimental scatter of the values from Wilde et al. [48] as could be seen from Fig. 2. One should also note an unrealistic increase in the heat capacity values close to the melting point. At the same time a small increase in the heat capacity values of gold close to the melting point may be expected due to formation of vacancies.

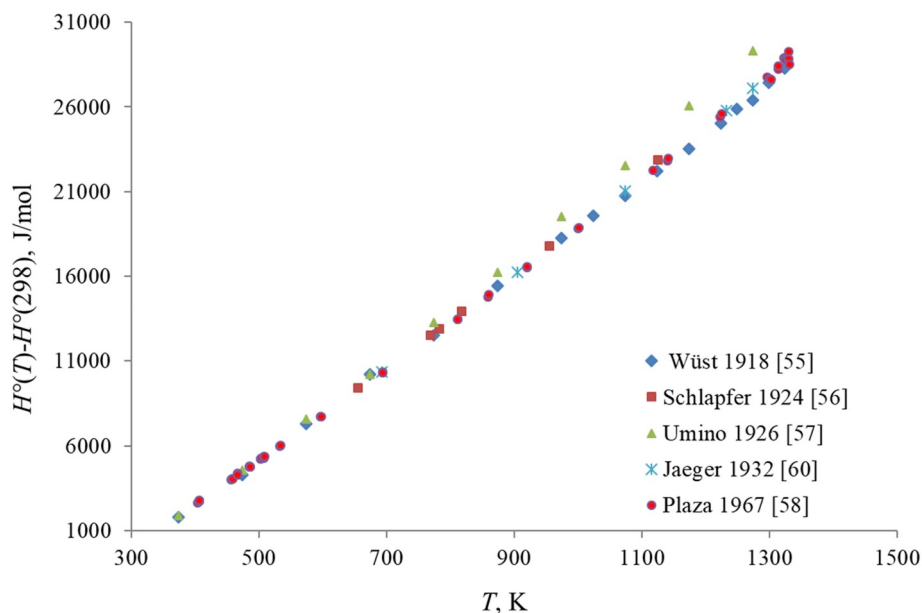


Fig. 3. Enthalpy increment measurements for solid gold $H^\circ(T) - H^\circ(298.15)$. The values were recalculated from the original temperatures to 298.15 K for comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

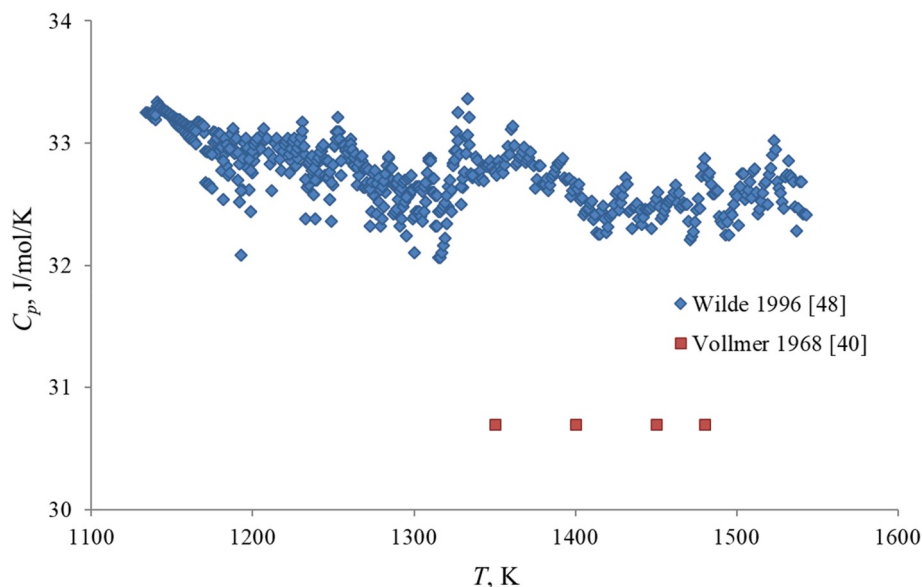


Fig. 4. Experimental heat capacity data for the liquid gold. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Kraftmakher and Strelkov [43] calculated the formation energy of vacancies taking into account the almost linear behavior of the heat capacity in their measurements between 700 and 900 K and a more rapid increase of the values at higher temperatures. They reported that the concentration of vacancies should be 0.4%, which is slightly higher than that reported in the other works [51–54]. One should also note that there is a large scatter in the experimental values for the energy of formation of vacancies (0.56–1.28 eV) and vacancy concentration values 0.07–0.3% measured by different methods [51–54]. At the same time the values for the energy of formation are rather large and seem to correspond to the process of fusion rather than just vacancy formation. Because of the high uncertainty in these measurements no attempt was made in the present work to describe this rapid pre-melting increase of the heat capacity.

The values from the works of [37,42,43,45–46] were given higher

weight in the present work.

2.3. Enthalpy increment measurements of crystalline Au

Enthalpy increments on crystalline gold were measured in the works of [55–60] (Table 2). The results from Umino [57] are thought to be too high at temperatures above 800 K, while the values from the works of [55–56,58] are in a good agreement with each other up to temperatures close to the melting point (Fig. 3). Investigations from Plaza [58] give rather high values for enthalpy increments at the melting point. During combined critical evaluation of the data from heat capacities and enthalpy increments it was found that the high values at the melting point reported by Plaza [58] were dragging the C_p vs T curve too high which is not in agreement with the direct C_p measurements. At the same time there is an increasing scatter in the results from Plaza at these

Table 3

Experimental values of the enthalpy increments for liquid gold.

Temperature interval, K	Relative uncertainty, %	Method	Purity as reported in the original publications %	Units to be used for transfer into J	Measured value	Reference
1337.15–1573.15	5%	Drop calorimetry	n/a	15 °C calorie	$H^\circ(T)-H^\circ(273.15)$	Wüst et al. [55]
1373.15–1523.15	1%,	Drop calorimetry	n/a	15 °C calorie	$H^\circ(T)-H^\circ(273.15)$	Umino [57]
1331.25–1485.98	3%	Bunsen drop calorimetry	99.999%	Thermochemical calorie	$H^\circ(T)-H^\circ(298.15)$	Plaza [58]
1352–1806	1.5%	Drop calorimetry	99.99%	Thermochemical calorie	$H^\circ(T)-H^\circ(310)$	Tester et al. [61]
1337–3820	6%	Pulse heating method	99.999%	Thermochemical calorie	$H^\circ(T)-H^\circ(293)$	Kaschnitz et al. [62]

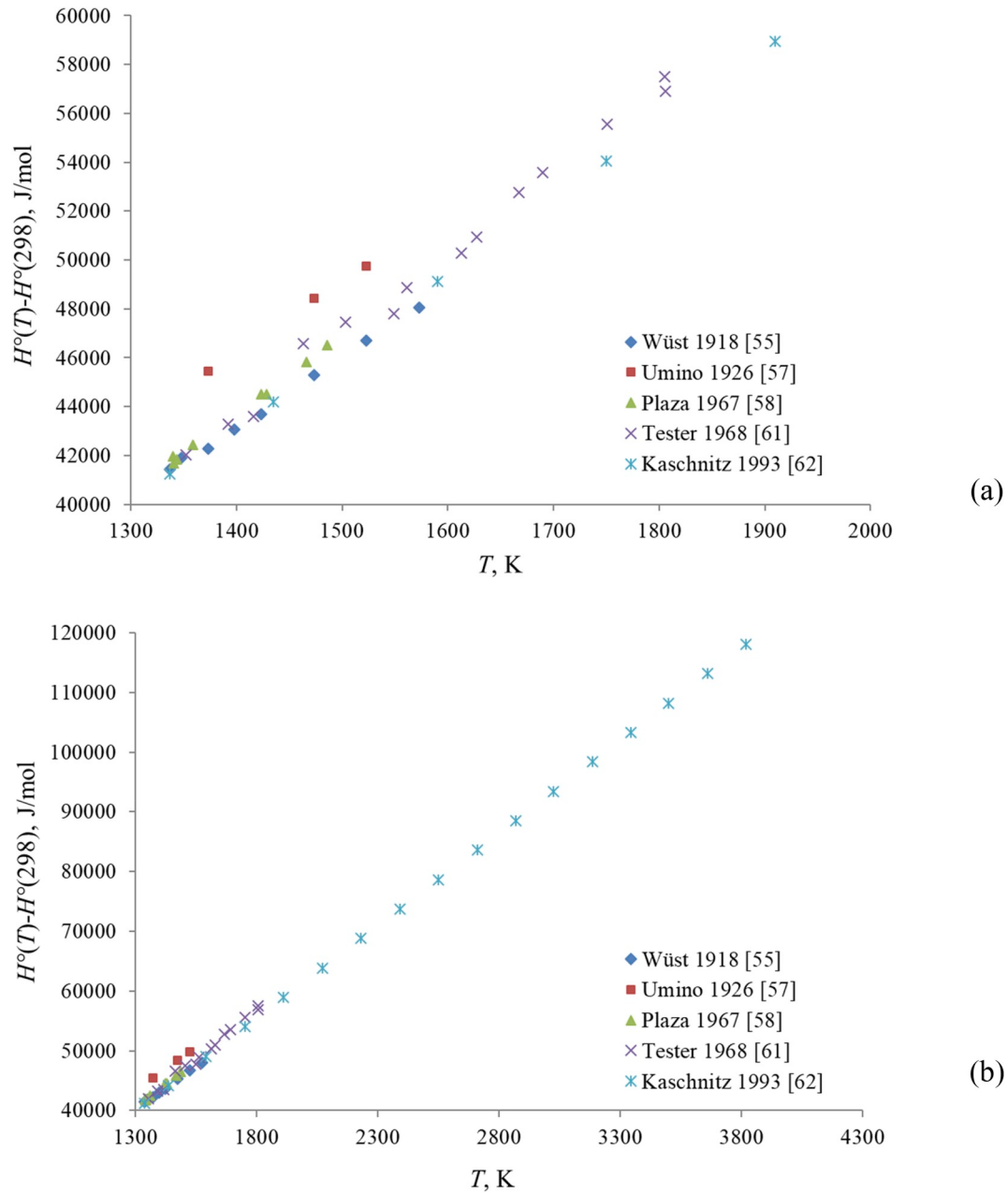
**Fig. 5.** Enthalpy increment measurements for liquid gold $H^\circ(T)-H^\circ(298.15)$. Values were recalculated from original temperatures to 298.15 for comparison: a) 1300–2000 K; b) 1300–3800 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4

Experimental enthalpies of fusion.

T, K	$\Delta_m H$ J/mol	Relative uncertainty, %	Method	Purity as reported in the original publications, %	Units to be used for transfer into J	Reference/date
n/a	13463	15%	DTA	n/a	15 °C calorie	Roberts-Austen [64]
n/a	12119	15%	–	n/a	15 °C calorie	Ludwik [65]
1337	13083	5%	Drop calorimetry	n/a	15 °C calorie	Wüst et al. [55]
n/a	12968	2%	Drop calorimetry	n/a	15 °C calorie	Umino [57]
1339.09	12326	3%	Bunsen drop calorimetry	99.999%	Thermochemical calorie	Plaza [58]
1336	12700	1%	Quasi-adiabatic calorimetry	99.96%	Thermochemical calorie	Vollmer and Kohlhaas [40]
n/a	12389	1.5%	Drop calorimetry	99.99%	Thermochemical calorie	Tester et al. [61]
1337	12212	5%	Impulse heating method	99.999%	Thermochemical calorie	Kaschnitz et al. [62]
1336	12606	5%	DSC	99.999%	n/a	Wilde et al. [48]
n/a	13788	3%	Impulse heating method	99.99%	n/a	Lebedev et al. [66]
1337.85	12823	n/a	DSC	n/a	Thermochemical calorie	Radenac et al. [68]

temperatures, which makes it unreasonable to give high weight to these data.

2.4. Heat capacity of liquid Au

There is a lack of data for the heat capacity of liquid gold. There have been only two direct measurements using quasi-adiabatic calorimetry by Vollmer and Kohlhaas [40], and using a DSC technique by Wilde et al. [48]. The data from Vollmer and Kohlhaas shows a constant heat capacity [40]. Wilde et al. [48] carried out measurements for liquid gold above the melting point and also supercooled below the melting point. The obtained results have an uncertainty of 5%. There are some doubts about the supercooled values for liquid gold as a clear peak at the melting point is seen, and it is possible that some partial crystallization took place (Fig. 4). Moreover the values from Wilde et al. [48] are higher than those from Vollmer and Kohlhaas [40] by ~9%.

2.5. Enthalpy increments measurements of liquid Au

Enthalpy increment measurements for liquid gold were reported in the works of [55,57,58,61,62] (Table 3). As with the solid phase, the results from Umino [57] give too high values (Fig. 5a) and are not considered further. Plaza [58] reported enthalpy increments which were rather higher than those from Wüst et al. [55]. The enthalpy increment values from Plaza [58] for the solid phase at the melting point are inconsistent with the experimental C_p . As a result lower weight was given to these. Tester et al. [61] carried out measurements using a drop calorimetry technique in the temperature range between 1352 and 1806 K. It can be seen that these measured values have a rather larger scatter than in previous works, but nevertheless it could be noted that they are in good agreement with the data from Plaza [58] (Fig. 5a). The most recent measurements were carried out by Kaschnitz et al. [62]. Special attention was paid in this work in order to prevent vaporization and boiling of the samples by application of pressures from 1 to 2000 bar and maintaining visual control of the stability of the melt. The obtained results are slightly lower than those from Plaza [58] and Tester et al. [61], but are slightly higher than the results from Wüst et al. [55] (Fig. 5b).

2.6. Fusion

The temperature of fusion of pure gold is fixed by the international temperature scale ITS-90 as 1337.33 K [63]. There have been very few measurements of the fusion enthalpy reported in the literature (Table 4). The earliest measurements were made by Roberts-Austen [64] and Ludwik [65]. Surprisingly the more recent investigations carried out during the last 100 years hardly managed to narrow the scatter of the

experimental values and obtain a more reliable value. The scatter between the more recent reported values varies between 12212 J/mol and 13804 J/mol. The lowest value was obtained by Kaschnitz [62] using a pulse method, which is traditionally given a lower weight in comparison to drop calorimetry or adiabatic measurements. The same method was used by Lebedev et al. [66], however the obtained result of 13788 J/mol is close to the upper limit. Stølen and Grønvold [67] analyzed the results published prior to 1999 and recommended the average value of 12720 J/mol. Arblaster [20] included into his assessment the values obtained by Wilde et al. [48], but the reported weighted average value appeared to be the same as that evaluated by Stølen and Grønvold [67].

3. Methodology of current work

3.1. Ab initio calculation method

The Helmholtz free energy $F(V,T)$ of pure gold (with V and T , respectively, the volume and temperature) is the thermodynamic potential that we aim at during modelling in order to derive C_p . The temperature dependence of $F(V,T)$ arises mainly from the lattice vibrations and these must be treated with an approach beyond the simple harmonic approximation [11] in order to obtain the volume dependence that is needed to derive C_p [11]. Here, we model the anharmonic contribution to $F(V,T)$ by the quasi-harmonic approximation (QHA) [69]. In the QHA, $F(V,T)$ is expressed as the sum of two components, i.e., $F(V,T) = E_{\text{tot}}(V) + F_{\text{vib}}(V,T)$, where $E_{\text{tot}}(V)$ is the total energy at zero temperature and the vibrational free energy $F_{\text{vib}}(V,T)$ retains the form it has within the harmonic approximation but with the phonon frequencies now assumed to be volume dependent. With the resulting volume-dependent $F(V,T)$ a whole range of thermal properties can be calculated, including C_p .

To calculate the phonon frequencies at a given volume, we applied the supercell small-displacement method [70–72]. Within this scheme, the interatomic force constants (i.e., the derivatives of the atomic forces with respect to the equilibrium atom positions at the given volume) are calculated by the finite difference method. A supercell of the equilibrium unit cell is constructed, a small displacement is applied to each atom in the cell, and the forces that arise in response on all atoms in the supercell are calculated. The derivatives of the forces are calculated by finite differences. To obtain the full matrix of interatomic constants, these displacements should be applied to all atoms in the supercell and along all the three Cartesian directions. However, the translational and space-group symmetries of the (equilibrium) FCC crystal of Au allows one to reduce the number of displacements needed to just one.

The derivation of the interatomic force constants from the *ab initio* forces and then the calculation of the phonon frequencies and the QHA thermal properties were performed using the PHONOPY package [73–74]. To calculate the phonons, we used $3 \times 3 \times 3$ supercells of the

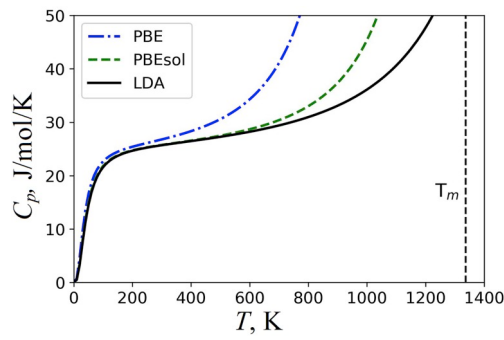


Fig. 6. Constant-pressure heat capacity C_p of Au calculated within the QHA using the GGA-PBE, GGA-PBEsol, and LDA. In these QHA calculations, we used a $3 \times 3 \times 3$ supercell with a $6 \times 6 \times 6$ k-point grid.

conventional FCC unit cell that contain 108 atoms and displacements of 0.01 Å. The *ab initio* total energies and atomic forces were calculated with the DFT PAW (Projector-Augment Waves) method as implemented in the MedeA distribution of the VASP package [75]. The values of C_p were obtained using the local-density-approximation (LDA) exchange and correlation functional. The plane-wave energy cut-off was set to 299 eV and the Methfessel-Paxton scheme with a width of 0.2 eV was used for the smearing of the occupations of the electron bands. We set the convergence threshold of the electronic self-consistent field loop to 10^{-8} eV to obtain numerically precise forces (as required in finite-difference phonon calculations). For the integration over the Brillouin zone of the supercells we used a $4 \times 4 \times 4$ regular mesh that corresponds to a density of ~ 6900 k-points per atom. The dynamical matrix and the spectrum of phonon frequencies were calculated at the q -points sampled by the chosen supercell and then Fourier interpolated over a q -point mesh of dimensions $48 \times 48 \times 48$. The interpolated phonon frequencies were then used to calculate $F_{\text{vib}}(V, T)$ [69]. The static total-energy contribution $E_{\text{tot}}(V)$ to the free energy was obtained by

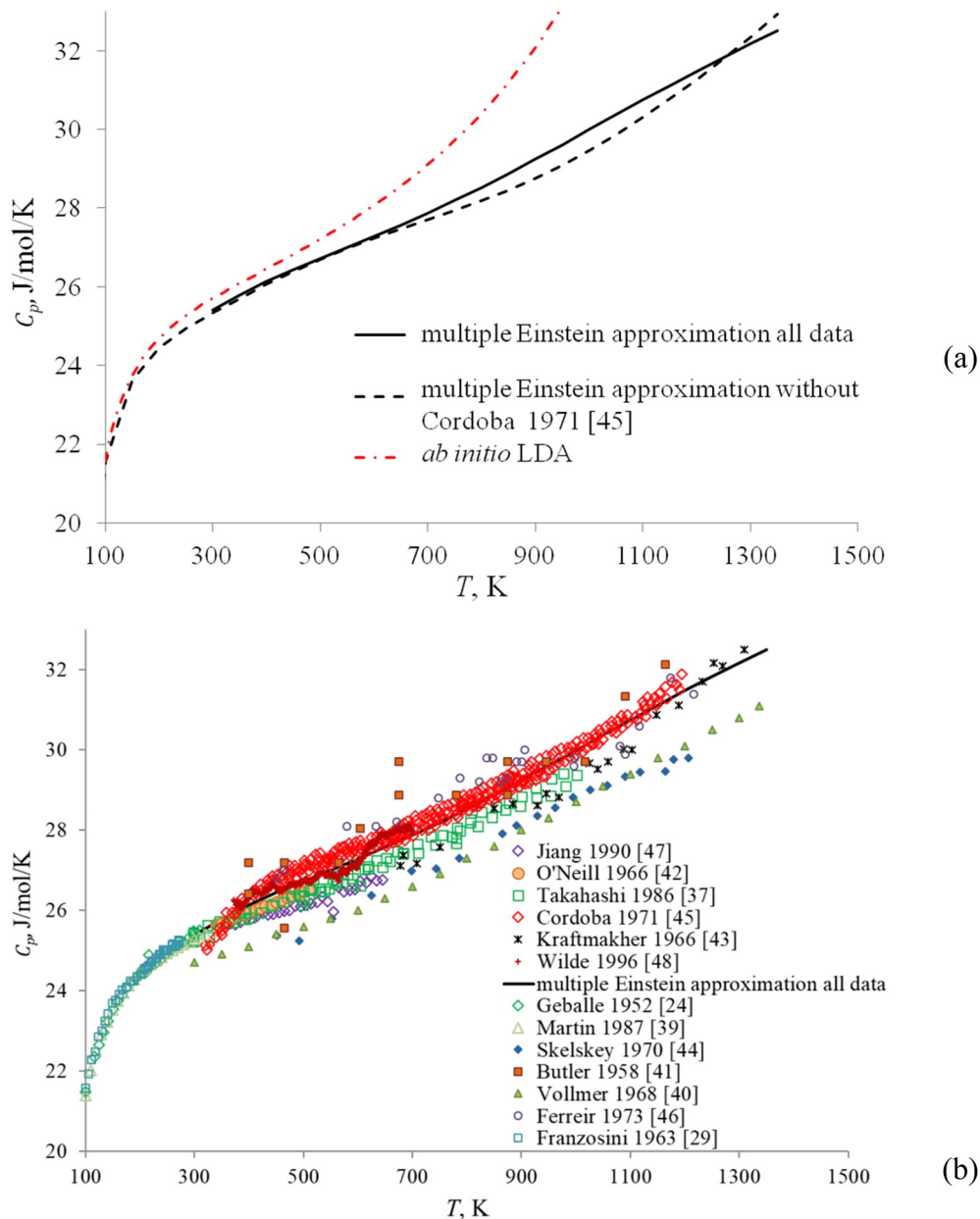


Fig. 7. *ab initio* calculations (a) and comparison of the values approximated with multiple Einstein functions with existing experimental results (b).

Table 5Parameters for the joint approximation $C_p(T)$ data for Au.

N ^o	α_i	Θ_i	α_i	Θ_i	α_i	Θ_i
	Heat capacity data				Heat capacity and heat content data	
	below 300 K		up to melting point			
1	0.437442 ± 0.02	85.0669 ± 1.9	0.491679 ± 0.05	4939.49 ± 314	0.491718 ± 0.05	4940.19 ± 303
2	0.579977 ± 0.02	182.925 ± 3.0	0.361171 ± 0.03	76.4958 ± 3.0	0.361198 ± 0.03	76.4978 ± 2.9
3	0.010543 ± 0.001	21.1325 ± 0.96	0.119903 ± 0.01	1519.9 ± 122	0.119939 ± 0.01	1520.35 ± 117
4	–	–	0.656488 ± 0.03	169.127 ± 4.7	0.656467 ± 0.03	169.133 ± 4.6

Table 6

Standard thermodynamic functions of solid Au at 298.15 K.

T, K	C_p	$S^o(T)$	$H^o(T)-H^o(0)$	$s(C_p)$	$s(S)$	$s(H)$
	J/(mol·K)		J/mol	J/(mol·K)		J/mol
298.15	25.122	47.350	6011	0.01	0.03	2.3

calculating the total energy on a regular grid of 15 unit-cell volumes centered around the equilibrium volume and then fitting the Vinet equation of state to the calculated values. Following Ref [76–77] we neglect the contribution of the electronic excitations to the free energy that were found to be negligible due to the low electronic density of states at the Fermi level.

3.2. Thermodynamic models

The modelling part was carried out in a similar way to that published earlier for Pb and Sn [3–4] following the recommendation of the Ringberg seminar [1] and using an evaluation procedure for S^o_{298} based on the approach of Voronin and Kutsenok for obtaining a precise description of $C_p(T)$ [14].

The heat capacity at constant pressure representing a combination of the Einstein model and a polynomial correction term is described as:

$$C_p = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} + aT + bT^2 + cT^3 + dT^4 \quad (1)$$

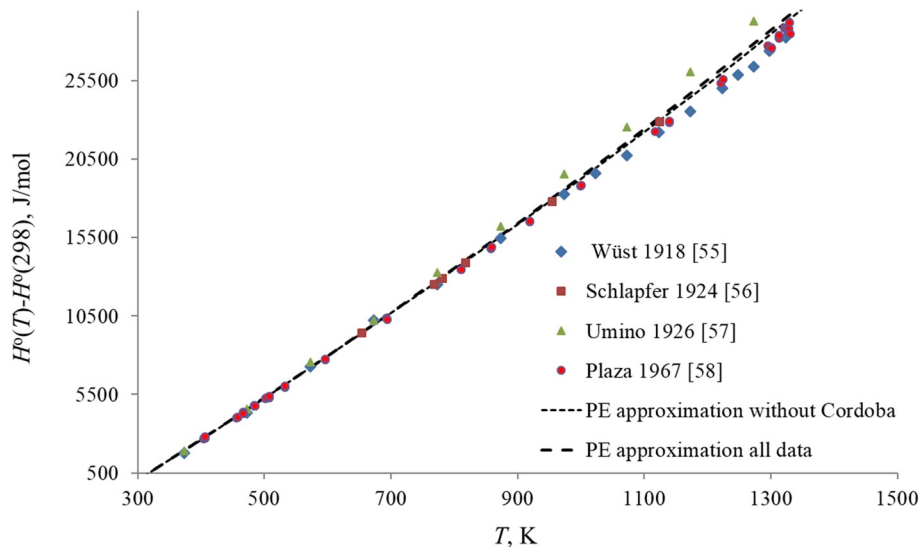
Here the polynomial takes into account the anharmonic and electronic effects and the conversion from C_V to C_p , etc and θ_E is the Einstein temperature of Au.

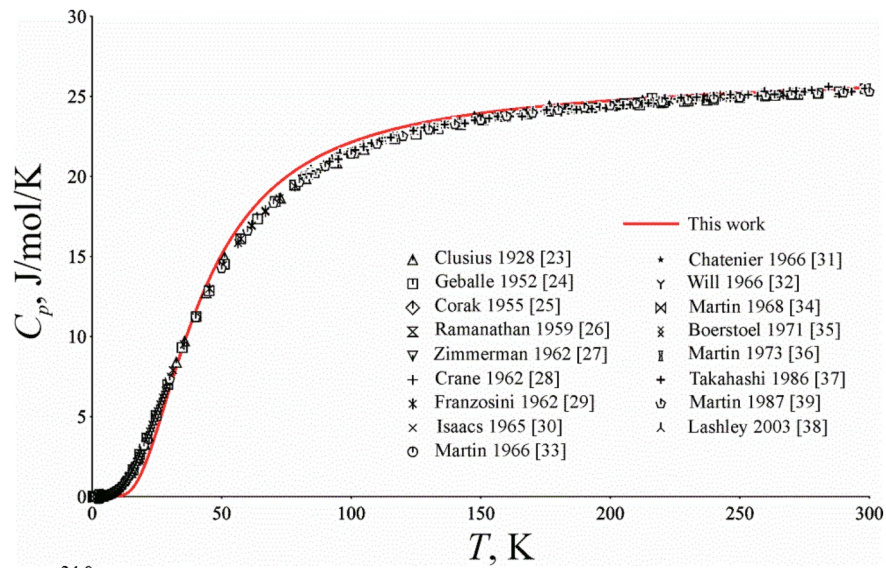
Integration of this equation allows us to obtain equations for other

Table 7

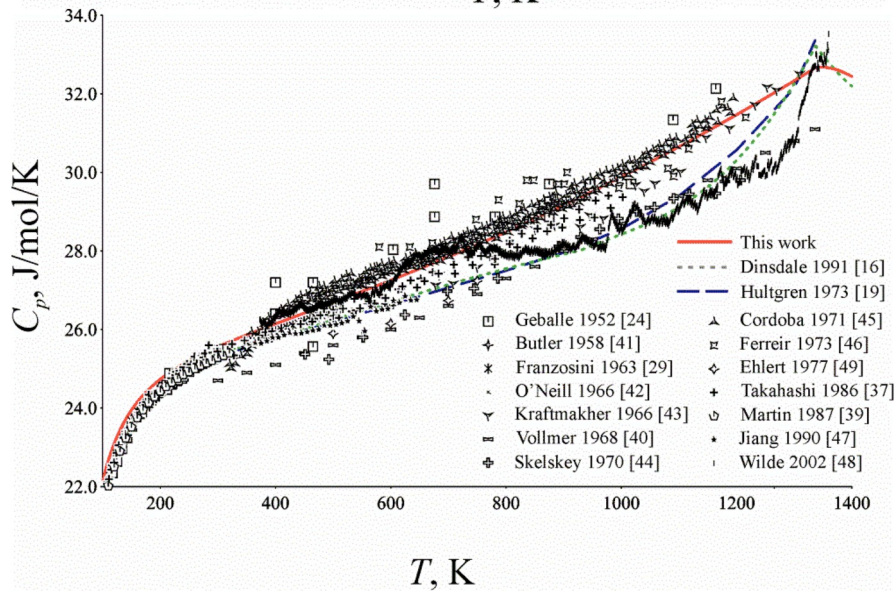
Assessed parameters for pure gold.

Phase	
FCC_A1 Gold 1 E	$\theta_E = 126.68742 \text{ K}$
Temperature	$0 < T < 1337.33 \text{ K}$
	$G = -7683.67045 + \frac{3}{2}R\theta_E - 3RT \ln \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)} -$ $\frac{+2.56203705E - 03}{2}T^2 - \frac{2.41366968E - 06}{6}T^3$ $T > 1337.33 \text{ K}$
	$G = -7683.67045 + 3898.778 + \frac{3}{2}R\theta_E -$ $3RT \ln \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)} + 9.807219T - 2.0566206T \ln T +$ $\frac{-6.83244E + 19}{30}T^{-5} + \frac{2.04767E + 38}{132}T^{-11}$
Liquid	$\theta_E = 126.68742 \text{ K}$
	$G = -1906.4 + \frac{3}{2}R\theta_E + 3RT \ln \frac{(e^{\theta_E/T} - 1)}{e^{\theta_E/T}} - 6.7E -$ $4 \cdot T^2 \Delta G_{diff} = G_m^{trans} - G_m^{vib} = 19700 - 14.917T$

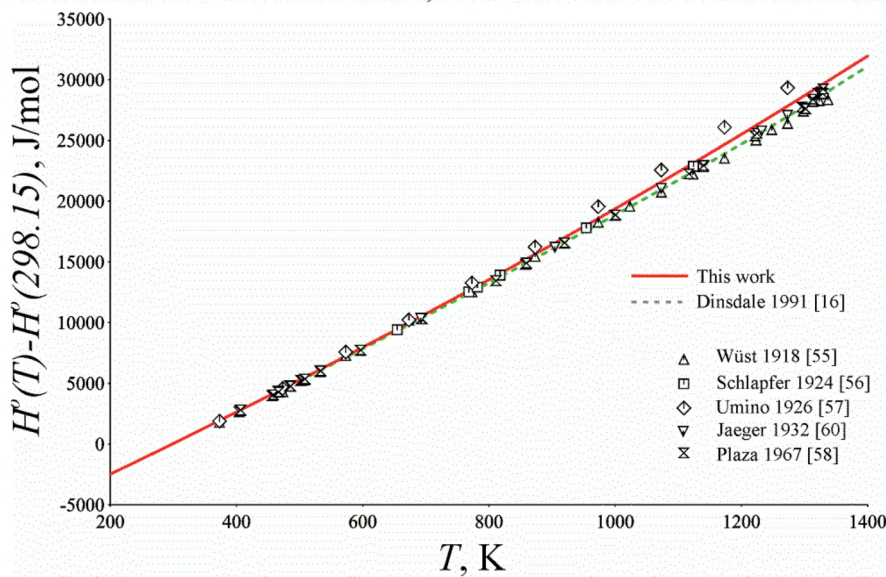
**Fig. 8.** Comparison of the values calculated with multiple Einstein functions $H^o(T)-H^o(298.15)$ with experimental results.



(a)



(b)



(c)

Fig. 9. Calculated thermodynamic functions using model with 1 E temperature a) heat capacity in the temperature interval 0–300 K, b) heat capacity in the temperature interval 300 K to the melting point and c) calculated and experimental data for $H^{\circ}(T) - H^{\circ}(298.15)$.

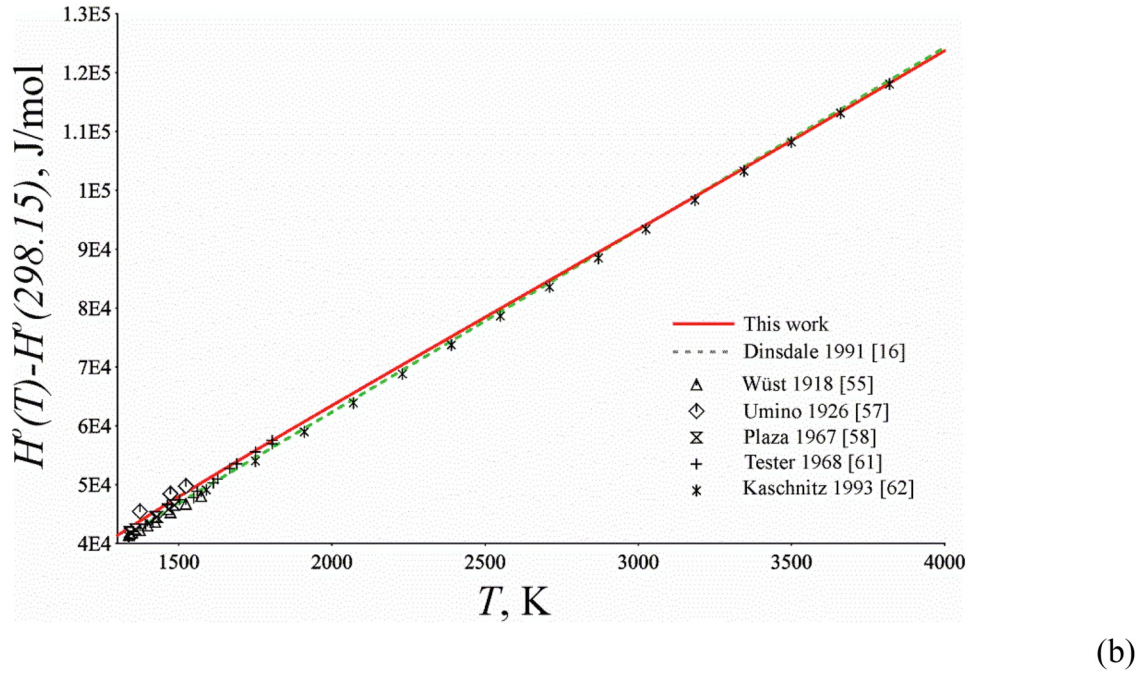
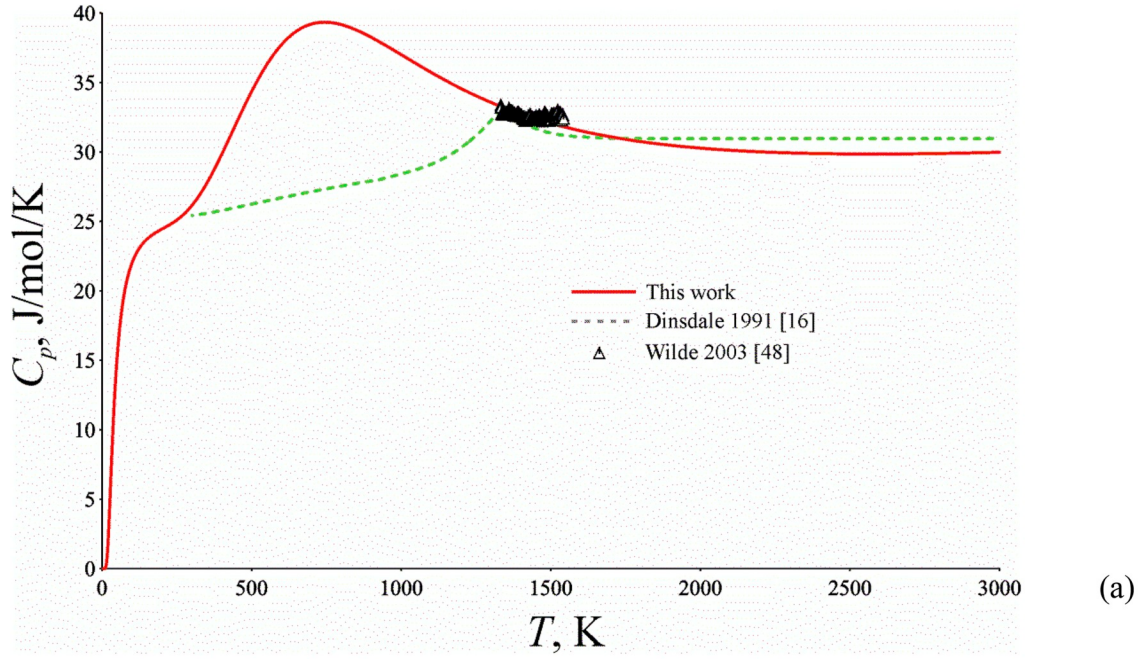


Fig. 10. Calculated heat capacity in comparison with the experimental data from the literature (a); calculated enthalpy increments for the liquid phase in comparison with literature data [55,57,58,61,62] (b).

thermodynamic functions (with the inclusion of a term $3/2R\theta_E$ to H and G [11]):

$$S^o(T) = 3R \left[\frac{\theta_E/T}{e^{\theta_E/T} - 1} + \ln \left(\frac{e^{\theta_E/T}}{e^{\theta_E/T} - 1} \right) \right] + aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \frac{d}{4}T^4 \quad (2)$$

$$H_T^o(T) - H_0^o = E_0 + \frac{3}{2}R\theta_E \left(\frac{e^{\theta_E/T} + 1}{e^{\theta_E/T} - 1} \right) + \frac{a}{2}T^2 + \frac{b}{3}T^3 + \frac{c}{4}T^4 + \frac{d}{5}T^5 \quad (3)$$

$$G_T^o(T) = E_0 + \frac{3}{2}R\theta_E - 3RT \ln \left(\frac{e^{\theta_E/T}}{e^{\theta_E/T} - 1} \right) - \frac{a}{2}T^2 - \frac{b}{6}T^3 - \frac{c}{12}T^4 - \frac{d}{20}T^5 \quad (4)$$

In order to ensure that the crystalline phase does not become stable at very high temperatures the following equation is used to describe the

thermodynamic properties of the crystalline phases above the melting point.

$$C_p = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} + a' + b'T^{-6} + c'T^{-12} \quad (5)$$

with the coefficients a' , b' and c' selected so that the heat capacity and its derivative are continuous at the melting point and merge with those of the liquid phase at some high temperature.

The two state model [12-13] was used to describe the thermodynamic properties of the liquid phase. According to this model it is assumed that the liquid phase consists of the two types of atoms mixing ideally: atoms with vibrational motion with no translational degrees of

freedom and atoms with translational motion. The atoms with vibrational motion can be thought of as representing a pure amorphous phase. This could also be expressed in terms of different energy states, an increase in space or degrees of translational and vibrational freedom available to the atoms.

At each temperature a transition of atoms takes place from one state to another in order to achieve equilibrium with χ of translational atoms and $1-\chi$ fraction of vibrational atoms. The equilibrium value of χ is determined by the equation:

$$\chi = \frac{e^{-\Delta G_{dif}/RT}}{1 + e^{-\Delta G_{dif}/RT}}, \quad (6)$$

where ΔG_{dif} is the difference in Gibbs energy between the translational and vibrational atoms. The Gibbs energy of the vibrational atoms can be approximated by the extended Einstein equation, which includes additional parameters which may be optimized in order to obtain agreement with experimental data.

$$G^{vib} = E_0 + \frac{3}{2}R\theta_E + 3RT \ln \frac{(e^{\theta_E/T} - 1)}{e^{\theta_E/T}} + A + aT^2 + bT^3 \quad (7)$$

The value for the Einstein temperature was taken initially to be the same as that of the crystalline phase. The parameters A , a and b were optimized. These parameters here refer only to the liquid phase. The Gibbs energy difference between the vibrational atoms and the translational atoms can be described as:

$$\Delta G_{dif} = G^{trans} - G^{vib} = B + CT + D T \ln T \dots \quad (8)$$

Thus the total Gibbs energy G^L will then be given by:

$$G^L = G^{vib} - RT \ln [1 + e^{(-\Delta G_{dif}/RT)}]. \quad (9)$$

The optimization of data for the liquid phase (A , a , b , B , C and D) was carried out using experimental data for the liquid phase.

3.3. Voronin and Kutsenok method

In order to evaluate S_{298}^0 the heat capacity data were fitted using multiple Einstein functions as described in the work of Voronin and Kutsenok [14]. The method allows standard thermodynamic functions to be approximated with an accuracy corresponding to experimental measurements from 0 K up to the melting point.

Using this approach the experimental $C_p(T)$ data can be approximated using following equation

$$C_p(T) = 3R \sum_i \alpha_i \frac{(\Theta_i/T)^2 e^{\Theta_i/T}}{(e^{\Theta_i/T} - 1)^2} \quad (10)$$

Then an integration of the equation (10) with addition of $3/2R\theta_E$ (which corresponds to zero-point lattice vibration) leads to the following expressions for thermodynamic functions [6]:

$$S^0(T) = 3R \sum_i \alpha_i \left(\frac{\Theta_i/T}{e^{\Theta_i/T} - 1} - \ln(1 - e^{-\Theta_i/T}) \right) \quad (11)$$

$$H_T^0(T) - H_0^0 = \frac{3}{2}R\theta_E + 3R \sum_i \alpha_i \Theta_i \left(e^{\Theta_i/T} - 1 \right)^{-1} \quad (12)$$

$$G_T^0(T) - H_0^0 = \frac{3}{2}R\theta_E + 3RT \sum_i \alpha_i \ln \left(1 - e^{-\frac{\Theta_i}{T}} \right) \quad (13)$$

where α_i , Θ_i ($i = 1, 2, \dots$) are parameters determined by fitting the experimental heat capacity data to equation (10), $3/2R\theta_E$ is the same term as in Eq.(3 and (4).

4. Results and discussion

4.1. Results of the *ab initio* calculations

The QHA C_p curves obtained in the present work with the PBE, PBEsol and LDA functionals are shown in Fig. 6. In the QHA calculations with all three functionals we used a 3x3x3 supercell and a 6x6x6 k-point grid. Fig. 7a compares the *ab initio* LDA-QHA values of C_p to the values modeled by the multiple Einstein equation. The LDA-QHA values track closely the multiple Einstein curve up to about 300 K showing only a slight overestimation in this range. At higher temperatures, the difference between the two curves becomes wider and the LDA-QHA values lie above all the experimental data points with the exception of the measurements from Butler and Inn [41] (Fig. 7b). The LDA-QHA curve traverses the region of experimental C_p values reported by Butler and Inn [41] showing general good agreement between 300 K and 700 K. If the comparison between *ab initio* and experimental data were based on the data set from Butler and Inn [41], one might conclude that the LDA-QHA scheme is an adequate approach to model the C_p of Au. However, the fact that the LDA-QHA curve overestimates all the other experimental measurements roughly above 300 K and that it diverges above 700 K, indicates that in the case of Au the LDA-QHA approach is not adequate to model C_p over the full temperature range.

Previous studies [77–79] have shown that the QHA predictions of C_p are sensitive to the choice of the exchange and correlation functional. It was shown that when the GGA-PBE (generalized-gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) formulation) functional is used within the QHA, one predicts higher values of C_p and that the divergence starts at lower temperatures than when the LDA is used. We tested the more recent PBEsol exchange and correlation functional to determine whether it gives better predictions of C_p at the QHA level than the GGA-PBE functional. To the best of our knowledge the PBEsol functional has not yet been used in QHA calculations of the C_p of Au. With the PBEsol functions we obtain C_p values closer to those obtained with the LDA and that start to diverge at much higher temperatures than the GGA-PBE-QHA values. However, also the GGA-PBEsol-QHA approach overestimates the experimental values across most of the temperature range and predicts a divergence above 700 K. Recent *ab initio* studies [77–78] modeled the anharmonic effects on the lattice vibrations beyond the QHA to determine how important is their contribution to the C_p for a range of transition metals including Au. These studies applied both the LDA and GGA-PBE functionals and found that, regardless of the exchange and correlation functional, for gold and the other transition metals that were considered, the anharmonic contribution to C_p beyond the QHA is roughly of the same order of magnitude as the QHA contribution but with the opposite sign. Therefore, the two contributions largely compensate each other with the result of correcting for the overestimation and the divergence of C_p obtained at the QHA level.

4.2. Evaluation of $S_{298.15}^0$

Equal weights were given to all existing low temperature experimental data (between 0 and 298.15 K) since all sets of results are in a good agreement with each other.

The first step of $S_{298.15}^0$ estimation was a joint approximation of heat capacity data below 300 K. To increase the accuracy of the fitting procedure the relative deviations $(C_p^{cal} - C_p^{ex})/C_p^{ex}$ were applied in the target function between ~0 and 50 K as opposed to the absolute deviations $(C_p^{cal} - C_p^{ex})$ between $T > 50$ K. For an adequate description of the experimental data, three pairs of multiple Einstein functions were sufficient (see Table 5). As a result, the standard thermodynamic functions of solid Au at 298.15 K were calculated (see Table 6).

Only a subset of the experimental heat capacity data above room temperature were used for the combined analysis of the low and high temperature data due to the large uncertainty in the high temperature

measurements (Fig. 7b). Extra weight was given to the adiabatic low temperature data description due to the fact that these values are believed to be more reliable. The consistency of the low-temperature data set with the high-temperature measurements of C_p was carried out by successively adding data from individual works and evaluating the quality of the description of the entire data set. As a result of this analysis, some data were selected to which $w = 1$ are attributed [24,29,37,39,42–43,45,47,48]. The weighting factors of the remaining data were less than 0.1. As a result of the joint processing of the low temperature and the reliable high temperature data (a total of 1199 points, of which 427 refer to temperatures below room temperature), the parameter values of Eq. (10) were obtained (listed in Table 5). It should be noted that an assessment of the heat capacities without using the data from the work of Cordoba [45] would give lower values of the heat capacity and a sharper rise at very high temperatures (Fig. 7a).

The obtained sets of parameters (Table 5) were used to calculate enthalpy increment values in order to compare them with existing experimental results. It should be noted that above 1000 K the experimental data for $H^0(T) - H^0(298.15)$ give slightly low results (Fig. 8). So the next step of the calculation was to derive a single approximation for both the most reliable heat capacity data from 0 K to the melting point and the heat content data (1285 data points). All data sets were given to equal weights, but the various types of deviations were minimized: the absolute deviations between the calculated and measured values in the case of C_p and relative deviations in the case of enthalpy increments. The estimated values of parameters to Eq. (10) are listed in the two rightmost columns of Table 5; within the error, they coincide with the values given in the first two columns of Table 5. The calculated standard thermodynamic functions at 298.15 K are listed in Table 6. Fig. 8 illustrates the agreement of the values calculated with multiple Einstein functions $H^0(T) - H^0(298.15)$ with the experimental results.

4.3. SGTE modelling

4.3.1. Crystalline phase

It is recommended that 1 Einstein temperature be used for the FCC A1 structure phases to simplify the modelling during extrapolation of data into multicomponent systems. The obtained set of parameters and the calculated heat capacity and $H^0(T) - H^0(298.15)$ are presented in Table 7 and Fig. 9(a–c). It appeared to be impossible to make a good fit of the C_p data below 200 K with just 1 Einstein temperatures and, at the same time, to fit the assessed value of $S^0_{298.15}$. As a result it was decided to make a precise fit to $S^0_{298.15}$, allowing the data for the C_p to be bit higher than experimental values in the temperature interval between 50 and 200 K. The calculated values for the standard entropy is $S^0_{298.15} = 47.35$ J/(mol·K).

4.3.2. Liquid phase

The temperature of fusion was fixed as 1337.33 K in accordance with the ITS-90 [63]. There is a large uncertainty in the enthalpy of fusion data and it appears to be rather difficult to justify giving more weight to any of the existing values. For this reason the more or less average value accepted by Stolen and Grønvdal [67], $\Delta_m H = 12720 \pm 304$ J/mol, was used. Additionally the existing experimental data on the heat capacity from Wilde et al. [48], and the enthalpy increment data [55,57,58,61,62] were used for the optimization of the parameters using the two state model.

It appeared to be almost impossible to achieve an exact fit to the heat capacity data of Wilde et al. [48] (Fig. 10a). However, good agreement (within the experimental uncertainty) was obtained for the enthalpy increment data of the liquid phase (Fig. 10b). Still it should be mentioned that the vapor pressure above liquid gold is significant, which may increase the uncertainty of the measurements in addition to the expected increase in uncertainty with an increase in temperature. The calculated value for the enthalpy of fusion is 12720.443 J/mol. The calculated value for the temperature of fusion is 1337.3K, which is in

exact agreement with the ITS-90 [63] values.

5. Summary

During the critical evaluation of the thermodynamic data it was concluded that despite the existence of a large amount of experimental data for the heat capacity of the solid phase of Au, there is still an extremely large uncertainty in the experimental values at high temperatures, which has not been discussed in previous critical evaluations and reviews. At the same time the low temperature experimental data (below 200 K) are sufficiently reliable.

A description of the thermodynamic data for pure gold was obtained using an extended Einstein model for the crystalline phases and a two state model for the liquid phase.

Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical issues concerned with the web page. They will be later available to download from www.tmsrc.misis.ru. The new webpage is under preparation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.calphad.2019.101724>.

References

- [1] M. Chase, I. Ansara, A. Dinsdale, G. Eriksson, G. Grimvall, H. Hoglund, H. Yokokawa, Group 1: heat capacity models for crystalline phases from 0 K to 6000 K, *Calphad* 19 (4) (1995) 437–447.
- [2] Q. Chen, B. Sundman, Modeling of thermodynamic properties for BCC, FCC, liquid and amorphous iron, *J. Phase Equilibria* 22 (6) (2001) 631–644.
- [3] A.V. Khvan, A.T. Dinsdale, I.A. Uspenskaya, M. Zhilin, T. Babkina, A.M. Phiri, A thermodynamic description of data for pure Pb from 0 K using the two state model for the liquid phase, *Calphad* 60 (2018) 144–155.
- [4] A.V. Khvan, T. Babkina, A.T. Dinsdale, I.A. Uspenskaya, I.V. Fatushna, A. I. Druzhinina, A.B. Syzdykova, M.P. Belov, I.A. Abrikosov, Thermodynamic properties of tin: Part I Experimental investigation, ab-initio modelling of α - β -phase and a thermodynamic description for pure metal in solid and liquid state form OK, *Calphad* 65 (2019) 50–72.
- [5] Z. Li, S. Bigdeli, H. Mao, Q. Chen, M. Selleby, Thermodynamic evaluation of pure Co for the third generation of thermodynamic databases, *Phys. Status Solidi B* 254 (2) (2017) 1600231.
- [6] S. Bigdeli, H. Ehteshami, Q. Chen, M. Selleby, New description of metastable hcp phase for unaries Fe and Mn: coupling between first-principles calculations and Calphad modelling, *Phys. Status Solidi B* 253 (9) (2016) 1830–1836.
- [7] S. Bigdeli, H. Mao, M. Selleby, On the third-generation Calphad databases: an updated description of Mn, *Phys. Status Solidi B* 252 (10) (2015) 1–10.
- [8] S. Bigdeli, Q. Chen, M. Selleby, A new description of pure C in developing the third generation of calphad databases, *J. Phase Equilibria Diffusion* 39 (6) (2018) 832–840.
- [9] W. Xiong, P. Hedström, M. Selleby, J. Odqvist, M. Thuvander, Q. Chen, An improved thermodynamic modelling of the Fe-Cr system down to zero Kelvin coupled with key experiments, *Calphad* 35 (3) (2011) 355–366.
- [10] W. Xiong, Q. Chen, P.A. Korzhavyi, M. Selleby, An improved magnetic model for thermodynamic modelling, *Calphad* 39 (2012) 11–20.
- [11] G. Grimvall, *Thermophysical Properties of Materials*, North Holland, Amsterdam, 1986.
- [12] J. Ågren, Thermodynamics of Supercooled liquids and their glass transition, *J. Phys. Chem. Liq.* 18 (1988) 123–139.
- [13] J. Ågren, B. Cheynet, M.T. Clavaguera-Mora, K. Hack, J. Hertz, F. Sommer, U. Kattner, Group 2: extrapolation of the heat capacity in liquid and amorphous phases, *Calphad* 19 (4) (1995) 449–480.

- [14] G.F. Voronin, I.B. Kutsenok, Universal method for approximating the standard thermodynamic functions of solids, *J. Chem. Eng. Data* 58 (2013) 2083–2094.
- [15] A.L. Voskov, I.B. Kutsenok, G.F. Voronin, CpFit program for approximation of heat capacities and enthalpies by Einstein-Planck functions sum, *Calphad* 61 (2018) 50–61.
- [16] A.T. Dinsdale, SGTE data for pure substances, *Calphad* 15 (1991) 317–425.
- [17] R.J. Corruccini, J.J. Gniwew, Specific heats and enthalpies of technical solids at low temperatures, *Natl. Bur. Stand. Monogr.* 21 (1960).
- [18] G.T. Furukawa, W.G. Saba, M.L. Reilly, Critical analysis of the heat-capacity data of the literature and evaluation of thermodynamic properties of copper, silver, and gold from 0 to 300, °K NSRDS—NBS 18 (1968).
- [19] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, D.D. Wagman, Selected Values of the Thermodynamic Properties of the Elements, American Society For Metals, Metals Park, Ohio, 1973.
- [20] J.W. Arblaster, Thermodynamic properties of gold, *J. Phase Equilibria Diffusion* 37 (2016) 229–245.
- [21] D.R. Stull, G.C. Sinke, Thermodynamic Properties of the Elements: Tabulated Values of the Heat Capacity, Heat Content, Entropy, and Free Energy Function of the Solid, Liquid, and Gas States of the First 92 Elements, 18, Am. Chem. Soc., Washington DC, 1956. Adv. Chem. Series 18.
- [22] K.K. Kelley, Contributions to the data on theoretical metallurgy. XIII high-temperature heat-content, heat capacity, and entropy data for the elements and inorganic compounds, US Dep Int. Bureau Mines, Bulletin 584 (1960).
- [23] K. Clusius, P. Hartek, Über die spezifischen Wärmen einiger fester Körper bei tiefen Temperaturen, *Z. Phys. Chem.* 134 (1928) 243–263.
- [24] T.H. Geballe, W.F. Giaque, The heat capacity and entropy of gold from 15 to 300K, *J. Am. Chem. Soc.* 74 (1952) 2368–2369.
- [25] W.S. Corak, Atomic heats of copper, silver and gold from 1K to 5K, *Phys. Rev.* 98 (6) (1955) 1699–1707.
- [26] K.G. Ramanathan, T.M. Srinivasan, The atomic heats of gold, platinum and antimony at liquid helium temperatures, *Ind. Acad. Sci. A* 49 (1959) 55–60.
- [27] J.E. Zimmerman, L.T. Crane, Anomalous lattice specific heat of gold and zinc at liquid helium temperatures, *Phys. Rev.* 126 (2) (1962) 513–516.
- [28] L.T. Crane, Specific heats of dilute Au-Co alloys between 1.2 and 5K, *Phys. Rev.* 125 (6) (1962) 1902–1904.
- [29] P. Franzosini, K. Clusius, Ergebnisse der Tieftemperaturforschung XLI Atomwärme und Entropie des Goldes zwischen 12K und 273K, *Z. Naturforschung* 18a (12) (1963) 1244–1246.
- [30] L.L. Isaacs, Low temperature specific heat of gold silver and copper, *J. Chem. Phys.* 43 (1965) 307–308.
- [31] F.J. Du Chatenier, J. De Nobel, B.M. Boerstol, Specific heats of Gold and dilute alloys of manganese, chromium, iron and vanadium in gold at low temperatures, *Physica* 32 (1966) 561–570.
- [32] T.A. Will, B.A. Green, Specific heats of Au and AuSn at low temperatures, *Phys. Rev.* 150 (2) (1966) 519–522.
- [33] D.L. Martin, Specific heats of copper, silver and gold below 30K, *Phys. Rev.* 141 (2) (1966) 576–582.
- [34] D.L. Martin, Specific heats below 3K of pure copper, silver and gold and of extremely dilute gold-transition-metal alloys, *Phys. Rev.* 170 (3) (1968) 650–655.
- [35] B.M. Boerstol, J.J. Zwart, J. Hansen, The specific heat of palladium, platinum, gold and copper below 30K, *Physica* 54 (1971) 442–458.
- [36] D.L. Martin, Specific heat of copper, silver and gold below 30K, *Phys. Rev. B* 8 (12) (1973) 5357–5360.
- [37] Y. Takahashi, H. Akiyama, Heat capacity of gold from 80 to 1000K, *Thermochim. Acta* 109 (1986) 105–109.
- [38] J.C. Lashley, M.F. Hundley, A. Migliori, J.L. Sarrao, P.G. Pagliuso, T.W. Darling, M. Jaime, J.C. Cooley, W.L. Hults, L. Morales, D.J. Thoma, J.L. Smith, J. Boerio-Goates, B.F. Woodfield, G.R. Stewart, R.A. Fisher, N.E. Phillips, Critical examination of heat capacity measurements made on a Quantum Design physical property measurement system, *Cryogenics* 43 (2003) 369–378.
- [39] D.L. Martin, The specific heats of copper, silver, and gold below 300 K, *Can. J. Phys.* 65 (1987) 1104–1110.
- [40] O. Vollmer, R. Kohlhaas, Die Atom- und Schmelzwärme von Kupfer, Silber und Gold, *Z. Metallkde* 59 (4) (1968) 273–277.
- [41] C.P. Butler, E.C.Y. Inn, A radiometric method for determining specific heat at elevated temperatures, U.S. Naval Radiological Defense Lab., Tech. Rep. USNRDL-TR- 235 (1958) (AD 200 857).
- [42] M.J. O'Neill, Measurements of specific heat functions by differential scanning calorimetry, *Anal. Chem.* 38 (1) (1966) 1331–1336.
- [43] YaA. Kraftmakher, P.G. Strelkov, Energy of formation and concentration of vacancies in Gold, *Fiz. Tverd. Tela* 8 (1966) 580–582.
- [44] D. Skelskey, J. van den Sype, High temperature specific heat of gold using the modulation method, *J. Appl. Phys.* 41 (1970) 4750–4751.
- [45] G. Cordoba, C.R. Brooks, The heat capacity of gold from 300 to 1200K: experimental data and analysis of contributions, *Phys. Status Solidi A* 6 (2) (1971) 581–595.
- [46] A. Ferrier, As Cited in AGARD Report 6060 Thermophysical Properties of Solid Materials. Project Section II, E. Fitzer, 1973.
- [47] Q. Jiang, R. Lück, B. Predel, Eine verfeinerte Methode zur Messung der spezifischen Wärme mit dem Differential-Scanning-Kalorimeter, *Z. Metallkde* 81 (1990) 94–99.
- [48] G. Wilde, C. Mitsch, G.P. Görlner, R. Willnecker, Specific heat and related thermodynamic functions of undercooled Cu-Ni and Au melts, *J. Non-Cryst. Solids* 205–207 (1996) 425–429.
- [49] T.C. Ehler, Differential Scanning calorimeter studies of the heat capacities of copper difluoride and gold, *Thermochim. Acta* 21 (1977) 111–115.
- [50] M. Braun, R. Kohlhaas, O. Vollmer, Zur hochtemperatur- kalorimetrie von Metallen, *Z. Angew. Phys.* 25 (1968) 365–372.
- [51] T. Mori, M. Meshii, J.W. Kauffman, Quenching rate and quenched-in lattice vacancies in gold, *J. Appl. Phys.* 33 (9) (1962) 2776–2780.
- [52] P. Jongenburger, Energy of formation of vacancies in copper and gold, *Phys. Rev.* 106 (1957) 66–69.
- [53] R.O. Simmons, R.W. Balluffi, Measurement of equilibrium concentrations of lattice vacancies in gold, *Phys. Rev.* 125 (1962) 862–872.
- [54] W. DeSorbo, Calorimetric studies on annealing quenched-in defects in gold, *Phys. Rev.* 117 (1960) 444–450.
- [55] F. Wüst, A. Meuthen, R. Durrer, Die Temperatur- Wärmehaltskurven der technisch wichtigen Metalle, Forschungsarbeiten auf dem gebiete des ingenieurwesens 204 (1918) 1–63.
- [56] P. Schlapfer, P. Debrunner, Zur Kenntnis der spezifischen Wärme des graphitischen Kohlenstoffes und des Koks, *Helv. Chim. Acta* 7 (1924) 31–58.
- [57] S. Umino, On the latent heat of fusion of several metals and their specific heats at high temperatures, *Sci. Rep. Tohoku Univ.* 15 (1926) 597–617.
- [58] E.M. Plaza, Thermodynamics of Solid and Liquid AuSn and Heat Contents of Gold and Tin, Lawrence Berkeley National Laboratory, 1967. LBNL Report #: UCRL-17401.
- [59] H. Schimpff, Über die Wärmekapazität von Metallen und Metallverbindungen, *Z. Physikalische Chemie* 71 (1910) 257–300.
- [60] F.M. Jaeger, E. Rosenbohm, J.A. Bottema, The exact measurement of the specific heats of solid substances at high temperatures: VII. Metals in stabilized and nonstabilized condition: copper and gold, *Proc. Acad. Sci. Amsterdam* 35 (1932) 772–779.
- [61] J.W. Tester, R.C. Feber, C.C. Herrick, Calorimetric study of liquid gold, *J. Chem. Eng. Data* 13 (3) (1968) 419–421.
- [62] E. Kaschnitz, G. Nussbaumer, G. Pottlacher, H. Jäger, Microsecond-resolution measurements of the thermophysical properties of liquid gold, *Int. J. Thermophys.* 14 (2) (1993) 251–257.
- [63] M.L. McGlashan, The International temperature scale of 1990 (ITS-90), *J. Chem. Thermodyn.* 22 (1990) 653–663.
- [64] W.C. Roberts-Austen, On certain properties of metals considered in relation to the periodic law, *Proc. R. Soc. Lond.* 49 (1890) 347–356.
- [65] P. Ludwik, Kohäsion und Atomvolumen, *Z. Phys. Chem.* 88 (1914) 632–637.
- [66] S.V. Lebedev, A.I. Savvatimskii, YuB. Smirnov, Exploding- wire measurement of heat of fusion and electrical conductivity of refractory metals, *Zh. Tekh. Fiz.* 42 (1972) 1752–1760 (Sov. Phys. Tech. Phys. 1973, 17, 1400–1406).
- [67] S. Stølen, F. Grønvald, Critical assessment of the enthalpy of fusion of metals used as enthalpy standards at moderate to high temperatures, *Thermochim. Acta* 327 (1999) 1–32.
- [68] A. Radenac, C. Chesneau, M. Rapin, Differential calorimeter for high temperatures (up to 1800 K), *Rev. Int. Hautes Temp. Refract.* 7 (3) (1970) 230–235.
- [69] S. Baroni, P. Giannozzi, E. Isaev, Density-functional perturbation theory for quasi-harmonic calculations, *Rev. Mineral. Geochem.* 71 (1) (2010) 39–57.
- [70] K. Parlinski, Z.Q. Li, Y. Kawazoe, First-Principles determination of the soft mode in cubic ZrO₂, *Phys. Lett.* 78 (1997) 4063–4066.
- [71] G. Kresse, J. Furthmüller, J. Hafner, Ab initio force constant approach to phonon dispersion relations of diamond and graphite europphys, *Lettres* 32 (1995) 729–734.
- [72] D. Alfé, G.D. Price, M.J. Gillan, Thermodynamics of hexagonal-close-packed iron under Earth's core conditions, *Phys. Rev. B* 64 (2001), 045123.
- [73] A. Togo, I. Tanaka, First principles phonon calculations in materials science, *Scr. Mater.* 108 (2015) 1–5.
- [74] A. Togo, L. Chaput, I. Tanaka, G. Hug, First-principles phonon calculations of thermal expansion in Ti₃SiC₂, Ti₃AlC₂, and Ti₃GeC₂, *Phys. Rev. B* 81 (2010) 174301–174306.
- [75] J. Hafner, Ab initio simulations of materials using VASP: density-functional theory and beyond, *J. Comput. Chem.* 29 (2008) 2044–2078.
- [76] A. Glensk, B. Grabowski, T. Hickel, J. Neugebauer, Understanding anharmonicity in fcc materials: from its origin to ab initio strategies beyond the quasi-harmonic approximation, *Phys. Rev. Lett.* 114 (2015) 195901.
- [77] B. Grabowski, S. Wippermann, A. Glensk, T. Hickel, J. Neugebauer, Random phase approximation up to the melting point: impact of anharmonicity and nonlocal many-body effects on the thermodynamics of Au, *Phys. Rev. B* 91 (2015) 201103 (R).
- [78] B. Grabowski, T. Hickel, J. Neugebauer, Ab initio study of the thermodynamic properties of nonmagnetic elementary fcc metals: exchange-correlation-related error bars and chemical trends, *Phys. Rev. B* 76 (2007), 02430.