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Heat Capacity of Transition Metals at High Temperatures[1]

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In recent years better data have appeared for thermophysical properties of some transition elements at high temperatures (e.g., Ta, Nb, Mo, W, Pt) using subsecond techniques and refinements in thermometry. These data enable us to deduce values for the heat capacity at a constant volume C_v and compare them with the expected lattice vibrational contribution. We attribute the differences chiefly to electronic effects and compare these with results of low-temperature measurements. While calculating the C_p-to-C_v correction, we obtain values for the Grüneisen parameter γ which are useful in assessing the "reliability" of the measured data.

KEY WORDS: Grüneisen parameter; heat capacity; high temperatures; transition elements.

1. INTRODUCTION

It has been at least 50 years since it was recognized that the electronic heat capacity, $C_e^0 = \Gamma T$, determined near $T = 0$ is a measure of the electronic density of states, $N(E)$, at the Fermi surface. For some transition elements such as Mo and W, the coefficient Γ is small compared with that for Nb or Pd. The Fermi energy E_F is near a minimum in the $N(E)$ curve for the former and near a maximum for the latter. At high temperatures, the nonlattice part of the heat capacity for Mo, W, and Cr was shown to be much greater than the extrapolation of ΓT would predict, while for the elements V, Nb, etc., the measured value is smaller [1].

Generally there has been a lack of attention by theorists to these "discrepancies" at high temperatures. One reason has been the lack of

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agreement in experimental data due to inherent difficulties in measurement; another is the theoretical difficulty in dealing with electron energies or band structure for temperatures T for which $kT \sim E_F$. In recent years the first difficulty has been partially overcome by using subsecond measuring techniques with computers and improved thermometry.

This paper looks at selected C_p data, evaluates C_v, and asks how we explain the excess of C_v above the Debye lattice background C_D, which is sensibly constant for $T > \theta_D$, the characteristic Debye temperature.

First we should recognize that some other treatments have evaluated C_v (or C_p) and simply subtracted an extrapolated electron contribution $C_e^0 = \Gamma T$ and ascribed the difference $C_v - C_D - C_e$ to contributions from vacancies or anharmonicity. We reject this approach because it puts the "cart before the horse." The electronic contribution at high temperatures cannot be calculated from $C_e = \Gamma T$ even when allowance is made for the disappearance of the electron–phonon enhancement factor $(1 + \lambda)$ at high temperatures. This is because the electron energy bands, particularly for the transition elements, have a structure which is complex and fine on a scale compared with kT [2]. Regarding vacancies, the experimental evidence shows that the contribution is negligible at temperatures less than 80 or 90% of T_m [3, 4]. The anharmonic contribution is predicted theoretically to be linear in T and either positive or negative in sign. The magnitude is small, judged from experimental values of C_v in nonmetals such as Al_2O_3 [5] and alkali halides [6].

Using data sources described below, we convert the "best" values of C_p to C_v using the relation

$$C_p = C_v(1 + \beta\gamma T)$$

where β is the volume coefficient of thermal expansion and γ is the Grüneisen parameter given by $\gamma = \beta V B_s / C_p$ [7]. V is the molar volume and B_s is the adiabatic bulk modulus.

2. DATA SOURCES

2.1. Heat Capacity

First we used the critical evaluation and sources listed by Hultgren et al. [8] together with more recent data to produce a graph and then smoothed these to produce a table of "best" values. Also, for some elements, new critical evaluations have been published with which we are in substantial agreement. In such cases we list only these for economy of space (Table I). Otherwise, we list a few selected primary sources. Figure 1 is an example of selected C_p data for platinum, with the curve of $C_v(T)$ deduced from our estimates of best values.

2.2. Linear Expansivity α

We have used $\beta = 3\alpha$, taking α values recommended by the AIP Handbook [9] or in the TPM tables [10] together with more recent sources listed in Table I. Note that these sources usually tabulate the

Table I. Data Sources for Heat Capacity and Bulk Modulus

Element	C_p	α	B_s
Ti	Desai [13][a]	AIP [9],[a] TPM [10][a]	Fisher & Renken [14], 4–1155 K
Zr	Hultgren et al. [8],[a] Guillermet [15][a]	AIP [9],[a] TPM [10][a]	Fisher & Renken [14], 4–1155 K
V	Desai [16][a]	AIP [9],[a] TPM [10][a]	Walker [17], 300–2100 K
Nb	Hultgren et al. [8],[a] Righini et al. [18], Cezairliyan [19]	AIP [9],[a] Righini et al. [20], Miiller & Cezairliyan [21]	Bujard et al. [22], 300–2400 K
Ta	Hultgren et al. [8][a]	AIP [9],[a] Cezairliyan et al. [23]	Walker & Bujard [24], 300–3000 K
Cr	White et al. [25],[a] Andersson [26][a]	White et al. [25]	Katahara et al. [27] 50–700 K
Mo	Desai [28],[a] Guillermet [29][a]	Amatumi et al. [30], Miiller & Cezairliyan [31]	Bujard et al. [21], 300–2400 K
W	White & Collocott [32, 4],[a] Gustafson [33][a]	Swenson et al. [34][a]	Lowrie & Gonas [35], 300–2100 K
Rh	Hultgren et al. [8],[a] Vollmer [36]	AIP [9],[a] Ebert [37]	Bridgman [38]
Ir	Hultgren et al. [8],[a] Trukhanova & Filippov [39]	AIP [9][a]	Macfarlane et al. [40], 4–300 K
Ni	Desai [41][a]	Kollie [42], Totskii [43]	Alers et al. [44], 4–750 K
Pd	Hultgren et al. [8],[a] Miiller & Cezairliyan [45]	AIP [9][a]	Weinmann & Steinemann [46], 4–430 K
Pt	Hultgren et al. [8],[a] Righini & Rosso [47]	Hahn & Kirby [48], Amatumi et al. [28]	Macfarlane et al. [49], 4–300 K

[a] A compilation or critical evaluation.

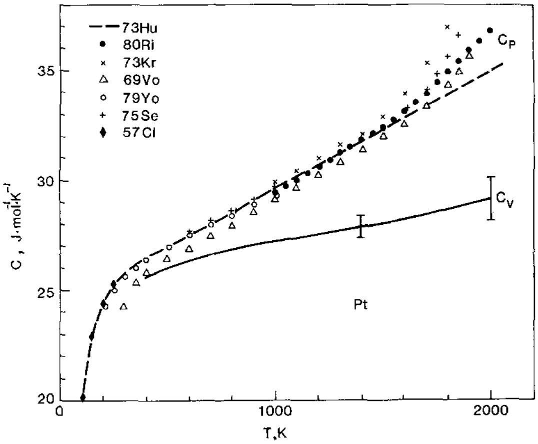

Fig. 1. Selected experimental values of C_p for Pt including the evaluation by Hultgren et al. [8] (— —) and C_v deduced from our estimate of C_p.

practical value $\alpha^* = (1/l_0)\, dl/dT$ rather than the thermodynamic quantity $\alpha = d \ln l/dT = \alpha^*[1 + \Delta l/l]^{-1}$.

2.3. Bulk Modulus B_s

Values of B_s are calculated from the elastic constants listed in the complications of Hearmon [11] and Simmons and Wang [12] and more recent measurements given in Table I. In some cases values have not been determined at high temperatures and we have extrapolated using the empirical information that dB_s/dT is constant for temperatures $T \geqslant \theta_D$.

2.4. Grüneisen Parameter γ

We are not concerned primarily with $\gamma(T)$ except as a means of calculating $(1 + \beta\gamma T)$ and C_v. It is a useful guide to the presence of possible errors in C_p or β, as we expect $\gamma(T)$ to be relatively constant or at least varying only slowly with T in the absence of phase transitions.

3. EVALUATION OF $C_v - C_D$ AND ERRORS

We use the "high-temperature" values of θ_D (denoted θ in Table II) to determine the lattice or Debye term, C_D. At temperatures $T > 2\theta$, C_D is within 1% of the classical value $3R = 24.94\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ so that errors arising from the wrong choice of θ are small. For $T \leqslant \theta$ our estimate of C_D

from the Debye function may be in error due to uncertainty in the choice of θ. Values for the factor $(1+\beta\gamma T)$ vary from ~1.02 at 500 K to ~1.2 at the highest temperatures. Therefore maximum probable errors of 5% in $\beta\gamma T$ will introduce errors of only 1% or less in converting C_p to C_v.

Therefore at high temperatures the error bars shown in Figs. 2–5 are the maximum likely errors in C_p judged from deviation plots of selected data (see Fig. 1).

For a few metals, notably Rh and Ir, uncertainties in α or in our extrapolation of B_s may contribute significantly by introducing errors in the conversion factor $1+\beta\gamma T$.

Table II. Values of Debye Temperature, Electronic Heat Capacity ($T \rightarrow 0$) [50], and Electron–Phonon Enhancement Factor, λ [51]: Bulk Modulus B_s and γ Are Given at Two Temperatures (Generally 500 and 1500 K)

	θ (K)	C_e^0/T ($\mathrm{mJ \cdot mol^{-1} \cdot K^{-2}}$)	λ	B_s (GPa)	γ
Ti	360	3.34	0.4_5	105	1.19 at 500 K (α)
				93[a]	2.11 at 1500 K (β)
Zr	250	2.80	0.4_5	93	0.92 at 500 K (α)
				84[a]	1.25 at 1500 K (β)
V	380	9.8	0.8	155	1.52 at 500 K
				136	1.46 at 1500 K
Nb	285	7.8	0.9	166	1.62 at 500 K
				149	1.60 at 2000 K
Ta	230	6.0	0.8	190	1.61 at 500 K
				168	1.59 at 2500 K
Cr	~550	1.42	0.1	194	1.44 at 500 K
		2.3[b]		182.5[a]	1.46 at 1500 K
Mo	380	1.84	0.3	257	1.53 at 500 K
				218	1.76 at 2500 K
W	315	1.00	0.2	307	1.62 at 500 K
				273[a]	1.70 at 2500 K
Rh	350	4.7	0.2	260	2.24 at 300 K
				230[a]	2.40 at 1500 K
Ir	290	3.2	0.3	360	2.46 at 300 K
				332[a]	2.54 at 1500 K
Ni	390	7.05	0.1	179	1.78 at 500 K
				153	2.01 at 1500 K
Pd	290	9.40	0.4	184	2.24 at 400 K
				160[a]	2.31 at 1500 K
Pt	225	6.55	0.5	283	2.64 at 300 K
				248[a]	2.72 at 1500 K

[a] Extrapolated value of B_s.

[b] Value for "paramagnetic" Cr (+4% V).

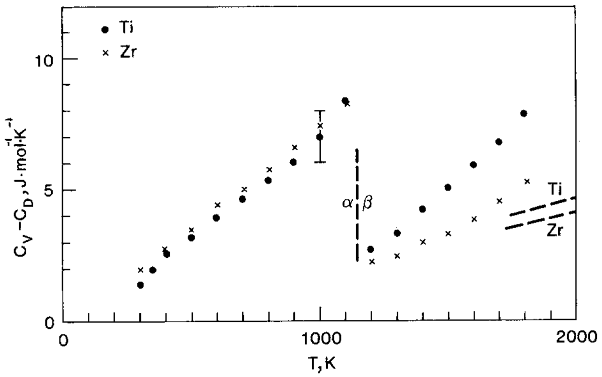

Fig. 2. Values of $C_v - C_D$ for Ti $[T(\alpha \to \beta) \approx 1160\,\mathrm{K},\ T_m = 1943\,\mathrm{K}]$ and Zr $[T(\alpha \to \beta) \approx 1124\,\mathrm{K},\ T_m = 2128\,\mathrm{K}]$; (– – –) extrapolation of $C_e^0/(1+\lambda) = \Gamma T/(1+\lambda)$.

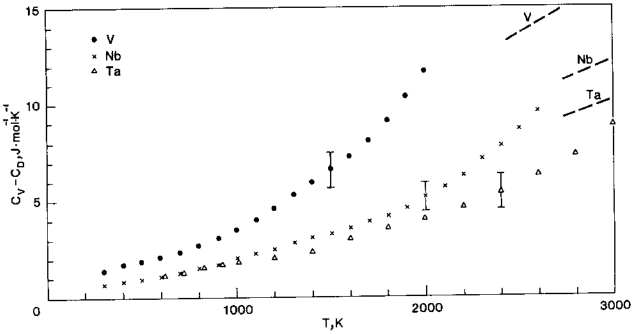

Fig. 3. Values of $C_v - C_D$ for V ($T_m = 2175$ K), Nb ($T_m = 2746$ K), and Ta ($T_m = 3260$ K); (– – –) extrapolation of $\Gamma T/(1+\lambda)$.

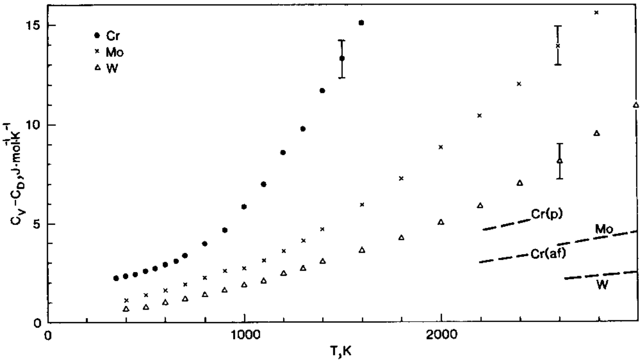

Fig. 4. Values of $C_v - C_D$ for Cr ($T_m = 2130$ K), Mo ($T_m = 2897$ K), and W ($T_m = 3693$ K); (– – –) extrapolation of $\Gamma T/(1+\lambda)$.

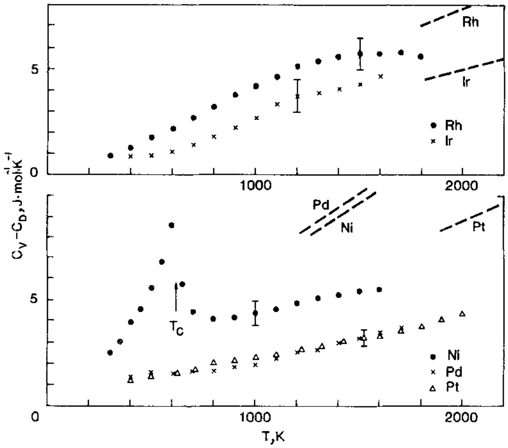

Fig. 5. Values of $C_v - C_D$ for Rh ($T_m = 2236$ K) and Ir ($T_m = 2720$ K) (top) and Ni ($T_m = 1728$ K, $T_c = 629$ K), Pd ($T_m = 1828$ K), and Pt ($T_c = 2042$ K) (bottom).

4. RESULTS

(a) For two group I elements (Ti, Zr), $C_e \approx C_v - C_D$ is similar and exceeds the low-temperature electronic value $C_e^0/(1+\lambda)$ for the hexagonal (α) form. In the bcc(β) form C_e is much less than in the hcp(α) phase.

(b) The group V elements (V, Nb, Ta) are similar to one another in that C_e^0 is less than the "low-temperature" value $C_e^0/(1+\lambda)$ except at temperatures approaching the melting point, where vacancies may become significant.

(c) In group VI (Cr, Mo, and W). C_e far exceeds the extrapolation from low temperatures. This is particularly marked for Cr whether we use the low-temperature value measured for "normal" antiferromagnetic chromium or for the paramagnetic material (containing a few percent vanadium [25]).

(d) In group VIII, Rh and Ir behave similarly to each other and values of $C_v - C_D = C_e$ are comparable with values extrapolated from low temperatures. For Pd and Pt, which have relatively large electronic terms at low temperatures, the high-temperature values are similar and small. Likewise for the paramagnetic form of Ni above the Curie temperature $T_c = 630$ K.

5. DISCUSSION AND CONCLUSIONS

We have used a rather better "data base" than Shimizu et al. did in 1962 [53] to reach similar qualitative conclusions. For those transition elements with a Fermi energy lying near a minimum in the electronic density of states, the electronic heat capacity at high temperatures greatly exceeds that extrapolated from low-temperature data. The reverse situation occurs for the elements with a large low-temperature electronic contribution, that is, with E_F near a maximum. So much for the qualitative picture. Can the present data encourage band structure theorists to improve the quantitative understanding? Also, there is the fascinating case of Cr, for which $C_v - C_D$ exceeds C_e^0 to a far greater extent than for Mo and W. This is true whether or not we take the low-temperature value of C_e^0 from normal antiferromagnetic chromium ($T_N = 311$ K) or from measurements on the paramagnetic *Cr*V (with 4 or 5% vanadium to prevent magnetic ordering). We should also note that the heat capacity measurements extending up to 625 K on *Cr*V alloys [54] give values which agree within experimental error of about 2% with values for pure Cr above T_N. This seems to indicate that remnants of magnetic order cannot be held responsible for the large "electronic" contribution at high temperatures. There remains the Moriya-type spin fluctuations [55] for which clear confirmatory evidence is still being sought in neutron scattering experiments [56]. Note that the high-temperature increase in C_v (and C_p) is accompanied by a similar increase in expansion coefficient so that the Grüneisen parameter remains fairly constant. This constancy is interesting and is apparent in the other metals despite the changing importance of electronic versus lattice contributions. It may be due partly to the fact that the electronic Grüneisen parameter for most transition elements is $\sim 5/3$ [7], which is rather similar to the average value for lattice vibrations.

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