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Comments on the calculation of the thermodynamic properties of metals at high temperatures

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In a series of recent papers an accurate theoretical calculation of some thermodynamic properties in a number of fcc and bcc metals has been presented. In order to compare the calculated values of the specific heat under constant volume with the experimental data, these papers also consider the vacancy contribution. By using recent thermodynamical concepts we clarify the point that generally the value of the vacancy contribution to the *isochoric* specific heat differs significantly from that of the corresponding contribution to the *isobaric* specific heat. However, in view of the fact that the vacancy contribution to C_V is generally less than 1%, the corrections suggested in the present paper would not materially change the results of the earlier calculations.

MacDonald and MacDonald[1] carried out a consistent calculation of the thermodynamic properties of monatomic fcc crystals at high temperatures. These properties were obtained from the Helmholtz free energy of the crystal $F(V,T)$ with the help of the appropriate thermodynamic relations.

The crucial point of their treatment was that they have been able to obtain successfully the *volume* dependence of the free energy. Among other properties they have calculated the specific heat at constant volume (C_V) and constant pressure (C_p).

Subsequently MacDonald, Shukla, and Kahaner[2] calculated the thermodynamic properties of alkali metals at high temperatures by employing a second-neighbor, central-force model of the bcc lattice. The same model was recently applied by MacDonald and Shukla[3] to the transition metals V, Nb, Ta, Mo, and W.

It is the object of the present paper to indicate that when the theoretical results are compared with the experimental data, one should consider that in the high-temperature region the vacancy contribution to the C_V value is significantly different from the corresponding contribution to the C_p value.

MacDonald and Shukla[3] assume that the lattice, electrons, and vacancies make additive contributions to the specific heat at constant volume, i.e.,

$$C_V^{\text{theor}} = C_V^l + C_{\text{el}} + C_{\text{vac}} . \tag{1}$$

The last term has been calculated from the relation [see Eq. (15) of Ref. 3]

$$C_{\text{vac}} = R\left[\frac{h^f}{kT}\right]^2 \exp\left[\frac{s^f}{k}\right] \exp\left[-\frac{h^f}{kT}\right] , \tag{2}$$

where s^f and h^f are, respectively, the entropy and enthalpy[4-7] of formation of single vacancies, k is Boltzmann's constant, and R is the gas constant.

MacDonald and Shukla[3] have estimated the quantity C_{vac} by using the experimental h^f and s^f values given in Ref, 8; then by inserting theoretical values of C_V^l and C_{el} to Eq. (1) they have estimated the quantity C_V^{theor} and compared it with C_V^{expt} where C_V^{expt} is determined from experimental quantities according to the thermodynamic relaxation

$$C_V = C_p(1 + TV\beta^2 B_s / C_p)^{-1} , \tag{3}$$

where B_s denotes the adiabatic bulk modulus and β the (volume) thermal expansion coefficient.

Current aspects of the contribution of vacancies to the specific heat. One defines as the contribution of vacancies to the specific heat the excess of the specific heat of a *real* crystal over that of a *perfect* crystal (see Ref. 4 and p. 86 of Ref. 7); the latter has therefore to be definitely stated in each case. As explained in Refs. 4–7 two types of *perfect* crystals have to be considered: (a) The *isobaric* perfect crystal (with specific heats C_p^0 and C_V^0) and (b) the *isochoric* perfect crystal (of which the specific heats C_p^* and C_V^{0*} are different from those of the isobaric perfect crystal just mentioned).

Therefore, when dealing with the contribution of vacancies to the specific heat C_V one has to consider either $C_V - C_V^0$ or $C_V - C_V^{0*}$. These quantities are given by[7]

$$C_V - C_V^0 = \frac{nu^{*2}}{kT^2} + n(c_p - \beta^2 T v^f B) , \tag{4}$$

$$C_V - C_V^{0*} = \frac{nu^{*2}}{kT^2} + nc_V , \tag{5}$$

where $c_p \equiv dh^f/dT\,|_p$, $c_V \equiv du^*/dT\,|_V$, B is the isothermal bulk modulus, v^f the vacancy formation volume, u^* the isochoric internal energy for the vacancy formation under isochoric conditions, and n denotes the number of vacancies. The latter quantity can be equivalently calculated from the following relations (N is Avogadro's number):[7]

$$\frac{n}{N} = \exp\left[\frac{s^f}{k}\right] \exp\left[-\frac{h^f}{kT}\right] \tag{6}$$

or

$$\frac{n}{N}=\exp\left[\frac{s^*}{k}\right]\exp\left[-\frac{u^*}{kT}\right], \tag{7}$$

where s^* denotes the entropy for vacancy formation under isochoric conditions.

In most cases the quantities $c_p-\beta^2Tv^fB$ and c_V are appreciably smaller than u^{*2}/kT^2 and hence Eqs. (4) and (5) coincide with the following approximate relations:

$$C_V-C_V^{0*}=\frac{nu^{*2}}{kT^2},$$

$$C_V-C_V^0=\frac{nu^{*2}}{kT^2},$$

or by using Eq. (6),

$$C_V-C_V^0=R\left[\frac{u^*}{kT}\right]^2\exp\left[\frac{s^*}{k}\right]\exp\left[-\frac{h^f}{kT}\right]. \tag{8}$$

This relation provides a first approximation of the contribution of vacancies to the isochoric specific heat and should be compared with Eq. (2). As we shall see, the quantities C_{vac} and $C_V-C_V^{0*}$ differ by a significant factor.

By considering that (see p. 45 of Ref. 7)

$$u^*=h^f-Tv^f\beta B,$$

a combination of Eqs. (8) and (2) gives

$$(C_V-C_V^{0*})/C_{\text{vac}}=\left[1-\frac{Tv^f\beta B}{h^f}\right]^2. \tag{9}$$

In other words, Eq. (9) gives the ratio of the "true" contribution of vacancies to the specific heat C_V over that estimated by R. MacDonald and co-workers. It should be clarified that this equation is valid for any pressure.

In order to get an idea of the values of $(C_V-C_V^*)/C_{\text{vac}}$ we proceed to an application of Eq. (9) to the transition metals (V, Nb, Ta, Mo, and W) studied by MacDonald and Shukla.[3] The application is carried out at a high temperature (e.g., $T/T_M=0.93$) where the contribution of vacancies is expected to be significant. For the sake of comparison we also apply Eq. (9) to a fcc metal (e.g., Al) and a bcc metal (e.g., Na). Note that due to the lack of direct experimental v^f values for the transition metals we have used the approximation $v^f/\Omega=0.4$ (Ω is the mean volume per atom) with a plausible uncertainty of no more than 25%.

Furthermore note that the B values of V, Ta, and Mo are obtained from the B_s values of Ref. 9 with the help of the thermodynamic relation

$$B^{-1}=B_s^{-1}+\frac{\beta^2TV}{C_p}. \tag{10}$$

An inspection of Table I indicates the following.

1. For the transition metals Eq. (2) overestimates the contribution of vacancies to the C_V value by an amount which (for $T/T_M=0.93$) lies between 50% and 130%.

2. For the case of Al the above overestimation is appreciably larger; for $T/T_M=0.98$, Eq. (2) leads to a vacancy contribution larger by a factor of 4–5 than the

TABLE I. Vacancy formation parameters and bulk properties used in the application of Eq. (9).

	T (K)	T/T_M	β (10^{-5} K^{-1})	B (10^{11} N/m^2)	Ω (10^{-29} m^3)	$\frac{v^f}{\Omega}$	h^f (eV)	$T\beta Bv^f$ (eV)	$\left[1-\frac{T\beta Bv^f}{h^f}\right]^2$
V	2011	0.930	5.16[a]	1.012[b]	1.482[c]	0.4	2.10[d]	0.389	0.66
Nb	2550	0.930	3.01[a]	1.29[e]	1.92[c]	0.4	2.60[d]	0.475	0.67
Ta	3040	0.930	6.50[a]	1.02[f]	1.92[c]	0.4	2.80[d]	0.970	0.43
Mo	2688	0.930	4.50[a]	1.73[g]	1.65[h]	0.4	3.00[d]	0.864	0.51
W	3425	0.930	3.48[a]	2.22[i]	1.683[i]	0.4	4.00[d]	1.111	0.52
Al	913	0.978	11.21[j]	0.57[j]	1.751[k]	0.6	0.76[l]	0.501	0.25
							0.66[m]	0.577	0.18
Na	370.2	0.998	23.17[n]	0.057[n]	4.007[n]	0.4	0.42[o]	0.049	0.78

[a] From Ref. 3 of Ref. 31.

[b] By inserting into Eq. (10) the following values: B_s from Ref. 9, C_p from Fig. 5 of Ref. 3, V from Fig. 1 and Table III of Ref. 3.

[c] From Fig. 1 and Table III of Ref. 3.

[d] Reference 8.

[e] By inserting into Eq. (10) the following values: B_s from Ref. 10, C_p from Ref. 11, and V from Fig. 1 and Table III of Ref. 3.

[f] By inserting into Eq. (10) the following values: B_s from Ref. 9, C_p from Ref. 11, and V from Fig. 1 and Table III of Ref. 3.

[g] By inserting into Eq. (10) the B_s value that results from a linear extrapolation of the adiabatic elastic data given in Ref. 9, for temperatures up to 2300 K; furthermore we have used the data of C_p and V depicted in Figs. 6 and 8 of Ref. 12.

[h] From Fig. 8 of Ref. 12.

[i] Reference 7, p. 221.

[j] Reference 13.

[k] Reference 7, p. 170

[l] Reference 14.

[m] Reference 15.

[n] Reference 7, p. 201.

[o] From Table IV of Ref. 2.

"true" one, given by Eq. (9). On the other hand, for the case of Na the overestimation is only around 30%.

By summarizing we can state from the contribution of vacancies to C_V is calculated from Eq. (8) and not from Eq. (2). As explained in Ref. 7 the latter equation is an appropriate one only for the case when one is interested in the vacancy contribution to C_p. In view of the fact that the vacancy contribution to C_V is generally less than 1%, the corrections suggested in the present comment would not materially change the results of Refs. 1–3.

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