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Note

An Analysis of the High-Temperature Entropy of Transition Metals

M. Thiessen[1]

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The high-temperature entropy at constant pressure, obtained from heat capacity data, is analyzed for Mo, Nb, Pd, Rh, Ru, Sc, Ti, V, W, Y, and Zr. The vibrational contribution to the entropy defines an entropy Debye temperature, $\theta_S(T)$. Due to anharmonicity, $\theta_S(T)$ decreases with the temperature T, typically by 10–20% between room temperature and the melting point. An unusual temperature dependence of $\theta_S(T)$ may indicate inadequacies in the underlying data. On this ground, the C_p data recommended by Hultgren et al. (1973) for W and Ru seem doubtful. A comparison is made between θ_S and the elastic-limit Debye temperature θ_D for the metals with a cubic lattice structure. θ_S of Nb is found to be almost independent of T, a feature related to the fact that the elastic constant c_{44} increases with T.

KEY WORDS: Debye temperature; heat capacity; high temperature; metals; vibrational entropy.

1. INTRODUCTION

The high-temperature heat capacity of solids is a quantity of wide interest, e.g., in a theoretical account of phase diagrams [1]. Rosén and Grimvall [2] analyzed the high-temperature heat capacity, $C_p(T)$, of nontransition metals, in terms of an entropy-related Debye temperature, $\theta_S(T)$. A study of the temperature dependence of $\theta_S(T)$ may reveal inaccuracies in the C_p data that are used to derive $\theta_S(T)$. For instance, unusual features in $\theta_S(T)$

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[1] Department of Theoretical Physics, The Royal Institute of Technology, S-100 44 Stockholm, Sweden.

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of calcium [3] subsequently led to a remeasurement of its heat capacity [4]. The magnitude and temperature dependence of $\theta_S(T)$ are also of great importance in themselves.

The analysis of Rosén and Grimvall [2] for nontransition metals was simplified by the fact that the electronic part of the heat capacity is approximately linear in T. For transition metals, this is not always the case, because the electronic heat capacity probes the electron density of states $N(E)$ in an interval around the Fermi level where $N(E)$ may vary considerably with the electron band energy E [5]. The high-temperature entropy S_p is obtained from the measured heat capacity C_p through

$$S_p(T) = \int_0^T \frac{C_p(T')}{T'}\, dT' \tag{1}$$

It is the purpose of this paper to analyze S_p for some nonmagnetic transition metals. Magnetic materials are excluded because the magnetic part of the entropy is poorly known and then the vibrational entropy, expressed as $\theta_S(T)$, cannot be accurately deduced.

2. THEORY

The theoretical background and the method of analysis have been described elsewhere [6], and only some key formulas are quoted here. In a Debye model, the vibrational entropy is given by

$$S_{ph} = 9Nk_B \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} x^2 \left[\frac{xe^x}{e^x - 1} - \ln(e^x - 1)\right] dx \tag{2}$$

N is the number of atoms in the specimen, k_B is Boltzmann's constant, T is the temperature, and θ is the Debye temperature. Thus S_{ph} is a function of θ/T. Then

$$S_p(T) = S_{ph}(\theta_S/T) + S_{el}(T) \tag{3}$$

$S_{el}(T)$ is the contribution to the entropy arising from the conduction electrons [5]. This defines an entropy Debye temperature θ_S, which varies with the temperature T.

A well-known expression for the Debye temperature, based on the elastic limit of the frequency spectrum, is

$$\theta_D = \frac{h}{k_B}\left(\frac{9N}{4\pi VI}\right)^{1/3} \tag{4}$$

where h is Planck's constant, V is the specimen volume, and I is an average over the sound velocities,

$$I = \left\langle \sum_{i=1}^{3} \frac{1}{C_i^3} \right\rangle = \frac{1}{4\pi} \iint \left(\frac{1}{C_1^3} + \frac{1}{C_2^3} + \frac{1}{C_3^3} \right) d\Omega \tag{5}$$

For a cubic lattice, the sound velocities C_1, C_2, and C_3 are functions of the three independent elastic constants, c_{11}, c_{44}, and c_{12} [7].

3. RESULTS

Figures 1–3 show ${}_{\mathrm{S}}$ as a function of T/T_{m}, where T_{m} is the melting temperature, for Mo, Nb, Pd, Rh, Ru, Sc, Ti, V, W, Y, and Zr. For the

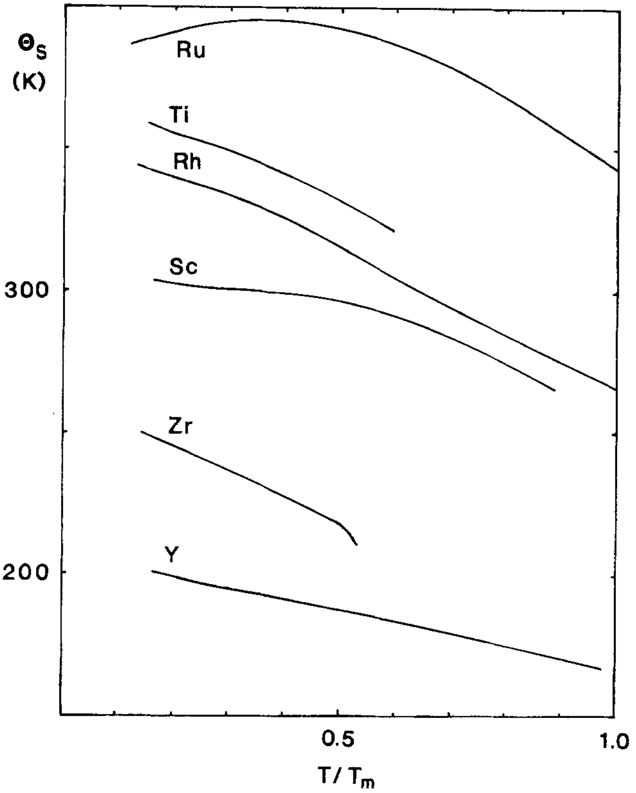

Fig. 1. The Debye temperature θ_{S} as a function of T/T_{m}, where T is the temperature and T_{m} is the melting point, for Rh, Ru, Sc, Ti, Y, and Zr. For Sc, Ti, Y, and Zr a phase transition occurs, and therefore the curves end below T_{m}.

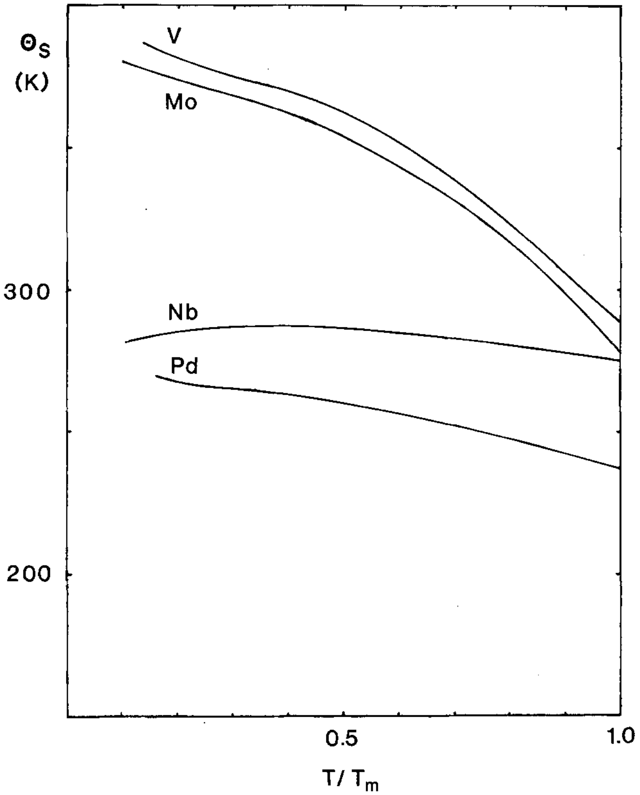

Fig. 2. The Debye temperature θ_S as a function of T/T_m for Mo, Nb, Pd, and V.

calculation of θ_S, recommended experimental data $S_{exp}(T)=S_p(T)$ are taken from Hultgren et al. [8]. The electron contributions to the entropy, $S_{el}(T)$, are calculated from electron densities of states [9] (from Ref. 10 for W).

Table I gives a comparison between θ_S obtained from the entropy and θ_D obtained from the elastic constants, c_{11}, c_{44}, and c_{12}, taken from Ref. 11, at room temperature and at $0.5T_m$ for Mo, Nb, Pd, V, and W, which all have cubic lattices.

4. DISCUSSION

For most of the metals considered, θ_S decreases smoothly by 10–20% when going from room temperature to the melting point. A decrease of the same magnitude was found by Rosén and Grimvall [2] for 16 non-

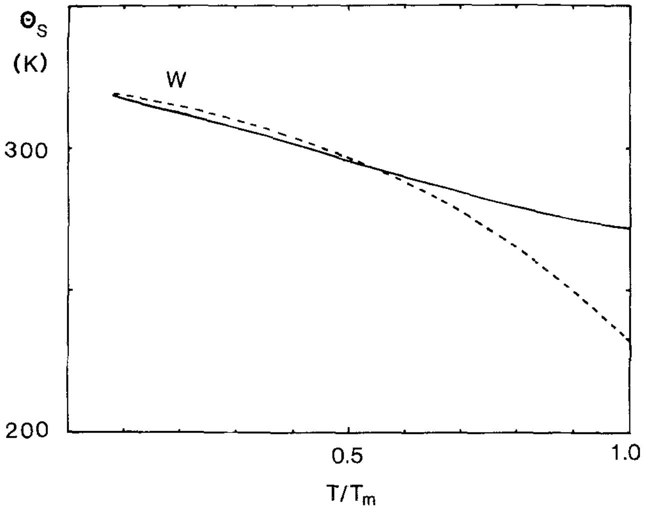

Fig. 3. The Debye temperature θ_S as a function of T/T_m for W. The dashed line shows θ_S calculated from C_p data given in Ref. 12.

transition metals. The three most notable deviations from the general behavior of $\theta_S(T)$ are observed for Ru, Nb, and W.

In the case of ruthenium, and to a lesser extent of Mo, Rh, Sc, and V, there is a "hump" in θ_S centered at approximately 500 K. In analogy to the case of Ca [3, 4], that feature suggests inadequacies in the C_p data of Ru. In fact, one notes that in the temperature range 272 to 573 K, Hultgren et al. [8] found no primary data and thus had to interpolate to get a recommended C_p.

For niobium $\theta_S(T)$ is almost independent of T. This is a very unusual case (cf. Ref. 2). However, the temperature dependence of $\theta_S(T)$ is

Table I. Debye Temperature (in K) for Various Elements

Element	S[a]	D[a]	S[b]	D[b]	$0.5T_m$
Mo	380	462	354	420	1445
Nb	282	268	286	272	1370
Pd	269	267	260	258	913
V	383	389	362	355	1088
W	319	381	295	343	1840

[a] $\theta_S(T)$ and $\theta_D(T)$ evaluated at room temperature.

[b] $\theta_S(T)$ and $\theta_D(T)$ evaluated at half the melting point.

consistent with that of the elastic-limit θ_D (Table I). An increase in c_{44} with T (cf. Fig. S13 in Ref. 11) compensates for the normal decrease of c_{11} and c_{12}, so that $\theta_D(T)$ is almost independent of T. Thus there is no reason to doubt the C_p data in this case.

In the case of tungsten, and with $\theta_S(T)$ derived from the data recommended by Hultgren et al. [8], $\theta_S(T)$ does not show the downward curvature at high T that is characteristic of $\theta_S(T)$ for other metals. If we use C_p data from an assessment by Gustafson [12] to obtain θ_S, we get quite a different shape (Fig. 3) which follows the normal behavior. This suggests that the $C_p(T)$ values in Ref. 8 are not quite correct, a conclusion also drawn by Gustafson [12] and White and Collocott [13], in their recent assessments. A more detailed analysis of the thermodynamics of tungsten is presented elsewhere [14].

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