

Heat Capacity of fcc Calcium

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The lattice entropy derived from the measured heat capacity at intermediate and high temperatures is analyzed to yield a weakly temperature dependent entropy Debye temperature. An unusual temperature dependence of this quantity may be a sign of error in the heat capacity data. When this analysis is applied to heat capacity data recommended by Hultgren et al. (1973) for 20 nontransition metals, the result for fcc Ca stands out as anomalous. We have reconsidered heat capacity data of fcc Ca and find that measurements by Eastman et al. (1924), which were given little weight by Hultgren et al., are consistent with a normal behavior of the entropy Debye temperature up to 450 K.

KEY WORDS: calcium; Debye temperature; entropy; heat capacity.

1. INTRODUCTION

The Debye temperature $\theta_S(T)$ associated with the vibrational entropy is a quantity which is slowly varying with the temperature T when $T \gtrsim \theta_S/3$. It is well defined and easy to calculate also when anharmonic effects, including thermal expansion, are present. See, e.g., Martin [1] for an analysis of alkali metals. Kinks or other unusual features in $\theta_S(T)$ may be a sign of error in the experimental heat capacity data used to evaluate $\theta_S(T)$. We have applied this idea in an analysis of almost all nontransition metals using the heat capacity data recommended by Hultgren et al. [2]. Most of the metals showed a very uniform behavior of $\theta_S(T)$ with fcc calcium as a conspicuous exception. In this paper, we shall argue that the heat capacity data by Eastman et al. [3] for fcc Ca, which were given little weight by Hultgren et al. [2], are to be preferred over a wide temperature interval.

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2. A DEBYE TEMPERATURE FIT TO THE LATTICE ENTROPY

Let C_p be the measured lattice heat capacity at constant pressure. S_p is the corresponding entropy and $S(\theta/T)$ is the entropy in a Debye model. We define an “entropy” Debye temperature $\theta_S(T)$ for each temperature T by

$$S(\theta_S/T) = S_p(T) = \int_0^T \frac{C_p(T')}{T'} dT' \quad (1)$$

When the phonon density of states $F(\omega)$ is that of a Debye model, $\theta_S(T)$ is constant and equal to the Debye temperature θ_D . For a general $F(\omega)$, but still with strictly harmonic lattice vibrations, $\theta_S(T)$ has a high temperature expansion related to frequency moments of $F(\omega)$. From ref. [4], we can write

$$\theta_S(T) = \theta(0) \left[1 + \sum_{n=1}^{\infty} a_n T^{-2n} \right] \quad (2)$$

(See the appendix.) In a real solid we have to add effects of anharmonicity. To lowest order in perturbation theory, a particular phonon mode (\mathbf{q}, λ) has the frequency

$$\omega(\mathbf{q}, \lambda) = \omega^0(\mathbf{q}, \lambda) + \Delta_2 + \Delta_3 + \Delta_4 \quad (3)$$

where ω^0 is the “harmonic” frequency at $T = 0$ K. Thermal expansion gives a shift $\Delta_2(\mathbf{q}, \lambda; V(T))$. The increased vibrational amplitude at finite T , present even at constant volume, gives rise to the shifts $\Delta_3(T)$ and $\Delta_4(T)$; see, e.g., Cowley and Cowley [5] for details. The shifts in Eq. (3) are not the same for all modes (\mathbf{q}, λ) , but at high temperatures, they are all linear in T . In an Einstein phonon model, all Δ_2 are proportional to n and all $\Delta_3 + \Delta_4$ are proportional to $n + 1/2$, where n is the Bose–Einstein factor $[\exp(\theta_E/T) - 1]^{-1}$. To lowest order in $(\Delta_2 + \Delta_3 + \Delta_4)/\omega^0$, we get a correct result for $\theta_S(T)$ if we add to the $\theta_S(T)$ of Eq. (2), which here refers to constant volume $V(T = 0)$, an anharmonic shift $\Delta\theta_S(T)$:

$$\Delta\theta_S(T)/\theta(0) = k[\exp(\theta_E/T) - 1]^{-1} \quad (4)$$

where k is a constant. The term $\Delta_3(T = 0) + \Delta_4(T = 0)$ will be included in $\theta(0)$. The Einstein temperature is chosen so that the Debye and the Einstein expressions for the heat capacity are equal at high temperatures, i.e., $\theta_E \simeq \sqrt{(3/5)} \theta(0) = 0.77\theta(0)$.

In a metal, the electronic heat capacity C_{el} must be subtracted from the measured C_p before we apply Eq. (1). At low temperatures, $C_{el} = \gamma_0 T$. The prefactor γ_0 can be written $\gamma_0 = \gamma_b(1 + \lambda)$ where γ_b is the band structure result and $1 + \lambda$ is an electron-phonon mass enhancement factor. At high temperatures the many-body correction is absent and the entropy is $\gamma_b T$. We shall use an Einstein phonon model to account for the gradual disappearance of the electron-phonon enhancement in the entropy. Details are given elsewhere [6]. In transition metals, it may also be necessary to allow for a rapidly varying electron density of states near the Fermi level and to find the electronic entropy by numerical integration.

The solid curve in Fig. 1 (for potassium) shows a typical behavior of $\theta_S(T)$ derived from the measured C_p [2] and corrected for C_{el} . At low temperatures, $\theta_S(T)$ varies because $F(\omega)$ does not have the Debye form. At high temperatures, $\theta_S(T)$ varies due to anharmonic effects, including thermal expansion. There is an intermediate temperature range, where the terms up to $n = 2$ in Eq. (2) give a good account of the variation due to the shape of $F(\omega)$, and Eq. (4) reasonably describes the anharmonicity. Higher order anharmonic effects and the vacancy contribution to C_p are small at such temperatures.

These considerations suggest that the expression

$$\theta_S^f(T) = \theta(0) \left\{ 1 + \frac{a_1(\theta(0), \theta(2))}{T^2} + \frac{a_2(\theta(0), \theta(2), \theta(4))}{T^4} + \frac{k}{\exp[(0.77\theta(0)/T] - 1]} \right\} \quad (5)$$

can be fitted to $\theta_S(T)$ over a rather wide range of temperatures around $\theta(0)$. In calculations for 20 nontransition metals, using C_p from Hultgren et al. [2], we find that numerically stable values of the parameters $\theta(0)$, $\theta(2)$, $\theta(4)$, and k are usually obtained if we make a least squares fit in the approximate temperature interval $0.5\theta(0)$ – $1.5\theta(0)$. A characteristic result is shown in Fig. 1. The middle curve (long and short dashes) is the fitted $\theta_S^f(T)$, extrapolated to high temperatures. The upper curve (short dashes) is $\theta_S^f(T)$ when $k = 0$, i.e., the “harmonic” part of $\theta_S(T)$. For the elements Li, Na, K, Rb, Cs, Be, Mg, Zn, Cd, Hg, Al, Ga, Sn, Pb, Cu, and Au, $(\theta_S^f(T) - \theta_S(T))/\theta(0) \equiv \delta(T)$ has the characteristic form exemplified by the shaded area in Fig. 1. The quantity $\delta(T)$ is zero below $T \sim T_m/2$ and, in most cases, has increased to $\delta = 0.02$ to 0.03 at the melting temperature T_m . We shall call this the “normal” behavior. Fcc calcium is a notable exception, which motivates a reconsideration of the recommended C_p data.

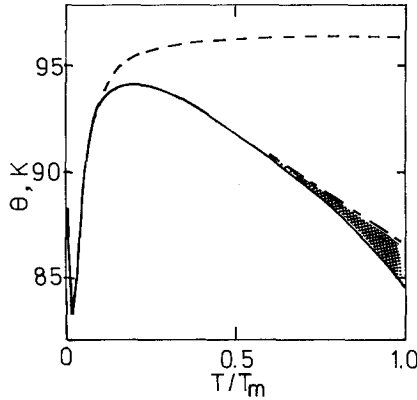


Fig. 1. The entropy Debye temperature $\theta_S(T)$ based on the experimental lattice heat capacity C_p for potassium [2] (solid line); our fitted $\theta_S^f(T)$ (---); and the "harmonic" $\theta_S(T)$ (- - -), which does not include the last term in Eq. (5). The shaded area defines $\delta(T)$.

Similar, but smaller, features in $\theta_S(T)$ are also found for In and Tl, and a small irregularity is present in $\theta_S(T)$ for Ag near $0.5T_m$. Results on the influence of anharmonicity and vacancy formation on $\delta(T)$, which was our main reason for a study of $\theta_S(T)$, will be published elsewhere [7].

3. RECONSIDERATION OF C_p DATA FOR FCC CALCIUM

Figure 2 shows $\theta_S(T)$ and $\theta_S^f(T)$ as obtained from the C_p data recommended by Hultgren et al. [2]. The fit to $\theta_S^f(T)$ was made in the interval 60–180 K, i.e., below the temperatures where we find significant

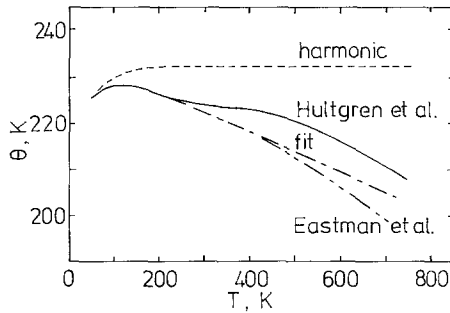


Fig. 2. The same results as in Fig. 1 but for fcc calcium, based on data recommended by Hultgren et al. [2]. The line --- is $\theta_S(T)$ when C_p has the form given in Fig. 3.

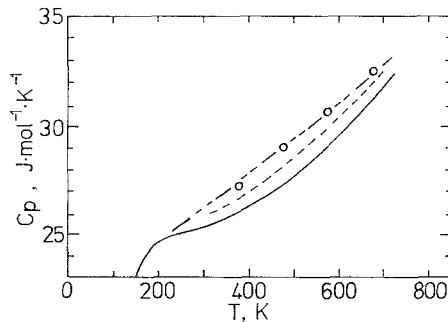


Fig. 3. The total heat capacity C_p recommended by Hultgren et al. [2] for fcc calcium (solid line), C_p used in the calculation of the lower $\theta_S(T)$ in Fig. 2 (-----), and C_p measured by Eastman et al. [3] (circles). The short dashed curve is derived from the values recommended in the Russian compilation [10].

anomalies in C_p . For C_{el} , we used $\gamma_0 = 3.00 \times 10^{-3} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $1 + \lambda = 1.3$, with an Einstein model ($\theta_E = 0.77\theta(0)$) representation of $\lambda(T)$ as described in [6]. Our fitted $\theta_S^f(T)$ has $\theta(0) = 233 \text{ K}$, $\theta(2) = 244 \text{ K}$, $\theta(4) = 253 \text{ K}$, and $k = 0.0269$. We had no difficulty in obtaining numerically stable values for the fitting parameters when the fitting interval was varied, and the regularity of $\theta(0)$, $\theta(2)$, and $\theta(4)$ is as expected. However, it is obvious from Fig. 2 that fcc Ca does not have a “normal” $\theta_S(T)$ at high temperatures.

Above 200 K there are few heat capacity measurements on calcium. Hultgren et al. chose to make a smooth interpolation which joins on to the heat content measurements of Jauch [8] (quoted by Kubaschewski [9]) in the interval 573–1234 K. In doing so, they discard data by Eastman et al. [3] for fcc Ca in the range 373–673 K.

Let us now assume that C_p is given by the upper (dashed) curve in Fig. 3, which goes approximately through the data points of Eastman et al. The corresponding $\theta_S(T)$ is shown in Fig. 2 as the lower curve (solid plus a dashed high temperature part). That result agrees very well with our anticipated “normal” behavior up to approximately 450 K. At still higher temperatures, the difference between the curves labelled “Eastman et al.” and “fit” is roughly twice as large as is “normal” for $\delta(T)$. (The T_m of bcc Ca is 1112 K.) We therefore expect that the true C_p of fcc Ca above 450 K gradually approaches the value recommended by Hultgren et al. [2]. It should be remarked that a recent compilation of thermodynamic properties [10] gives a C_p which lies roughly midway between the data of Hultgren et al. and Eastman et al.

4. CONCLUSIONS

We have analyzed the entropy Debye temperature $\theta_S(T)$ from $\sim\theta_S/2$ to $\sim T_m$ for Li, Na, K, Rb, Cs, Be, Mg, Ca, Zn, Cd, Hg, Al, Ga, In, Tl, Sn, Pb, Cu, Ag, and Au using the C_p values recommended by Hultgren et al. [2]. With the exception of Ca, In, Tl, and Ag, a very regular and "normal" behavior of $\theta_S(T)$ was found, which corroborates the recommended data. The most conspicuous exception was fcc calcium, which has led us to suggest that measurements by Eastman et al. [3] should be preferred over a wide range of temperatures. Indium and thallium show a $\theta_S(T)$ similar to that of fcc Ca, but not so pronounced, while Ag has only a minor irregularity in $\theta_S(T)$ near $T_m/2$.

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APPENDIX

Define frequency moments $\omega(n)$ for $n > -3$ by

$$\omega(n) = \left[\int_0^{\omega_{\max}} \omega^n F(\omega) d\omega / \int_0^{\omega_{\max}} F(\omega) d\omega \right]^{1/n} \quad (6)$$

with ω^n replaced by $\log \omega$ when $n = 0$. Corresponding Debye temperatures $\theta(n)$ are defined so that a Debye model, for a given n , yields the correct $\theta(n)$:

$$\left[\int_0^{\theta(n)} \omega^n \omega^2 d\omega / \int_0^{\theta(n)} \omega^2 d\omega \right]^{1/n} = \hbar \omega(n) / k_B \quad (7)$$

The parameters a_1 and a_2 in Eq. (2) are [4]

$$a_1 = \frac{1}{40} [\theta^2(0) - \theta^2(2)] \quad (8)$$

$$a_2 = \frac{1}{2240} [\theta^4(4) - \theta^4(0)] + \frac{a_1}{2} \left[a_1 + \frac{1}{10} \theta^2(0) \right] \quad (9)$$

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