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Thermodynamic properties of bcc crystals at high temperatures: The transition metals

Rosemary A. MacDonald
Thermophysics Division, National Bureau of Standards, Gaithersburg, Maryland 20899

Ramesh C. Shukla
Department of Physics, Brock University, Saint Catharines, Ontario, Canada L2S 3A1

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The second-neighbor central-force model of a bcc crystal, previously used in lowest-order anharmonic perturbation theory to calculate the thermodynamic properties of the alkali metals, is here applied to the transition metals V, Nb, Ta, Mo, and W. The limitations of the model are apparent in the thermal-expansion results, which fall away from the experimental trend above about 1800 K. The specific heat similarly fails to exhibit the sharp rise that is observed at higher temperatures. A static treatment of vacancies cannot account for the difference between theory and experiment. The electrons have been taken into account by using a model that specifically includes d-band effects in the electron ground-state energy. The results thus obtained for the bulk moduli are quite satisfactory. In the light of these results, we discuss the prerequisites for a better treatment of metals when the electrons play an important role in determining the thermodynamic properties.

I. INTRODUCTION

Since the first investigation by Fine[1] of the lattice dynamics of tungsten, several calculations for the other transition metals using Born—von Kármán force constants have been reported in the literature.[2–5] These calculations have primarily been concerned with the harmonic properties. The harmonic force constants for interactions between nearest and next-nearest neighbors have been determined from the elastic constants. The extension of these models for the investigation of the anharmonic properties of transition metals is not feasible. More recently, some attempts have been made[6,7] to formulate a theory where the dynamical matrix is broken down into the contributions from the various sources such as ions, electrons, etc., but the short-range interaction is still fitted to elastic constants. The extension of this approach to study the anharmonic properties of transition metals is also not feasible.

The reason for this impasse is that the lowest-order anharmonic perturbation-theory calculation of the Helmholtz free energy $F(V,T)$ for volume V and temperature T requires knowledge of the anharmonic force constants. These force constants can be determined from the third- and fourth-order elastic constants, if known, but they have not been measured for the transition metals. Even if such a model can be constructed, it is difficult to include the volume dependence of the free energy.

Recently, we have presented a well-defined procedure for calculating the anharmonic properties of fcc and bcc metals, using a modified Morse potential to represent the atomic interactions. The procedure was successfully applied by Shukla and MacDonald[8] and MacDonald and MacDonald[9] to the fcc metals in the nearest-neighbor approximation. $F(V,T)$, and thence the other thermodynamic properties, viz., the thermal expansion ε, the coefficient of linear expansion α, the isothermal and adiabatic bulk moduli B_T and B_S, respectively, and the specific heats at constant volume and constant pressure, C_V and C_P, respectively, were calculated for Cu, Ag, Ca, Sr, Al, Pb, and Ni. The same procedure has been applied to the alkali metals.[10] In the latter case, the calculation is complicated by the fact that a second-neighbor model is required for bcc metals because the first- and second-neighbor distances are nearly equal.[11] The exact calculation of the harmonic and anharmonic contributions to $F(V,T)$ now requires the calculation of 25 Brillouin-zone sums. These sums were evaluated for a range of volumes characterized by the three dimensionless parameters $\kappa_1,\kappa_2,\kappa_3$,[10] which depend on the first and second derivatives of the potential function $\varphi(r)$ evaluated at the nearest- and next-nearest-neighbor distances r_1 and r_2, respectively. For the alkali metals, this theory represented ε very well. The calculated C_V (after allowance for the vacancy contribution) were found to agree with experiment with 3%, but the agreement for C_P was not so good (within 6% of experimental values), largely, in our view, because the electrons were treated additively.

Since our interest in calculating the anharmonic contribution to the thermodynamic properties of crystals was aroused by the observation of exceptionally high heat capacities in the transition metals at high temperatures,[12–16] it is of particular interest to apply the theory outlined above to these metals also. This can be done directly for the thermal expansion and the lattice contribution to the specific heat and bulk modulus. In a preliminary report,[17] we have presented the results for ε and C_V^l, the lattice contribution to C_V, of niobium and tungsten, as representative of the 5-valent and 6-valent metals, respectively. However, because of the d-band electrons in the transition metals, the electron contribution to the thermodynamic properties must be treated differently from that for the alkali metals, though it will still be assumed to be additive.

TABLE I. Data used to obtain the potential parameters: The Debye temperature Θ_D (Ref. 18), the sublimation energy U (Refs. 19 and 20), and the lattice spacing a_0 at 0 K (Refs. 18 and 21). Parameters for the modified Morse potential in a second-neighbor model of the bcc lattice: $\varphi(r)=[D_0/(2b^2-1)]\{\exp[-2\alpha b(r-r_0)]-2b^2\exp[-\alpha(r-r_0)/b]\}$.

Metal	r_0 (Å)	α (Å^{-1})	D_0 (10^{-19} J)	b^2	Θ_D (K)	U (kJ/mol)	a_0 (Å)
V	2.7479	0.8963	1.2483	1.20	326	510.95	3.0184
Nb	3.0090	0.7530	1.7582	1.35	241	722.82	3.3017
Ta	2.9790	1.0294	1.9367	1.80	247	781.41	3.2935
Mo	2.8209	1.5135	1.6891	1.20	459	656.55	3.1376
W	2.8331	1.5568	2.1909	1.35	388	848.10	3.1559

In this paper, we present the results we have obtained for the thermodynamic properties of V, Nb, Ta, Mo, and W. Details of the theory pertinent to the transition metals are given in Sec. II. The results for ε, α, B_T, B_S, C_V, and C_P are presented in Sec. III. The discussion in Sec. IV concludes our study of bcc metals.

II. THEORY

Full details of the theory and the method of calculating $F(V,T)$ and its derivatives have been given in Ref. 10. It remains here to give details specifically for the transition metals.

The experimental data[18–21] used to determine the parameters of the modified Morse potential and the values of these parameters are given in Table I. It is also of interest to note the ranges of $\kappa_1,\kappa_2,\kappa_3$ values that are covered by each of the transition metals as it expands, since these are important in determining how well the theory survives its first test, viz., to reproduce the experimental values of the thermal expansion. The κ ranges are given in Table II. We note here that the parameter κ_2 lies in the range $0<\kappa_2<0.05$ for tunsten and also, for most of the temperature range, for molybdenum. This fact posed problems for the accuracy of the numerical procedures used to calculate the derivatives of $F(V,T)$ on two counts. First, the values $\kappa=0,0.05$ were the two lowest values of κ_2 used as mesh points in the interpolation procedure that evaluates the Brillouin-zone sums at any point $(\kappa_1,\kappa_2,\kappa_3)$, i.e., at any volume V. Second, κ_2 is defined as the difference between two terms that are nearly equal in these metals, viz.,

$$\begin{aligned}\kappa_2&=[\varphi''(r_2)-\varphi(r_2)/r_2]/B\\&=[\varphi''(r_2)/B]-\kappa_3\\&=\kappa_2'-\kappa_3\,,\end{aligned}\tag{1}$$

where

$$B=[\varphi''(r_1)-\varphi'(r_1)/r_1]\,.$$

To remedy the situation, the Brillouin-zone sums were evaluated for a new mesh of points with κ_2 in the range $0<\kappa_2<0.1$ and further, the parameter $\kappa_2'=\kappa_2+\kappa_3$ was used instead of κ_2 [see Eq. (1)]. With these two changes, satisfactory values of d^2F/dr^2 were obtained. Similar changes were made for tantalum, where the largest κ_2 value is only 0.12, and there was a significant improvement in d^2F/dr^2. As a check on the results with the original mesh points, a finer mesh was also used for niobium and vanadium. For niobium, there was a slight improvement, and for vanadium, the finer mesh had negligible effect on the results.

The only significant change in the theory lies in the expression we use for the electron ground-state energy. For the transition metals, it is important to take the d-band electrons into account. To this end we have used the formulation given by Wills and Harrison[22] for the total energy per ion [see Eqs. (2), (12), and (25) in Ref. 22]:

TABLE II. Ranges of lattice spacing r_2 and $\kappa_1,\kappa_2,\kappa_3$ values in the transition metals.

Metal	T (K)	r_2 (Å)	κ_1	κ_2	κ_3
V	0	3.0184	0.876 02	0.249 98	0.041 32
	2000	3.0884	0.936 47	0.208 38	0.057 70
Nb	0	3.3017	0.872 78	0.272 19	0.042 41
	2300	3.3650	0.915 39	0.244 93	0.054 17
Ta	0	3.2935	0.899 35	0.121 66	0.033 55
	3300	3.4133	0.975 09	0.075 91	0.055 17
Mo	0	3.1374	0.910 96	0.054 75	0.029 68
	2650	3.2000	0.960 26	0.003 88	0.040 66
W	0	3.1559	0.914 80	0.039 50	0.028 40
	2560	3.2000	0.943 00	0.010 10	0.034 60

$$E_{\mathrm{el}}=2.21(\hbar^2/2m)Z_s^{5/3}/r_0^2-0.916(e^2/2)Z_s^{4/3}/r_0-(e^2/2)\alpha_M Z_s^2/r_0+1.5e^2r_c^2Z_s^2/r_0^3$$
$$-0.5Z_d(1-Z_d/10)30.9n^{1/2}(\hbar^2/m)r_d^3/r_1^5+nZ_d(11.4)(\hbar^2/m)r_d^6/r_1^8\ , \tag{2}$$

where r_1 is the nearest-neighbor distance, r_0 is the radius of the sphere occupied by one atom, r_d is a characteristic length calculated from band theory, and r_c is the pseudopotential core radius. n is the number of nearest neighbors, e,m are the free-electron charge and mass, respectively, α_M is the Madelung constant, and Z_s,Z_d are the effective charges of the s and d bands, respectively, such that the total ionic charge Z is correct, i.e., $Z=Z_s+Z_d$. For the bcc lattice, r_0 is related to r_1 as follows:

$$r_0=r_1/(\pi\sqrt{3})^{1/3}\ , \tag{3}$$

and therefore Eq. (2) can be expressed in terms of r_1 as follows:

$$E_{\mathrm{el}}=A_1/r_1+A_2/r_1^2+A_3/r_1^3+A_5/r_1^5+A_8/r_1^8\ , \tag{2$'$}$$

where

$$A_1=-(0.916Z_s^{4/3}+\alpha_M Z_s^2)(8\pi/3)^{1/3}\sqrt{3}e^2/4\ ,$$
$$A_2=2.21(\hbar^2/m)0.75(8\pi/3)^{2/3}Z_s^{5/3}\ ,$$
$$A_3=(3\sqrt{3}\,\pi/2)e^2r_c^2Z_s^2\ , \tag{4}$$
$$A_5=Z_d(1-Z_d/10)30.9\sqrt{2}(\hbar^2/m)r_d^3\ ,$$
$$A_8=8Z_d(11.4)(\hbar^2/m)r_d^6\ .$$

By differentiation of Eq. (2′) with respect to r_1, we obtain the following expression for the electron contribution to the isothermal bulk modulus:

$$B_T^{\mathrm{el}}=(2r_1^2/9r_2^3)(4A_1/r_1^3+10A_2/r_1^4+18A_3/r_1^5$$
$$+40A_5/r_1^7+88A_8/r_1^{10})\ . \tag{5}$$

The total isothermal bulk modulus is then given as the sum

$$B_T=B_T^l+B_T^{\mathrm{el}}\ . \tag{6}$$

This is the value to be used in the calculation of the C_P-C_V correction,

$$C_P=C_V^l+C_{\mathrm{el}}+\tfrac{9}{2}N\alpha^2(r^*)^3B_TT\ , \tag{7}$$

where r^* is the equilibrium lattice spacing (second-neighbor distance) at temperature T, and C_{el} is the electronic contribution to the specific heat.

TABLE III. Lattice constant at room temperature, 293 K. Experimental values are taken from Ref. 21.

Metal	r_2 (Å) Theory	Experiment
V	3.0284	3.0231
Nb	3.3097	3.3066
Ta	3.3002	3.2980
Mo	3.1435	3.1405
W	3.1603	3.1586

III. RESULTS

A. Thermal expansion

The equilibrium lattice spacing $r^*(T)$ has been calculated over the desired range of temperature Θ_D to the melting point T_m for the each of the transition metals V, Nb, Ta, Mo, and W. At the reference temperature temperature, 293 K, we obtain quite good agreement with experiment,[21] as shown in Table III. The thermal expansion ε defined by

$$\varepsilon(T)=\frac{r^*(T)-r^*(293\text{ K})}{r^*(293\text{ K})}\ , \tag{8}$$

and the coefficient of linear expansion α,

$$\alpha(T)=\frac{1}{r^*(293\text{ K})}\left[\frac{dr^*}{dT}\right]\ , \tag{9}$$

are then calculated and the results are shown in Figs. 1—3. Comparison with the experimental values[18,23] tells us immediately that the theory will not be successful at temperatures much higher than 1500—2000 K, depending on the metal in question. We attribute this, in the first in-

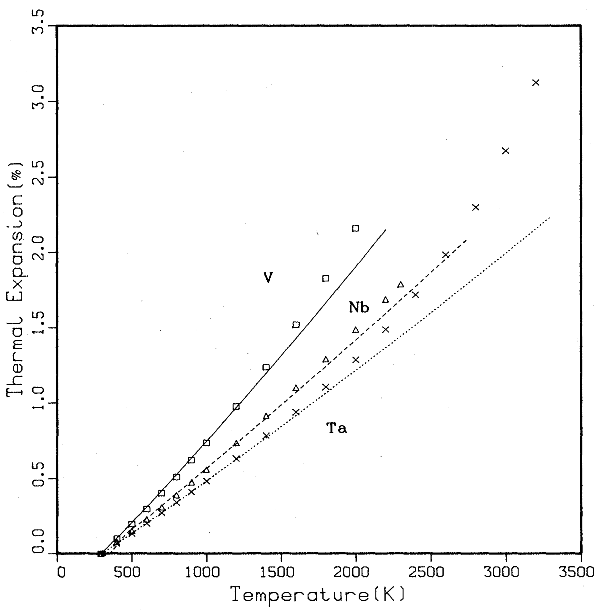

FIG. 1. Thermal expansion $\varepsilon(T)$ of 5-valent transition metals. Vanadium: theory (——), experiment (□); niobium: theory (— — —), experiment (△); tantalum: theory (· · · ·), experiment (×). All experimental values are taken from Ref. 18.

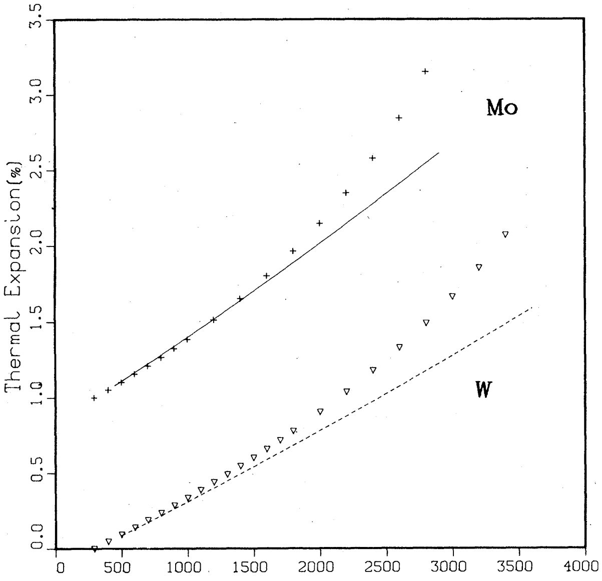

FIG. 2. Thermal expansion $\varepsilon(T)$ of 6-valent transition metals. Molybdenum: theory (——), experiment (Ref. 18) (+). Values have been increased by one unit. Tungsten: theory (— — —), experiment (Ref. 23) (▽).

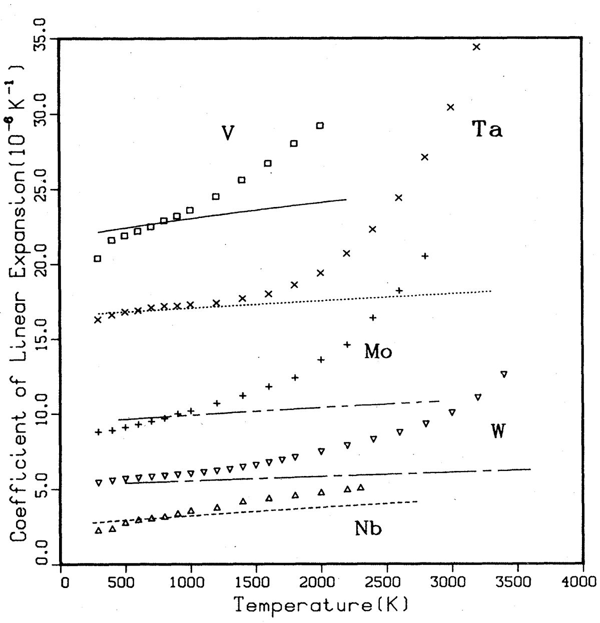

FIG. 3. Coefficient of linear expansion $\alpha(T)$ of vanadium, niobium, tantalum, molybdenum, and tungsten. Theory: V (——), Nb (— — —), Ta (· · · ·), Mo(——), and W (——). Experiment (Ref. 18): V (□), Nb (△), Ta (×), and Mo (+). Experiment (Ref. 23): W (▽). To avoid crossing of the curves, the results for the individual metals have been displaced as follows: V by 12 units, Nb by -5 units, Ta by 10 units, Mo by 4 units, and W by 1 unit.

TABLE IV. Parameters for electron ground-state energy. Total charge Z, d-band effective charge Z_d, d-state radius r_d, and pseudopotential core radius r_c (Ref. 22).

Metal	Z	Z_d	r_d	r_c
V	5	3.5	0.83	0.870
Nb	5	3.5	0.83	1.010
Ta	5	3.5	1.18	1.015
Mo	6	4.5	1.07	0.810
W	6	4.5	1.07	0.676

stance, to the inadequacies of the modified Morse potential as a representation of the interaction between atoms. The corresponding κ_2' values are so small, particularly in tungsten and molybdenum, that, as the lattice expands, we are approaching the unstable situation when $\varphi''(r_2) \leq 0$. For the Rydberg potential, higher values of κ_2' are obtained, but then the expansion is smaller than that observed experimentally over the whole range of temperature, as was the case for the alkali metals.[10] The differentiation necessary to obtain $\alpha(T)$ emphasizes differences between theory and experiment, as shown in Fig. 3.

B. Bulk modulus

The lattice contribution to the isothermal bulk modulus,

$$B_T^l = \frac{2}{9r^*}\left[\frac{d^2F}{dr^{*2}}\right]_{r^*,T} , \tag{10}$$

is about two-thirds of the total contribution (lattice plus electron) to the bulk modulus. The electron contribution $B_T^{\rm el}$ is quite sensitive to the values of r_d and r_c used in Eq. (4). We find that satisfactory results are obtained with the parameter values shown in Table IV. We obtain the adiabatic bulk modulus B_S from the relation

$$\frac{B_S}{B_T} = \frac{C_P}{C_V^l + C_{\rm el}} , \tag{11}$$

where B_T and C_P are given by Eqs. (6) and (7), respectively. We do not include the contribution of vacancies to the specific heat here, since we have no way of estimating their contribution to B_T. The results for all five transition metals are shown in Fig. 4, together with the available experimental values.[24] For Mo and W, there is quite good agreement between theory and experiment. It is less good for the 5-valent metals; certainly the theory cannot produce the upward trend shown in niobium. The slight wiggles in the curves are the result of inaccuracies in the numerical evaluation of d^2F/dr^2 discussed in Sec. II. They carry through to the specific-heat curves also.

C. Specific heat

In this theory, we assume that the lattice, electrons, and vacancies make additive contributions to the specific heat at constant volume, i.e.,

$$C_V^{\rm theor} = C_V^l + C_{\rm el} + C_{\rm vac} , \tag{12}$$

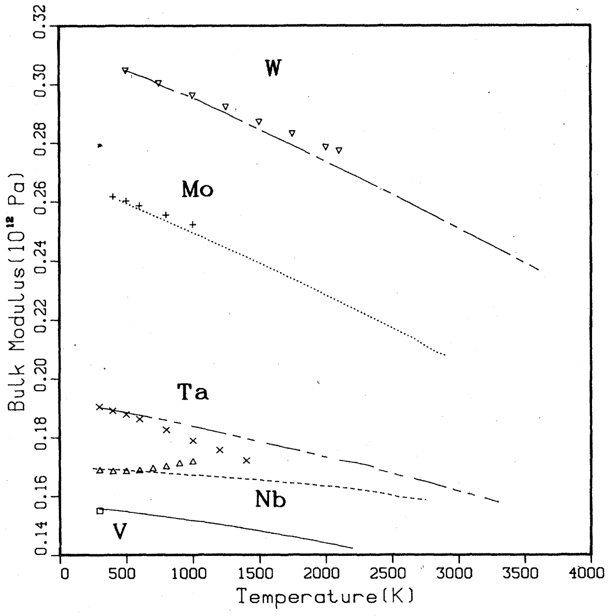

FIG. 4. Adiabatic bulk modulus $B_S(T)$ of the transition metals. Theory: V (——), Nb (— — —), Ta (----), Mo (· · · ·), and W (----). Experiment (Ref. 24): V (□), Nb (△), Ta (×), Mo (+), and W (▽).

where

$$C_V^l = -T\left[\frac{d^2F}{dT^2}\right]_V , \tag{13}$$

$$C_{\mathrm{el}} = \sigma_0 f\left[\frac{r^*(T)}{r^*(0)}\right]^2 T , \tag{14}$$

$$C_{\mathrm{vac}} = R\exp\left[\frac{S_f}{k}\right]\left[\frac{E_f}{kT}\right]^2\exp\left[\frac{-E_f}{kT}\right] . \tag{15}$$

S_f and E_f are, respectively, the entropy and energy of formation of single vacancies, k is Boltzmann's constant, R is the gas constant, and σ_0 is the coefficient of the electronic specific heat at 0 K. The values used for σ_0 (Ref. 25), S_f, and E_f (Ref. 26) are given in Table V. In Eq. (14) we have allowed for an explicit volume dependence of the electronic contribution arising from the volume dependence of the Fermi energy. Furthermore, we have introduced a factor f which represents the modification of the σ_0 values that is necessary if we are to represent the high-temperature density of states in the transition metals. That some modification is called for becomes apparent when we consider the implications of the high σ_0 values of the 5-valent metals. If we obtain C_V^l from Eq. (7) using experimental values for the other terms and with $C_{\mathrm{el}} = \sigma_0 T$ to represent the electronic contribution, we find that C_V^l(expt) is less than the lattice contribution calculated for our model,[17] a result which is quite unacceptable. For the 6-valent metals, the comparatively small values of σ_0 cause the experimental values of C_V^l to be larger than the theoretical values, the more usual result in such a calculation. Justification for a modification of σ_0 is given by Manning and Chodorow in their study of the density of states at the Fermi surface for tungsten and tantalum.[27] According to their estimates, the electron contribution to the specific heat is such that, at 500 K,

$$\sigma = 1.73\sigma_0 \text{ for W} , \tag{16a}$$

$$\sigma = 0.41\sigma_0 \text{ for Ta} , \tag{16b}$$

This estimate for tungsten was substantiated by the experimental data of Magnus and Holzman[28] and it has been further confirmed by the recent results of Ditmars.[29] With these values as a guide for the other transition metals, we have chosen f so that C_V^{theor} is in good agreement with C_V^{expt} near 500 K, where C_V^{expt} is determined from experimental quantities[12–16,18,24] according to the thermodynamic relation

$$C_V = C_P(1 + 9B_S\alpha^2VT/C_P)^{-1} . \tag{17}$$

TABLE V. Parameters for electron and vacancy contributions to the specific heat: The coefficient of electronic specific heat at 0 K, σ_0 (Ref. 25), high-temperature modification factor f (see text), and energy for vacancy formation E_f (Ref. 26). $\exp(S_f/k) = 7.39$ in all cases (Ref. 26).

Metal	σ_0 (10^{-4} J/mol K)	f	E_f (kJ/mol)
V	96.23	0.300	202.6
Nb	78.45	0.200	250.8
Ta	59.83	0.300	270.2
Mo	18.49	1.727	289.4
W	11.31	1.727	385.9

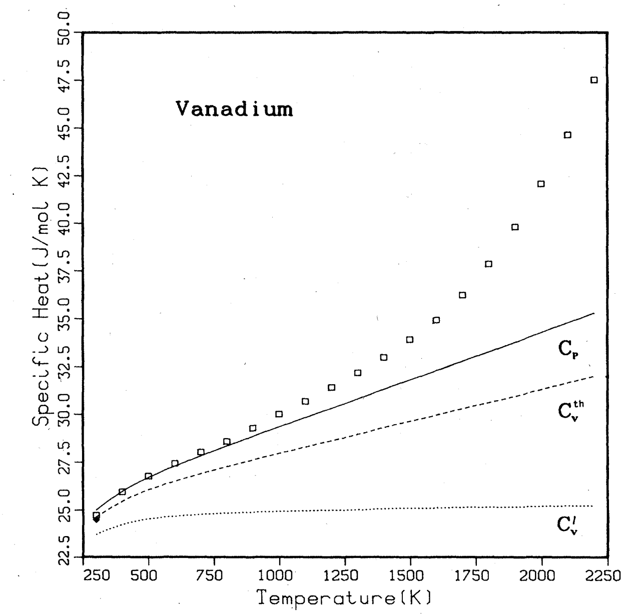

FIG. 5. Specific heat of vanadium. The lattice contribution C_V^l is denoted by a dotted line (· · · ·), the lattice-plus-electron-plus-vacancy contribution C_V^{theor} is denoted by a short dashed line (— — —), and C_P is denoted by a solid line (——). Experimental values of C_P (Ref. 12) are denoted by □. C_V^{expt} is denoted by ◆.

Details of this procedure for niobium and tungsten, as representative of the 5- and 6-valent metals, respectively, have been given in our preliminary report.[17] The values of f used here are given in Table V. We now proceed to calculate C_P, using Eqs. (7), (14) and the vacancy contribution C_{vac} [Eq. (15)]. The results are shown in Figs. 5–9. Although there is reasonable agreement with experiment over the first 1000-K rise in temperature, it is clear that the theory cannot account for the steep rise in specific heat observed at higher temperatures, unless the vacancy concentration is much greater than that derived from positron-annihilation experiments.[26] Not surprisingly, analysis of specific-heat data in terms of vacancy and nonvacancy contributions does indeed yield higher vacancy concentrations.[30,31] For molybdenum, if we use the estimates of Chekhovskoi and Petrov[30] [$E_f = 179.5$ kJ/mol, $\exp(S_f/k) = 50.9$] in Eq. (15), we obtain good agreement with experiment over the whole temperature range. The vacancy concentration is 2.9% at the melting point in this case. However, this analysis makes assumptions about the nonvacancy contribution to the specific heat, precisely the subject of our investigation here, so the parameters cannot be considered independent. Moreover, the analysis of a different set of specific-heat data by Kraftmakher[31] gives significantly different results. The vacancy concentration is 3.8% at the melting point in this case. For these reasons, we consider the vacancy data from positron-annihilation experiments to be the most reliable.

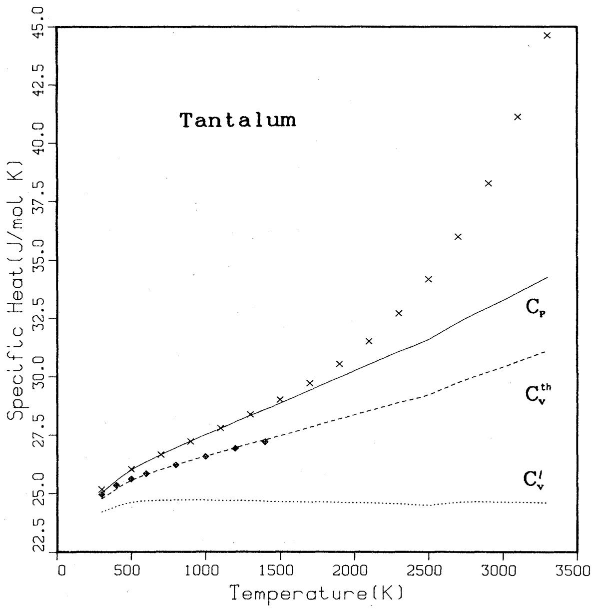

FIG. 7. Specific heat of tantalum. The lattice contribution C_V^l is denoted by a dotted line (· · · ·), the lattice-plus-electron-plus-vacancy contribution C_V^{theor} is denoted by a short dashed line (— — —), and C_P is denoted by a solid line (———). Experimental values of C_P (Ref. 14) are denoted by ×. C_V^{expt} is denoted by ◆.

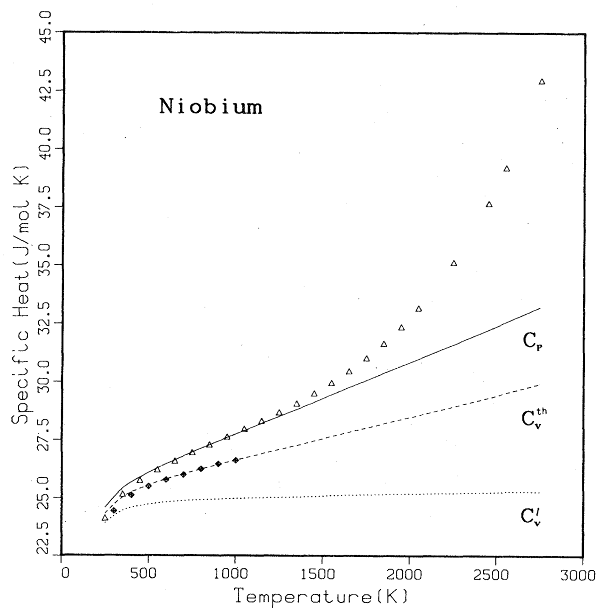

FIG. 6. Specific heat of niobium. The lattice contribution C_V^l is denoted by a dotted line (· · · ·), the lattice-plus-electron-plus-vacancy contribution C_V^{theor} is denoted by a short dashed line (— — —), and C_P is denoted by a solid line (———). Experimental values of C_P (Ref. 13) are denoted by △. C_V^{expt} is denoted by ◆.

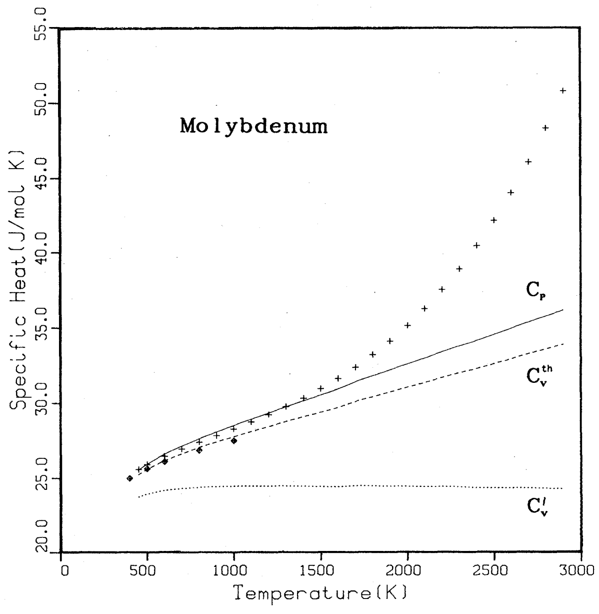

FIG. 8. Specific heat of molybdenum. The lattice contribution C_V^l is denoted by a dotted line (· · · ·), the lattice-plus-electron-plus-vacancy contribution C_V^{theor} is denoted by a short dashed line (— — —), and C_P is denoted by a solid line (———). Experimental values of C_P (Ref. 15) are denoted by +. C_V^{expt} is denoted by ◆.

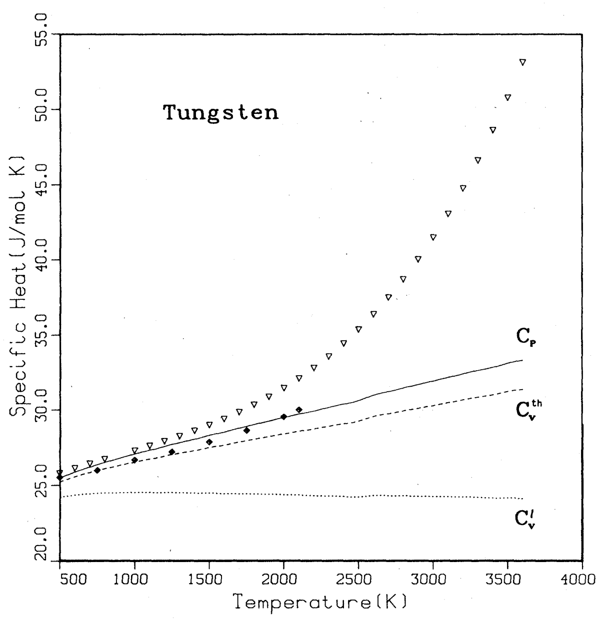

FIG. 9. Specific heat of tungsten. The lattice contribution C_V^l is denoted by a dotted line (· · · ·), the lattice-plus-electron-plus-vacancy contribution C_V^{theor} is denoted by a short dashed line (— — —), and C_P is denoted by a solid line (———). Experimental values of C_P (Ref. 16) are denoted by ∇. C_V^{expt} is denoted by ♦.

IV. DISCUSSION

We have calculated the thermodynamic properties of the transition metals V, Nb, Ta, Mo, and W from the second-neighbor central-force model of a bcc crystal that we used for the alkali metals. The results are reasonable up to about 1800 K, but fail to reproduce the rapid upward trend observed in the thermal expansion and specific heat at higher temperatures. Although we might expect the Morse potential to be a better representation of the interaction potential in the transition metals owing to their large core overlap, the limitations of the theory that were apparent in the alkali-metal results are felt more strongly here. However, we note that C_V^{theor} and C_V^{expt} are in very good agreement over the limited temperature range for which data are available. This was not the case for the alkali metals.

It is possible that higher-order perturbation-theory contributions will improve the theoretical results. For the inert-gas solids, it has been shown that the λ^4 terms[32] produce a significant increase in the specific heat when a Lennard-Jones potential is used.[33] A smaller increase has been obtained with the Morse potential.[34] Although we know that both the sign and magnitude of the lowest-order (λ^2) anharmonic contribution are very sensitive to the interatomic potential used in the model,[35] it is likely that the λ^4 contribution will increase the specific heat of the transition metals also, though not enough to account for the experimental results.

Clearly, the electrons should not be treated additively, as we have done here, but to do otherwise takes us into a vastly more complex situation owing to the long-range nature of the interactions, and the usefulness of our simple approach is lost. In our view, it is the vacancies that are most likely to be responsible for the high-temperature behavior in these crystals. To treat them as static entities is quite inadequate. They need to be treated dynamically if their contribution to the thermodynamic properties is to be correctly represented. Some support for this view is given by our earlier work on rubidium.[36] This Monte Carlo calculation indicated that an increased heat capacity was associated with large-scale atomic motions made possible by the presence of vacancies. Such motion cannot be dealt with by perturbation theory.

This summary of the limitations of the theory concludes our study of bcc metals.

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