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# Contributions to the Heat Capacity of Alpha (HCP) Titanium from 200–1000 K

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The heat capacity at constant pressure $C_P$ of alpha (HCP) titanium from 200 to 1000 K has been analyzed for contributions from lattice vibrations and electron excitations. Experimental data in the literature have been used to obtain the heat capacity at constant volume $C_V$ by the dilation correction. From $C_V$ has been subtracted an harmonic lattice contribution $C_{VH}$ given by the Debye heat capacity using a single Debye temperature and an electronic contribution $C_{VE}$. The difference $C_V - (C_{VH} + C_{VE})$ is positive, and from about 600 to 1000 K it is real in the sense that it is larger than the experimental uncertainty in $C_V$. This difference is attributed to an anharmonic lattice vibration contribution $C_{VA}$. Two models for $C_{VE}$ have been used. One, which includes electron-phonon enhancement, leads to a $C_{VA}$ of about 15% of $C_V$ at 1000 K. The other takes into account the shift in the density of states with temperature and leads to a $C_{VA}$ of about 5% of $C_V$.

**KEY WORDS:** anharmonic contributions to heat capacity; electronic heat capacity; heat capacity; lattice heat capacity; titanium.

## 1. INTRODUCTION

It is frequently assumed that the heat capacity of pure solid metals is composed of independent contributions associated with lattice vibrations and conduction electrons, and, at sufficiently high temperatures, the formation of equilibrium lattice defects. The lattice contribution is separated into components associated with harmonic ($C_{VH}$) and anharmonic ($C_{VA}$) lattice vibrations. Using models for the calculation of the contributions from conduction electrons $C_{VE}$, the formation of defects, and the harmonic

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lattice vibrations, the anharmonic contribution can be obtained by subtracting the sum of the other contributions from $C_V$.

Since the heat capacities of solids are measured at constant pressure, to apply the above procedure requires first obtaining $C_V$ from $C_P$ by the dilation correction [1], given by

$$C_D = C_P - C_V = \alpha^2 VT/K_T \tag{1}$$

where $V$ is the specific volume, $\alpha$ is the volumetric coefficient of thermal expansion, $K_T$ is the isothermal compressibility, and $T$ is the absolute temperature. For metals, $K_T$ usually is not available above 300 K, so that certain approximations must be employed to estimate the dilation correction.

In this paper, new measurements [2] of the heat capacity of alpha (hexagonal-close-packed) Ti are used to analyze the contributions to the heat capacity from 200 to 1000 K. All the quantities in Eq. (1) are available over this temperature range, so that $C_V$ can be calculated directly. It is

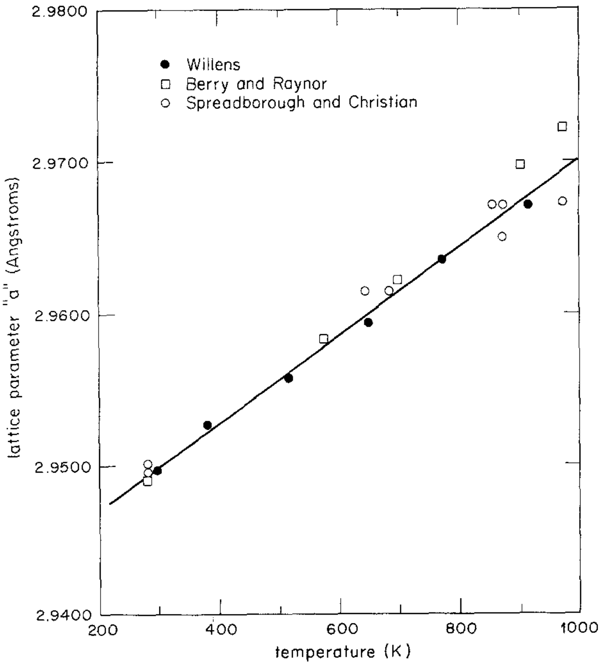

**Fig. 1.** Lattice parameter "a" of alpha titanium as a function of temperature.

assumed that the contribution to the heat capacity from harmonic lattice vibrations $C_{VH}$ is given by the Debye theory, using a single Debye temperature. For Ti, the contribution from the formation of lattice defects is negligible at these low temperatures [3]. Models for the contribution to the heat capacity from electron excitation $C_{VE}$ are examined, including electron-phonon interaction. The sum $C_{VH} + C_{VE}$ is subtracted from $C_V$ to obtain an estimate of the contribution $C_{VA}$ from anharmonic lattice vibrations.

## 2. CALCULATION OF $C_D$ AND $C_V$

$C_P$ for Ti above 300 K is taken from our recent measurements [2], in which the error is about ±1%. Comparison of these measurements to others in the literature is given in ref. [2] and is not repeated here. The data of Clusius and Franzosini [4], Stalinski and Bieganski [5], and Kothen and Johnston [6] were used to define a curve from 200 to 300 K from which $C_P$ values were taken. These data agree in this range within ±0.5%, and the curve smoothly matches the curve used above 300 K.

There have been several measurements of linear expansion and lattice parameters for Ti which allow determination of $V$ and $\alpha$ as functions of temperature. The lattice parameter data [7–9] are shown in Figs. 1 and 2 and are well represented by straight lines. These data were used to calculate $V$ as a function of temperature as shown in Fig. 3. The upper straight line was obtained from the straight lines fitted to the lattice parameters in Figs. 1 and 2. The curve of Yaggee et al. [10] was obtained from their density value measured at 25°C, and the coefficient of expansion was derived from their length measurements.

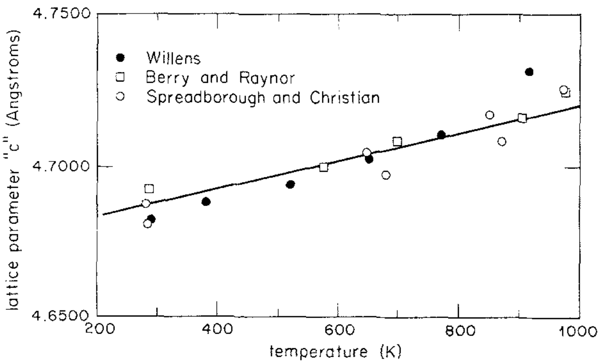

**Fig. 2.** Lattice parameter "c" of alpha titanium as a function of temperature.

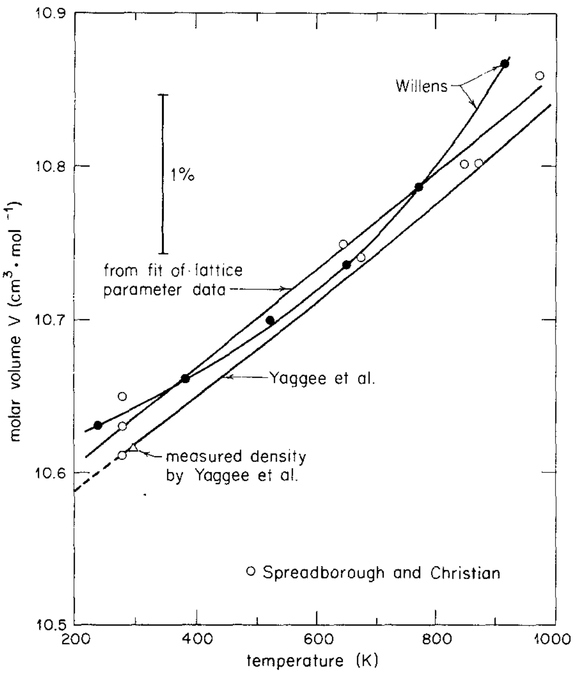

Fig. 3. The molar volume $V$ as a function of temperature for alpha titanium.

Values of $\alpha$ derived from the length measurements of Hidnert [11], Griener and Ellis [12], McCoy [13], and Yaggee et al. [10], are shown in Fig. 4. A necessity in deriving $\alpha$ from their linear thermal expansion coefficients $\alpha_l$ is that measurements must have been made on polycrystalline samples of random orientation. Since alpha Ti is HCP, any preferred orientation in the sample will give results from which $3\alpha_l$ will not be equal to $\alpha$. None of the investigators have determined the degree of preferred orientation, so that it is difficult to assess the accuracy of the experimental results.

The values of $\alpha$ and $V$ derived from the data of Yaggee et al. [10] have been chosen to use in calculating $C_D$. Their results are consistent with those of the other investigators and cover most of the requisite temperature range. From 300 to 200 K, we have extrapolated the $\alpha$ and $V$ curves based on their data. It is seen in Fig. 3 that $V$ scatters within $\pm 0.3\%$, which is taken as its uncertainty. For $\alpha$, the scatter or uncertainty is about $\pm 5\%$ (Fig. 4).

The only data for Ti from which the isothermal compressibility $K$ can be derived are those of Fisher and Renken [14]. They determined the velocity of sound in single crystals as a function of temperature, from

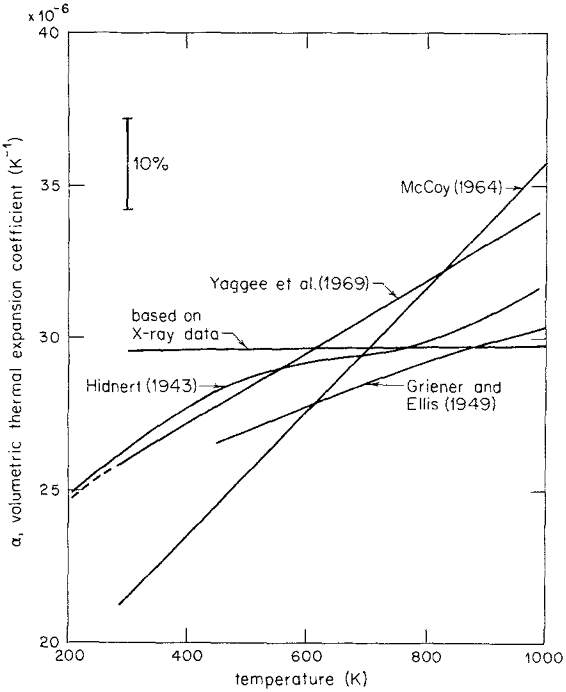

Fig. 4. The volumetric thermal expansion coefficient $\alpha$ as a function of temperature for alpha titanium.

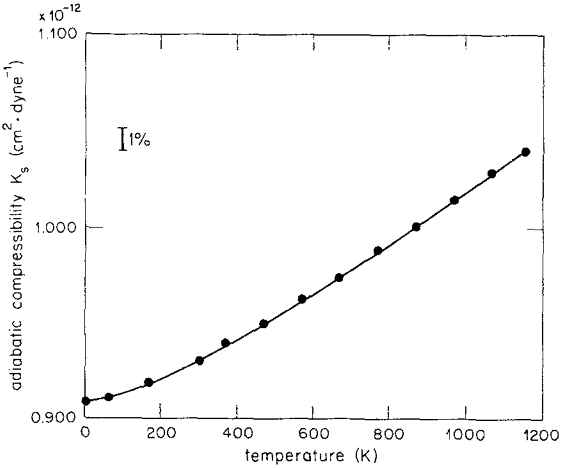

Fig. 5. Adiabatic compressibility $K_S$ for alpha titanium as obtained by Fisher and Renken [14].

which they calculated the elastic constants and the adiabatic compressibility $K_S$ (Fig. 5). Their reported accuracy in measuring the elastic constants gives an uncertainty in $K_S$ of about ± 1%.

The use of Eq. (1) to obtain $C_V$ requires converting $K_S$ to $K$ [1]. Incorporating this conversion gives

$$C_V = \frac{K_S}{\alpha^2 V T^2 + K_S C_P T} C_P^2 T \tag{2}$$

$C_V$ calculated from Eq. (2) using the selected values of $C_P$, $V$, $\alpha$, and $K_S$ is shown in Fig. 6. Using the uncertainties mentioned above for each

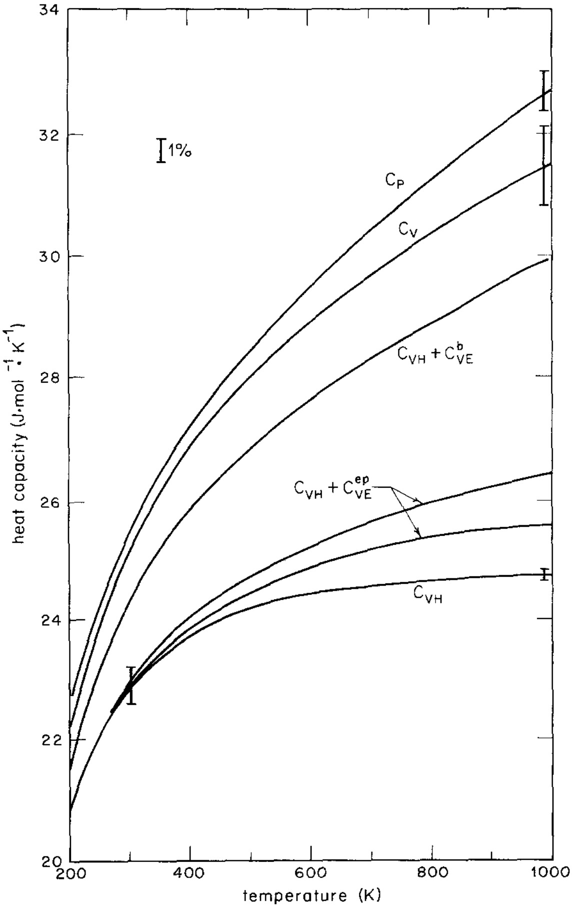

**Fig. 6.** The heat capacity of alpha (HCP) titanium from 200 to 1000 K. The bars at the ends of $C_P$, $C_V$, and $C_{VH}$ show the uncertainty in these quantities.

quantity, the uncertainty in $C_V$ is about ±2%, which is shown by the bar at the end of the curve at 1000 K.

At a temperature $T$, the calculated $C_V$ corresponds to the volume $V(T)$; for comparison of $C_V$ to theoretical models, it must be converted to $C_V$ at a volume usually taken at 0 K. The expression to obtain the correction is given by Korshunov [15]. The difference in $C_V$ at 1000 K for the volume at that temperature (Fig. 3) and that at 0 K is estimated to be 0.2 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$. This is within the uncertainty of the calculation of $C_V$ and is ignored here.

## 3. CALCULATION OF $C_{VH}$ AND $C_{VE}$

Now the agreement between the experimental $C_V$ and the sum of that estimated for a harmonically oscillating lattice ($C_{VH}$) and electron excitation ($C_{VE}$) is examined. To estimate $C_{VH}$, the Debye expression with a fixed Debye temperature $\theta_D$ is used. The review of Debye temperatures by Gschneidner [16] lists $\theta_D$ values from 370 to 430 K for Ti. $C_{VH}$ is not very sensitive to the value of $\theta_D$ at temperatures above the Debye temperature, so an intermediate value of $\theta_D = 400$ K has been chosen. A variation in $\theta_D$ of ±30 K alters $C_{VH}$ by about ±2.5% at 300 K, and about ±0.5% at 1000 K. $C_{VH}$ is shown in Fig. 6; the bars at each end of the curve show the uncertainty in $C_{VH}$ based on the uncertainty in $\theta_D$.

Free electron theory can be used to estimate $C_{VE}$ by the relation

$$C_{VE} = 1/3\pi^2 k^2 N(E_F)T \tag{3}$$

where $k$ is Boltzmann's constant, and $N(E_F)$ is the density of states at the Fermi surface. If the density of state is independent of temperature, then Eq. (3) gives $C_{VE}$ proportional to $T$, or $\gamma T$, where $\gamma$ is the low temperature heat capacity coefficient. Collins and Ho [17] obtained for Ti a value of $\gamma = 3.36 \times 10^{-3}\ \mathrm{J \cdot mol^{-1} \cdot K^{-2}}$ from their low temperature heat capacity measurements, which agrees within 2% with the other nine values which they surveyed. $C_{VE}$ using this value is shown in Fig. 7.

Shimizu et al. [18] deduced the density of states for Ti from low temperature heat capacity data of Ti and Ti alloys. Then they took into account the shift in the density of states with temperature to obtain a temperature dependent electronic heat capacity coefficient $\gamma(T)$, so that $C_{VE}^b = \gamma(T)T$. (The $b$ represents band theory here.) Their result is shown in Fig. 7 and is higher than that given by the free electron theory. The sum $C_{VE}^b + C_{VH}$ is shown in Fig. 6.

Grimvall [19] has derived an expression for a temperature dependent

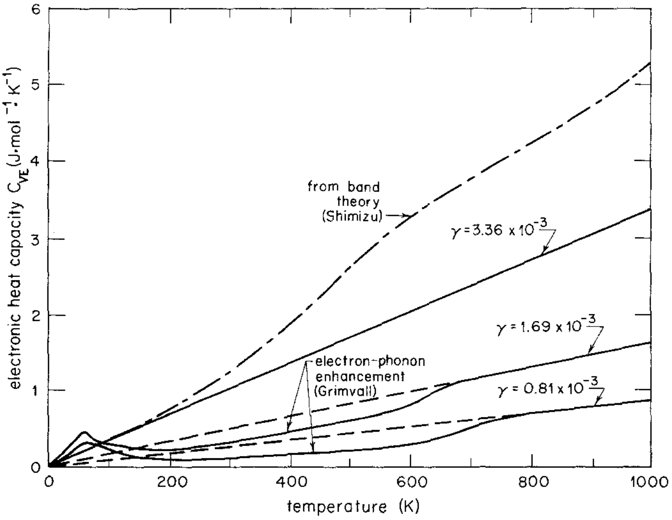

**Fig. 7.** The calculated electronic heat capacity $C_{VE}$ of alpha titanium based on the model by Shimizu et al. [18] and Grimvall [19].

coefficient due to electron-phonon interaction (see also, Fradin [20]):

$$C_{VE}^{ep} = (\gamma_0 + \gamma_T)T \tag{4}$$

Here $\gamma_0$ is the coefficient in the absence of electron-phonon interaction, which can be calculated via Eq. (3) if the density of states at the Fermi level is known. There appear to be only two density of state calculations in the literature for Ti. From the density of states distribution curve of Shimizu et al. [18], a value of about $1.69 \times 10^{-3}$ is obtained and from that of Altmann and Bradley [21] a value of about $0.81 \times 10^{-3}$. To obtain $\gamma_T$ from the calculation of Grimvall requires its value at absolute zero, taken to be the value of $\gamma$ given by Collins and Ho [17] from low temperature heat capacity measurements. Also required is the Einstein temperature, which was taken as 430 K; $\gamma_T$ is not very sensitive to the value chosen. Using these values, a curve for $C_{VE}^{ep}$ was calculated for each of the two values of $\gamma_0$ cited above. They are shown in Fig. 7. The sum $C_{VH} + C_{VE}$ for each of the three curves is shown in Fig. 6.

## 4. THE ANHARMONIC HEAT CAPACITY $C_{VA}$

In Fig. 8 is shown the difference between $C_V$ and $(C_{VE} + C_{VH})$. It is positive and is real in the sense that the sum obtained by either electronic model gives a result which is lower than the lower bound of the uncertainty in $C_V$ (see Fig. 6). The electronic contribution calculation of Grimvall

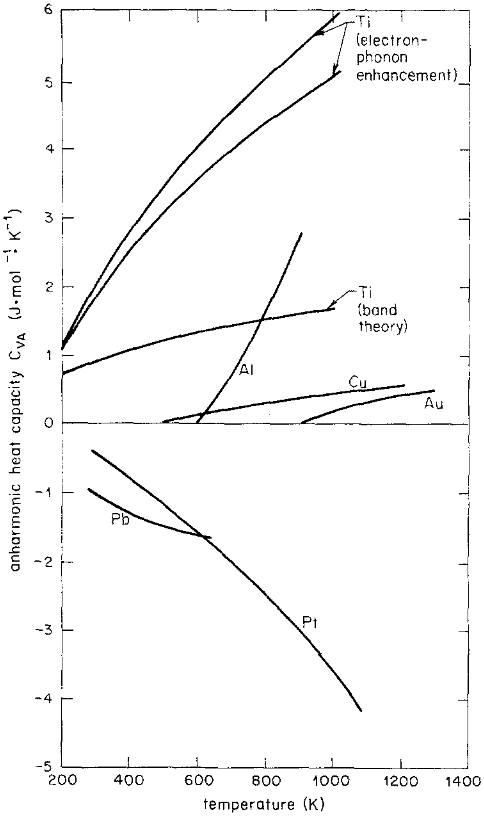

**Fig. 8.** The anharmonic heat capacity of Al, Cu, Au, Pb, Pt, and Ti. For Ti, curves are shown for $C_{VA}$ using two models for the electronic contribution to the heat capacity.

depends on the value of the density of states at the Fermi level. For the density of states distribution curves of both Shimizu et al. [18] and Altmann and Bradley [20], the Fermi level falls on or near a shoulder. Thus the value of the density of states depends sensitively on the location of the Fermi level and the shape of the curve. Until these are better defined, $C_{VE}$ cannot be determined more accurately. However, in spite of these uncertainties, it appears that the difference between $C_V$ and $(C_{VE} + C_{VH})$ is real and positive.

We attribute this "excess" heat capacity to anharmonic lattice vibrations. The heat capacities of Au [22], Al [23], Cu [24], Pb [25], and Pt [26, 27], for which the dilation correction can be made exactly (i.e., experimental data for $\alpha$, $V$, and $K$ are available as a function of temperature), have been analyzed in a fashion similar to that employed here for Ti. The results are shown also in Fig. 8. Examination of the uncertainties leading to the calculation of $C_{VA}$ indicates that the magnitude of $C_{VA}$ for Cu, Au, and perhaps Al is small, and the sign uncertain. However, for Pb, Al, Pt, and now Ti, the effect is real, and the sign well defined.

There have been some theoretical calculations of $C_{VA}$, but the magnitude (and in some cases the sign) is uncertain [28, 29]. Generally, the prediction is that $C_{VA}$ is linear with temperature, which, considering the uncertainties in calculating $C_{VA}$ from experimental data, is consistent with the results of the treatment here (Fig. 8). No theoretical calculations of $C_{VA}$ have been made for Ti, but the result of the treatment in this paper gives an estimate of $C_{VA}$ to which comparison now can be made.

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