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Analysis of thermodynamic properties of molybdenum and tungsten at high temperatures

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Using recent and accurate experimental information on various thermodynamic quantities up to the melting temperature T_f of molybdenum and tungsten, we make a detailed study of some of their high-temperature properties. In particular, we consider the entropy, reduced to a fixed crystal volume, and interpret the result in terms of an electronic part and a temperature-dependent entropy Debye temperature. The analysis reveals large explicit anharmonic effects. When plotted versus the reduced temperature T/T_f, various quantities of Mo and W related to anharmonicity show a striking similarity. For instance, the heat capacity C_P is the same for Mo and W, to better than 1%, for $T/T_f > 0.2$. We also make a detailed study of the temperature dependence of the Grüneisen parameter at constant pressure and at constant volume.

I. INTRODUCTION

An accurate theoretical account of the high-temperature heat capacity and related thermodynamic properties of transition metals has largely been lacking. Recently, it has even been questioned whether such an account in terms of current theories for electrons and lattice vibrations is at all adequate.[1] The analysis is complicated by the fact that simple analytic models, giving a linear temperature dependence of the electronic heat capacity and the low-order anharmonic effects, are insufficient at high temperatures. Further, experimental data near the temperatures of fusion T_f have been uncertain, and sometimes conflicting or lacking. However, the situation in regard to the experiments has improved considerably during the last decade. For instance, the width of the experimental scatter band for C_P data of many transition metals is less than about 9% close to T_f, and also data on the bulk modulus and the thermal expansion are known accurately enough to allow for a meaningful analysis.[1]

Theoretical models often refer to a fixed volume V_0 (e.g., the volume at 298 K), thus avoiding the complications due to the thermal expansion. Thermodynamic properties may be considered at constant pressure or at constant volume. As an example, the quantity $C_V=(\partial U/\partial T)_V$ is usually obtained by subtracting from C_P a term that accounts for the expansion of the solid. Then C_V is referred to as the heat capacity at "constant" volume. Actually, the standard $C_P - C_V$ correction implies that the $(\partial U/\partial T)_V$ derivative is evaluated at the volume $V(T,P_0)$ in equilibrium with the constant pressure P_0 at which the measurements were performed. In this paper we shall be particularly interested in properties at fixed volume V_0. Wallace[2] has compared C_V and C_{V_0} for 18 systems, mainly alkali halides and simple metals below 400 K. This paper focuses on transition metals, up to their melting temperature. We choose to consider molybdenum and tungsten, since their extreme melting temperatures ($T_f=2896$ K for Mo and 3695 K for W) cause features we wish to study to be pronounced. The shape of the electron density of states of the solid (bcc) phase, with a deep and broad minimum around the Fermi level, stabilizes the solid relative to the liquid and pushes up the melting temperature. One may thus view bcc Mo and W at high temperatures as "overheated" solids, which make them favorable for a study of high-order anharmonic effects in the lattice vibrations.

In a previous paper[3] we gave a qualitative account of many exceptional thermodynamic properties of tungsten, relying on the shape of the electron density of states. Those results remain valid, but we shall here reconsider W and extend the discussion to properties at fixed volume, using more recent experimental data. The analysis of molybdenum is presented in detail. That includes a critical evaluation of the heat capacity, the enthalpy, and the pressure and temperature dependence of the molar volume, from which we calculate the entropy $S(T,V_0)$ at fixed volume V_0. The contribution to S from conduction electrons is evaluated from the electron band structure. The remainder in S, of vibrational origin, gives information about the low- and higher-order anharmonic corrections. We shall also study in detail the temperature dependence of the Grüneisen parameter and comment on striking similarities between molybdenum and tungsten when some of their properties are compared at equal reduced temperatures T/T_f.

II. MICROSCOPIC THERMODYNAMICS

A. Electronic entropy

The entropy of the conduction electrons may be written, in terms of the Fermi-Dirac function f and the density of states $N(E)$,

$$S_{\text{el}}=-2k_B\int\{f(E)\ln f(E)+[1-f(E)]\ln[1-f(E)]\}N(E)dE\ . \qquad (1)$$

When $N(E)$ is constant within the energy range around the Fermi level where the integral in (1) gets its essential contributions, one obtains the usual linear dependence on the temperature T, $S_{\text{el}}=\gamma_b T$. For Mo and W this is not a valid approximation, and S_{el} has to be evaluated numerically, taking $N(E)$ from a band-structure calculation.[4] At the temperatures of interest here, there is no electron-phonon many-body correction for $N(E)$ or γ_b. However, the finite-electron lifetime due to the electron-phonon interaction leads to a broadening of the electron states, which should be accounted for in $N(E)$. We neglect this effect, which may lead to an underestimate of our parameter Θ_S by 1–2 % at T_f.[5]

B. Vibrational entropy

The entropy of harmonic lattice vibrations can be written

$$S_{\text{harm}}=k_B\sum_{\mathbf{q},s}\{[1+n(\mathbf{q},s)]\ln[1+n(\mathbf{q},s)]-n(\mathbf{q},s)\ln[n(\mathbf{q},s)]\}\ . \qquad (2)$$

The sum goes over all phonon states $(\mathbf{q},s)$ of wave vector $\mathbf{q}$ and mode index s. The Bose-Einstein functions n depend on the phonon frequencies $\omega(\mathbf{q},s)$. One can show[6] that in an anharmonic system and to lowest order, the entropy is correctly given by (2) if all ω are replaced by the shifted frequencies $\omega+\Delta_2+\Delta_3+\Delta_4$. Here Δ_2 refers to the effect of thermal expansion and Δ_3 and Δ_4 are the low-order shifts at fixed volume. All three shifts Δ vary linearly with T.

It is convenient to represent the vibrational entropy of a system by an entropy Debye temperature Θ_S chosen such that when Θ_S is inserted in a standard Debye model, it reproduces the experimental vibrational entropy. In a real system, $\Theta_S(T)$ is temperature dependent at low temperatures ($T<\Theta_S$) because the system does not have a true Debye spectrum, and at high temperatures ($T>\Theta_S$) because of anharmonic effects. The low-order anharmonic effects referred to above would affect Θ_S linearly in T. Further details on the interpretation of Θ_S are found in an account of simple metals.[7]

The high-temperature expansion of the entropy in the Debye model reads (R is the gas constant)

$$S_D=3R\{\tfrac{4}{3}+\ln(T/\Theta_S)+\tfrac{1}{40}(\Theta_S/T)^2+\cdots\}\ . \qquad (3)$$

Thus, when $T>\Theta_S$, an error ΔS is the entropy is equivalent with a shift $\Delta\Theta$ in Θ_S given by $\Delta\Theta/\Theta_S\approx-\Delta S/(3R)$.

III. MACROSCOPIC THERMODYNAMICS

A. Gibbs energy of a solid

All thermodynamic properties of a solid substance can be obtained if one knows its molar Gibbs energy, $G(T,P)$, as a function of temperature and pressure. Our evaluation of $G(T,P)$ is based on integrating the identity

$$(\partial G/\partial P)_T=V(T,P) \qquad (4)$$

which gives

$$G(T,P)=G(T,0)+\int_0^P V(T,P')dP'\ . \qquad (5)$$

The Gibbs energy function at zero pressure, $G(T,0)$, can be obtained from heat capacity, enthalpy, and entropy data. $V(T,P)$ is assumed to follow the Murnaghan[8] equation of state,

$$V(T,P)=V(T,0)[1+nP/B_T(T,0)]^{-1/n}\ . \qquad (6)$$

for pressures up to about 50 GPa (cf. Sec. IV B). In Eq. (6) B_T is the isothermal bulk modulus, n is the pressure derivative of B_T and assumed to be independent of P and T (cf. below), and $V(T,0)$ is determined from data on the thermal expansion versus the temperature. Equation (6) leads to a closed-form expression for the pressure contribution to the Gibbs energy in Eq. (5).[9] Once $G(T,P)$ is evaluated from experimental data, as will be discussed in Sec. IV, one can obtain various properties of the solid by using a computer program package for general thermodynamic calculations.[10]

B. Volume dependence of the heat capacity

Our evaluation of $G(T,0)$ in Eq. (5) uses as input information the heat capacity $C_P(T,P_0)$ obtained in experiments at constant (atmospheric) pressure P_0. From that we obtain the heat capacity C_V, corresponding to the equilibrium volume $V(T,P_0)$ at $P=P_0$, through

$$C_V=C_P-\alpha^2VB_TT\ . \qquad (7)$$

Here α is the thermal-expansion coefficient. The reduction of C_V to fixed volume [e.g., the equilibrium volume $V_0=V(T_0,P_0)$ where $T_0=298.15$ K and $P_0=1$ atm] involves an integration of the thermodynamic relation

$$(\partial C_V/\partial V)_T=T(\partial^2P/\partial T^2)_V \qquad (8)$$

which, combined with the identity

$$(\partial P/\partial T)_V=\alpha B_T\ , \qquad (9)$$

leads to

$$\begin{aligned}(\partial C_V/\partial V)_T&=[(C_P-C_V)/V][(1/\alpha^2)(\partial\alpha/\partial T)_P\\&\quad+(2/\alpha B_T)(\partial B_T/\partial T)_P\\&\quad+(\partial B_T/\partial P)_T]\\&=[(C_P-C_V)/V](\epsilon-2\delta_T+n)\ . \qquad (10)\end{aligned}$$

The last equality defines the dimensionless parameters n [cf. Eq. (6)], the Anderson-Grüneisen parameter[11] δ_T related to the isothermal bulk modulus, and ϵ.

C. Thermodynamic Grüneisen parameter

The thermodynamic Grüneisen parameter γ_G is often defined as

$$\gamma_G=\alpha V B_T/C_V \ . \qquad (11)$$

In theoretical work, the most convenient variables are T and V. Equation (11), combined with (9) and the Maxwell relation

$$(\partial S/\partial V)_T=(\partial P/\partial T)_V \ , \qquad (12)$$

yields

$$\gamma_G(T,V)=(V/C_V)(\partial P/\partial T)_V=(V/C_V)(\partial S/\partial V)_T \ . \qquad (13)$$

Experiments usually refer to the variables T and P_0. We find it convenient to use the expression

$$\gamma_G(T,P_0)=A(T,P_0)/[1-\alpha A(T,P_0)T] \ , \qquad (14)$$

containing the dimensionless quantity $A(T,P_0) \equiv \alpha V B_T/C_P$. Often, $\alpha A T \ll 1$, cf. Sec. V B.

IV. TREATMENT OF EXPERIMENTAL INFORMATION

A. General considerations

Following previous work on transition metals[12,13] the evaluation of the $G(T,P)$ functions for Mo and W uses polynomial representations for $C_P(T,0)$, $\alpha(T,0)$, and the isothermal compressibility $K_T(T,0)=1/B_T(T,0)$;

$$C_P(T,0)=C_0/T^2+C_1+C_2T+C_3T^2+C_4T^3 \ , \qquad (15)$$

$$\alpha(T,0)=a_1+a_2T+a_3T^2 \ , \qquad (16)$$

$$K_T(T,0)=k_1+k_2T+k_3T^2 \ . \qquad (17)$$

The constants in Eqs (15)–(17) were determined by searching for the best fit to experimental data. We used a computer program[14] for the optimization of thermodynamic model parameters, which can treat simultaneously various types of experimental data. The program minimizes the square sum of the differences between experimental and calculated values, while giving each piece of information a certain weight. The weights are selected by personal judgment, and changed by trial and error during the work, until the input data are accounted for within the expected uncertainty limits.

The n parameter in Eq. (6) was not determined by optimization but taken from ultrasonic measurements of the pressure dependence of the bulk modulus at room temperature. Those measurements give information on $(\partial B_S/\partial P)_T$ where B_S is the isentropic bulk modulus. A derivation of the thermodynamic relation between $(\partial B_T/\partial P)_T$ and $(\partial B_S/\partial P)_T$ has been reported by Overton.[15] Using the dimensionless parameters introduced in Sec. III B we express that relation as

$$(\partial B_T/\partial P)_T-(\partial B_S/\partial T)_T=[(C_P-C_V)/C_P]\{[(C_P-C_V)/C_P][\epsilon+1-(\partial B_S/\partial P)_T]-[\epsilon-2\delta_T+(\partial B_S/\partial P)_T]\} \ . \qquad (18)$$

Using experimental information[16] on $(\partial B_S/\partial P)_T$ at room temperature and zero pressure, i.e. $(\partial B_S/\partial P)_{T_0,0}$, and the values for $\epsilon(T_0,0)$ and $\delta_T(T_0,0)$ obtained in the present work (Sec. V) we find that the difference between n and $(\partial B_S/\partial P)_{T_0,0}$ is very small, viz. 0.5% of $(\partial B_S/\partial P)_{T_0,0}$ for Mo and 0.4% for W, which is probably smaller than the experimental error in the measurement of $(\partial B_S/\partial P)_{T_0,0}$. Therefore we determined the parameter n in Eq. (6) from ultrasonic data at room temperature, using the approximation $n \approx (\partial B_S/\partial P)_{T_0,0}$. The effects of temperature upon the n parameter are further discussed in Sec. V A.

B. Molybdenum

A critical evaluation of the thermodynamic properties of Mo has been given by Fernández Guillermet.[17] The results for $C_P(T,0)$ were directly used here, and the reader is referred to a detailed description[17] of the information used in evaluating the coefficients C_i in Eq. (15). A description of $V(T,0)$ has also been given earlier,[17] based on combining experimental information from x-ray and dilatometric measurements,[18–22] expressed as molar volumes. Here we reanalyzed $V(T,0)$, by adding to the data files values of the experimental linear thermal expansion $\Delta l/l_0=[l(T)-l(T_0)]/l(T_0)$ recommended by Touloukian *et al.*,[23] Amatuni *et al.*,[24] and recent results by Miiller and Cezairliyan[25] and Chekhovskoi *et al.*[26] We also compared our calculated $\Delta l/l_0$ with measurements by Suh, Ohta, and Waseda.[27] $B_T(T,0)$ was evaluated from measurements of the elastic constants by Bujard *et al.*[28] for temperatures up to $0.82T_f$. The bulk modulus at higher temperatures was obtained by a smooth extrapolation of their data in a B_S vs T/T_f plot. The pressure dependence of the bulk modulus was described by the room-temperature value $n=4.46$ based on ultrasonic data by Katahara,[16] see above. Using that value and B_T we calculated $V(T,P_0)$ for pressures up to 50 GPa using the Murnaghan model, and found very good agreement with the static compression data of Bridgman[29] and Vaidya and Kennedy[30] using piston-cylinder techniques, by Ming and Manghnani[31] using a high-pressure x-ray cell, and with the $V(T_0,P)/V(T_0,P_0)$ ratios recommended by Kennedy and Keeler[32] and Mao *et al.*[33] An analysis of Hugoniot data from shock-wave experiments referred to in Sec. V A also indicates that the Murnaghan equation of state accounts reasonably well for the P-V relation of Mo for pressures up to about 50 GPa.

C. Tungsten

The parameters C_i in $C_P(T,0)$ of tungsten were taken from an analysis by Gustafson,[34] who used heat-capacity,[35,36] enthalpy,[35,37] and room-temperature entropy[35] data. His description of C_P agrees well with the values recently recommended by the CODATA (Committee on Data for Science and Technology) group;[38] see a comparison in Fig. 2 of Ref. 3. The parameters describing $V(T,0)$ [Eq. (6)] were evaluated in the present work by treating simultaneously molar-volume data from high-temperature x-ray measurements[20] and values of $\Delta l/l_0$ recommended by the CODATA group[39] and determined by Miiller and Cezairliyan[40] using a subsecond technique. We also compared our calculated $\Delta l/l_0$ values with those previously reported by Kirby,[41] Pethukov and Chekhovskoi,[21] those recommended by Touloukian *et al.* (Ref. 23, p. 354), and recent measurements by Suh, Ohta, and Waseda.[27] The isothermal bulk modulus $B_T(T,0)$ was evaluated from the measured elastic constants of W at room temperature[42,43] and at temperatures up to 2073 K,[44] as tabulated by Simmons and Wang.[45] Values for B_S at high temperatures were estimated by us through a smooth extrapolation in a B_S vs T/T_f plot. The pressure dependence of the bulk modulus was described by the room-temperature value $n=4.32$, based on ultrasonic data by Katahara.[16] It yields $V(T_0,P)$ in agreement with the static-compression data obtained by Ming and Manghnani[31] for pressures up to about 10 GPa.

V. RESULTS

In this section we shall examine quantities like ϵ, δ_T, and γ_G, which play a key role in the reduction of measured data to the condition of a fixed volume, and in an account of the thermodynamic behavior of solids. We shall also compare the effect of temperature on various thermodynamic properties of Mo and W, and investigate the consequences of adopting T/T_f as a variable in treating high-temperature data.

A. Volume effects on C_V and S

The volume effect on C_V was expressed by Eq. (10) in terms of the dimensionless parameters n, δ_T, and ϵ. Wallace[2] examined thermodynamic data on various substances, mainly simple metals and alkali halides, and noted that there is often a strong cancellation between the terms in $\epsilon-2\delta_T+n$. The sign of this sum may even change with temperature, for a given solid. We study this issue for Mo and W, using the thermodynamic description of the preceding section. Calculated values of ϵ and $-2\delta_T$, as a function of T/T_f at $P=0$, are given in Table I, together with the differences ΔC_V and ΔS between the values corresponding to the equilibrium volume at zero pressure $V(T,0)$ and to fixed volume $V(T_0,0)$. ΔC_V was calculated (a) from Eq. (10) by neglecting the volume dependence of the right-hand side, i.e., as

$$\Delta C_V \approx (\Delta V/V)(C_P-C_V)(\epsilon-2\delta_T+n) \qquad (19)$$

and, (b), from the full $G(T,P)$ function evaluated before. There is a strong cancellation between ϵ and $-2\delta_T$ for Mo and W, at high temperatures. The difference ΔC_V is an appreciable fraction of C_P-C_V as derived from Eq. (7), viz. 8% at $T/T_f=0.3$ and as much as 40% when $T=T_f$. Neglecting the volume dependence of the right-hand side in Eq. (10) leads to an underestimate of the correction to fixed volume, and the error increases with T.

The calculations in Table I were based on the assumption that the Murnaghan parameter n does not vary with T, an approximation necessitated by the lack of direct measurements of $(\partial B_T/\partial P)_T$ at high temperatures. In connection with our analysis of the vibrational entropy at fixed volume it is important to know how large would be the effect of a change in n. We study that by performing a series of calculations at $T=T_f$ where the Murnaghan parameter is given values between $n'=0.3n$ and $n'=1.7n$, and n is the experimental value at T_0,P_0. The effect of those variations in n upon the heat capacity at fixed volume V_0, C_{V_0} (ΔC_{V_0}), and S (ΔS) is shown in Table II. The effect upon C_{V_0} at the melting point would be comparable to the difference $\Delta C_V=C_P-C_V$, shown in Table I, only if the Murnaghan parameter at $T=T_f$ has changed by ±70% of its room-temperature value. It is therefore important to know whether such a large increase is reasonable for the elements Mo and W. This problem was studied for Mo by performing a thermodynamic analysis of shock-wave data, using a method previously applied[13] to Zr. The analysis of bcc Mo will be reported elsewhere.[46] It treated information on the pressure, the volume, and the internal energy of samples studied in the shock-wave experiments by McQueen *et al.*[47] starting from 293 K and by Miller, Ahrens, and Stolper[48] starting from 1673 K. The thermodynamic

TABLE I. Comparison of calculated thermodynamic quantities corresponding to the equilibrium volume at zero pressure $V(T,0)$ and to fixed volume $V(T_0,0)$.

Element	T/T_f	ϵ	$-2\delta_T$	n	$\epsilon-2\delta_T+n$	ΔC_V[a] J/K mol	ΔC_V[b] J/K mol	ΔS[b] J/K mol	$\Delta S/3R$ (%)	C_P-C_V J/K mol	$\Delta C_V/(C_P-C_V)$ (%) from a	(%) from b
Mo	0.3	21.274	−13.178	4.46	12.556	0.075	0.073	0.377	1.5	0.649	11.6	11.2
	0.5	16.872	−13.018	4.46	8.314	0.272	0.272	0.982	3.9	1.579	17.2	17.2
	0.8	11.438	−11.278	4.46	4.620	0.850	0.967	2.485	10.0	4.263	19.9	22.7
	1.0	8.812	−9.826	4.46	3.446	1.560	2.022	4.056	16.3	7.298	21.4	27.7
W	0.3	14.589	−11.906	4.32	7.003	0.059	0.057	0.488	2.0	0.734	8.0	7.8
	0.5	14.570	−11.689	4.32	7.201	0.284	0.288	1.132	4.5	1.665	17.1	17.3
	0.8	11.381	−9.905	4.32	5.796	1.219	1.387	2.764	11.1	4.483	27.2	30.9
	1.0	9.027	−8.466	4.32	4.881	2.58	3.205	4.586	18.4	7.939	32.5	40.4

[a] First-order approximation, Eq. (19).

[b] From the full $G(T,P)$ expression, evaluated in Sec. IV.

TABLE II. Effect of changes in the Murnaghan parameter n on C_{V_0} and S at $T=T_f$, $V=V_0$.

Element	n'/n	ΔC_{V_0} J/K mol	ΔS J/K mol	$\Delta S/3R$ (%)
Mo	0.3	1.664	0.415	1.7
	0.5	1.222	0.302	1.2
	0.8	0.627	0.261	1.0
	1.0	0	0	0
	1.2	−0.540	−0.130	−0.5
	1.5	−1.409	−0.334	−1.3
	1.7	−2.031	−0.477	−1.9
W	0.3	1.988	0.486	1.9
	0.5	1.460	0.354	1.4
	0.8	0.610	0.146	0.6
	1.0	0	0	0
	1.2	−0.647	−0.152	−0.6
	1.5	−1.690	−0.393	−1.6
	1.7	−2.439	−0.562	−2.3

description of the present paper was used, but the parameter n in Eq. (6) was allowed to vary linearly with temperature. From a consideration of the data on the low-pressure range ($P \leq 50$ GPa) an average increase in n with temperature, $\Delta n/\Delta T = 7.3\times10^{-5}$ K^{-1}, was obtained.[46] That implies an increase in n by $\Delta n = 0.19$ between 298.15 K and T_f, which corresponds to $n' = 1.04n$ and leads to an effect upon $\Delta S/(3R)$ (Table II) smaller than 0.5%. Since $\Delta\Theta_S/\Theta_S \approx -\Delta S/(3R)$ (Sec. II B) we conclude that the approximation of a constant n probably affects our Θ_S (Sec. VI) at T_f by less than 1%.

The calculations in Tables I and II were directed at studying the behavior of the various thermodynamic quantities involved in the correction to fixed volume. The C_{V_0} values finally obtained from $C_P(T,P_0)$ of Mo and W are plotted in Figs. 1(a) and 1(b), respectively. We also give values for the vibrational part, C_{vib}, obtained by subtracting from C_{V_0} the electronic heat capacity (Sec. II A).

B. Temperature effects on the Grüneisen parameter

The properties of the Grüneisen parameter are of interest in the analysis and extrapolation of termophysical[1] and equation-of-state[49] data for solids, and in the treatment of anharmonic shifts in the phonon frequencies.[50] Analyses of experimental data in terms of Eq. (11), with C_V corresponding to $V(T,P_0)$, often show a weak variation of $\gamma_G(T,P_0)$ with T, and it has been suggested[1] that such a regular behavior can be used to detect errors in C_P or α. Since our treatment of experimental data for Mo and W does not involve explicit assumptions or approximations about the Grüneisen parameter, it allows us to study the variation of $\gamma_G(T,P_0)$ in a large temperature range. In Figs. 2(a) and 2(b) we give $\gamma_G(T,P_0)$ as a function of T/T_f, for Mo and W. Within the temperature range $0.1 < T/T_f < 1$, $\gamma_G(T,P_0)$ deviates from its mean value by less than 10%, with a decrease above $T/T_f = 0.65$. We can gain insight on its behavior from expression (14). Its denominator, $1-\alpha AT$, varies linearly with T/T_f, whereas $A(T,P_0) = \alpha V B_T/C_P$ decreases with T at high temperatures, due to the rapid increase in C_P, cf. Figs. 1(a) and 1(b). When plotted versus T/T_f, the functions $\gamma_G(T,P_0)$ and $A(T,P_0)$ in Mo and W are almost equal for $T/T_f > 0.55$, and there is no significant difference in the quantity $1-\alpha AT$ of Mo and W for $T/T_f > 0.1$. Using Eq. (7) we can write $1-\alpha AT = C_V/C_P$. Then, from Fig. 2, both Mo and W can be described by the relation

$$C_V/C_P \approx 1 - 0.144T/T_f \tag{20}$$

for $0.1 < T/T_f < 1$. A further discussion of similarities between Mo and W is given in Sec. V C.

The Grüneisen parameter $\gamma_G(T,V_0)$ at fixed volume $V_0 = V(T_0,P_0)$ is, by Eq. (13), the product of the two quantities V/C_V and $(\partial P/\partial T)_V$. In Figs. 3(a) and 3(b) we plot, for Mo and W, these two factors (referring to T_0,P_0) and the resulting $\gamma_G(T,V_0)$, as a function of T/T_f. The thermal pressure $(\partial P/\partial T)_{V_0}$ increases with T/T_f, while the variation in C_V makes V/C_V decrease. The two competing effects cause $\gamma_G(T,V_0)$ to be constant, within ±10%, for $0.1 < T/T_f < 1$.

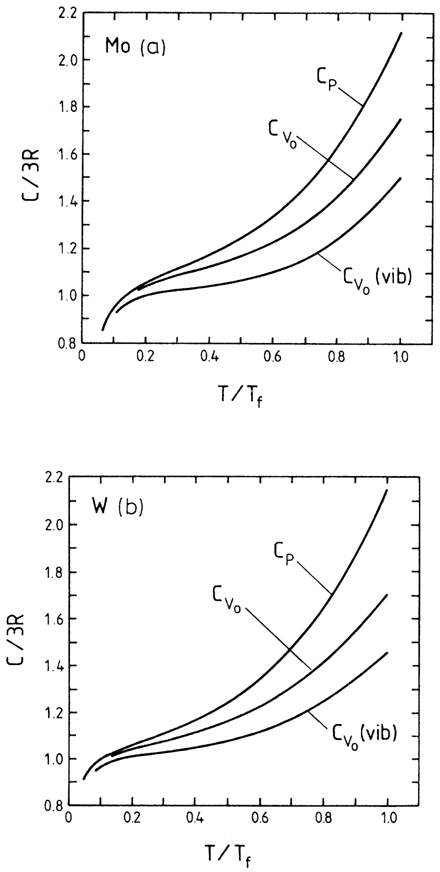

FIG. 1. The total heat capacity at constant pressure, C_P, the heat capacity at fixed volume, C_{V_0}, and the vibrational heat capacity at fixed volume, C_{V_0}(vib), as a function of the reduced temperature T/T_f for (a) Mo and (b) W.

From the positive slope of $(\partial P/\partial T)_V$ vs T/T_f in Fig. 3 and by Eq. (8), we infer that $(\partial C_V/\partial V)_T > 0$ when $V/V_0 = 1$. The Murnaghan equation of state with a temperature-independent n parameter predicts [cf. Eq. (16) in Ref. 9] that $(\partial P/\partial T)_V$ decreases with P, and the effect is proportional to $n - \delta_T(T,0)$. Since $\delta_T(T,0)$ varies with T for Mo and W (Table I) and shows a maximum, the $(\partial P/\partial T)_V$ vs T/T_f graphs for $V/V_0 < 1$ fall below the ones in Fig. 3 and will exhibit a minimum, implying that $(\partial C_V/\partial V)_T$ can change sign as a function of T when $V/V_0 < 1$.

C. Homology relations in high-temperature properties

Several room-temperature properties related to the strength of the interatomic forces are in a roughly constant ratio, when one compares 4*d* and 5*d* transition metals from the same group in The Periodic Table. This fact, previously referred to by us[51] as homology, has been used in estimations of lacking thermodynamic information, e.g., the standard entropy of Tc (Ref. 52) and the bulk modulus of Os.[51] In view of the theoretical and practical interest in such regularities, we now investigate how well they hold in the range from room temperature to the melting point.

In Fig. 4 we plot, as a function of the reduced temperature T/T_f, the ratios $V^{\mathrm{Mo}}(T,P_0)/V^{\mathrm{W}}(T,P_0)$, $B_S^{\mathrm{Mo}}(T,P_0)/B_S^{\mathrm{W}}(T,P_0)$, and $B_T^{\mathrm{Mo}}(T,P_0)/B_T^{\mathrm{W}}(T,P_0)$, respectively. The molar-volume ratio is remarkably constant. The ratios for the isentropic bulk modulus B_S and the isothermal bulk modulus B_T vary weakly in the temperature range covered by experiments ($T/T_f < 0.56$, full-drawn curves in Fig. 4). At higher temperatures, B_S^{W} (and from that B_T^{W}) results from a smooth extrapolation of data from lower temperatures (Sec. IV C). Hence it

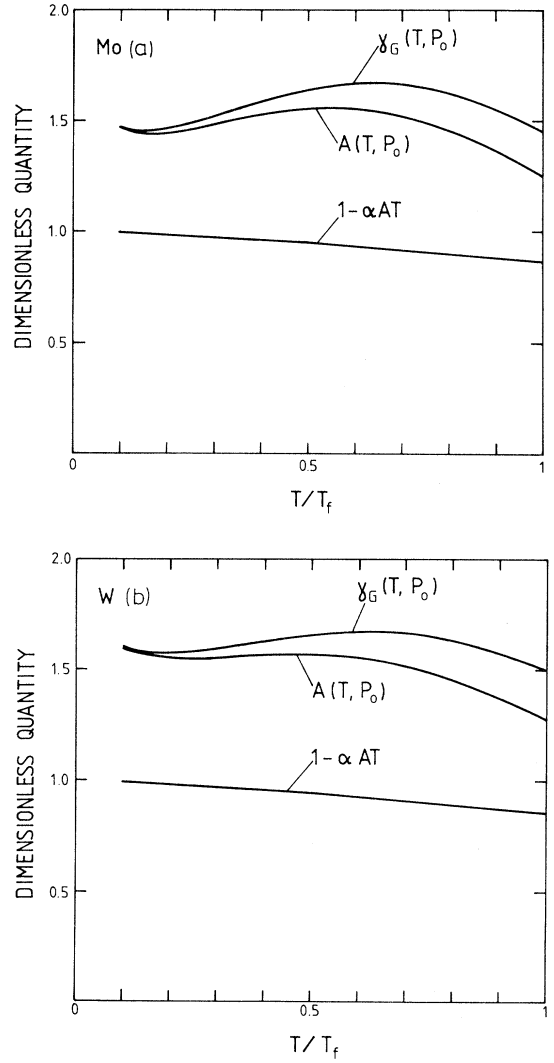

FIG. 2. The Grüneisen parameter at constant pressure, $\gamma_G(T,P_0)$, and the quantities $A(T,P_0) = \alpha V B_T / C_P$ and $1-\alpha A(T,P_0)T$, as a function of T/T_f for (a) Mo and (b) W.

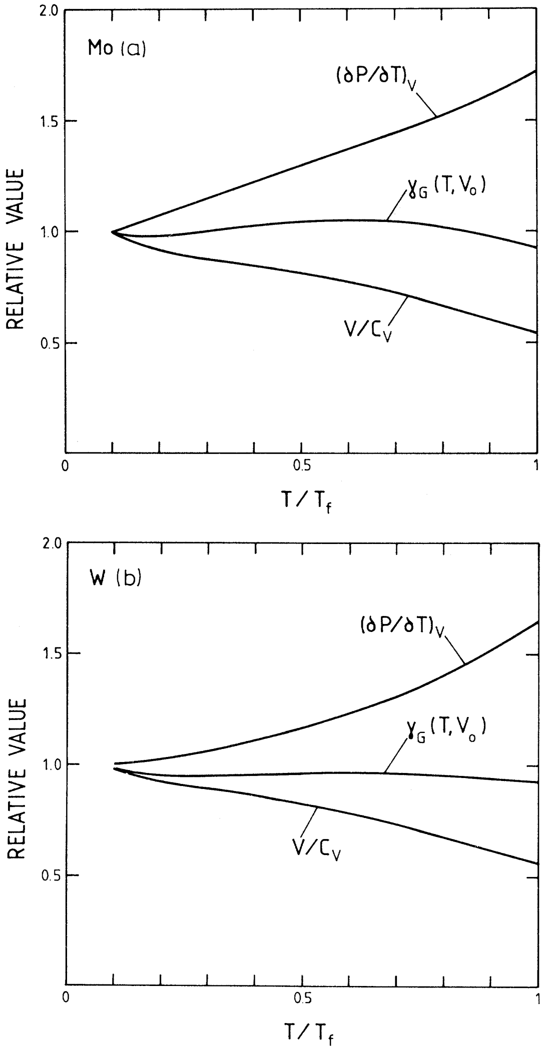

FIG. 3. The Grüneisen parameter at fixed volume, $\gamma_G(T,V_0)$, and the quantities $(\partial P/\partial T)_V$ and (V/C_V), normalized to 1 for $T = T_0$, $V = V_0$, as a function of T/T_f for (a) Mo and (b) W.

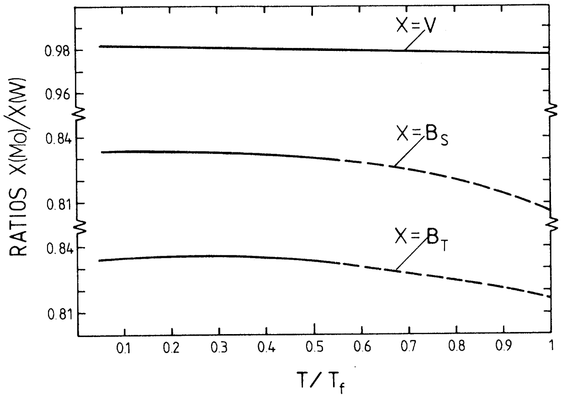

FIG. 4. The ratios $V^{\mathrm{Mo}}(T,P_0)/V^{\mathrm{W}}(T,P_0)$, $B_S^{\mathrm{Mo}}(T,P_0)/B_S^{\mathrm{W}}(T,P_0)$ and $B_T^{\mathrm{Mo}}(T,P_0)/B_T^{\mathrm{W}}(T,P_0)$, as a function of T/T_f.

cannot be ruled out that the bulk modulus ratios remain essentially constant also for $T/T_f > 0.56$.

Figure 5 gives ratios for three quantities of the dimension of a force constant (force per length). Two of them, $B_S V^{1/3}$ and $B_T V^{1/3}$, are obtained from the properties shown in Fig. 4. The ratio $k_S^{\mathrm{Mo}}/k_S^{\mathrm{W}}$ in Fig. 5 is between average interatomic force constants k_S which are derived from the vibrational entropy through the relation $k_S = M(k_B \Theta_S/\hbar)^2$, where M is the atomic mass and Θ_S is the entropy Debye temperature to be discussed in Sec. VI. We have previously[51] found an interesting constancy among $4d$ and $5d$ transition metals in the same group in The Periodic Table, $k_S^{4d}/k_S^{5d} = 0.76 \pm 0.01$ at room temperature. Figure 5 shows that for Mo-W this ratio does not vary much for Mo-W up to $T = T_f$.

Figure 6 gives ratios for two properties involving anharmonic effects at high temperatures, the thermal-expansion coefficient α and the heat capacity at constant pressure C_P. The ratio of thermal-expansion coefficients remains essentially constant above $T/T_f = 0.5$. For the heat-capacity ratio, $C_P^{\mathrm{Mo}}/C_P^{\mathrm{W}} = 1.00 \pm 0.01$, i.e., a most remarkable constancy.

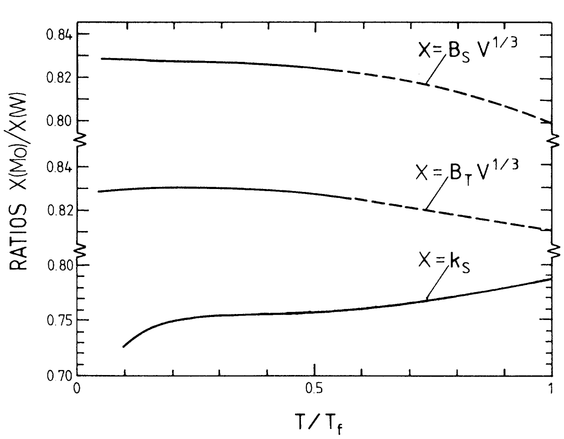

FIG. 5. The ratios $(B_S V^{1/3})^{\mathrm{Mo}}/(B_S V^{1/3})^{\mathrm{W}}$, $(B_T V^{1/3})^{\mathrm{Mo}}/(B_T V^{1/3})^{\mathrm{W}}$, and $k_S^{\mathrm{Mo}}/k_S^{\mathrm{W}}$, as a function of T/T_f.

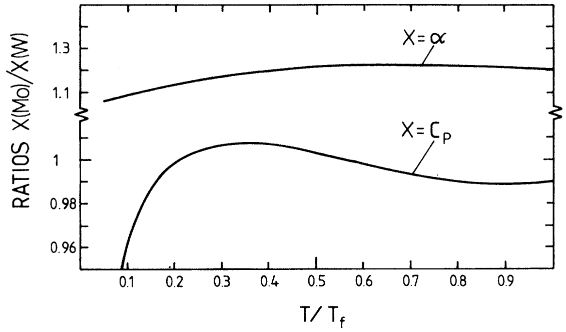

FIG. 6. The thermal expansivity ratio $\alpha^{\mathrm{Mo}}/\alpha^{\mathrm{W}}$ and the heat-capacity ratio $C_P^{\mathrm{Mo}}/C_P^{\mathrm{W}}$, as a function of T/T_f.

VI. DISCUSSION OF ANHARMONIC LATTICE VIBRATIONS

We obtain the vibrational entropy $S(T,P_0)$ from the total entropy by subtracting an electronic entropy (Sec. II A), and then find $\Theta_S(T,P_0)$. Our $\Theta_S(T,V_0)$ refers to the vibrational entropy reduced to fixed volume V_0. We have not allowed the electronic entropy to $S(T,P_0)$ to vary with the thermal expansion of the solid. This approximation, which is unimportant for our conclusions, may give $\Theta_S(T_f,P_0)$ which are too high by 1–2%. Figures 7(a) and 7(b) show $\Theta_S(T,P_0)$ and $\Theta_S(T,V_0)$ for Mo and W. We shall now discuss anharmonic effects, with the main emphasis on how they are revealed in the temperature dependence of Θ_S at fixed volume.

At intermediate temperatures there is an approximately linear decrease in Θ_S followed by a much more rapid decrease at high temperatures which is not well described merely by a T^2 term. The linear variation in Θ_S is simply related to the shifts in the phonon frequencies (cf. Sec. II B). Its magnitude and sign may vary with the solid. Some metals [Au (Refs. 7 and 53)] have an increasing Θ_S with increasing T, while others [Al (Ref. 54)] show such a weak temperature dependence that it has sometimes been taken as evidence that anharmonic effects in the heat capacity at fixed volume are almost negligible, and that the Dulong-Petit limit of $3R$ should generally be a very good approximation at high temperatures. The behavior of $\Theta_S(T)$ seen here for Mo and W is the most common for solids, but the rapid decrease at high temperatures is more pronounced than observed for simple metals.[7] We interpret that as being due to the suppression of melting (Sec. I) which allows higher-order anharmonic effects to be strongly developed. It may be tempting to view the rapid decrease in Θ_S at high temperature as an incipient dynamical instability of the type discussed by Stroud and Ashcroft[55] or as related to an "entropy catastrophe"[56] that may occur well above the actual melting temperature. We shall refrain from such speculations, and note that there seem to be metals [Pb (Ref. 54)] where $\Theta_S(T,V_0)$ would bend upwards at high T. We also remark that close to T_f the nonlinear shifts in Θ_S may not be given a simple interpretation in terms of shifted phonon frequencies, but we still find $\Theta_S(T)$ a very convenient

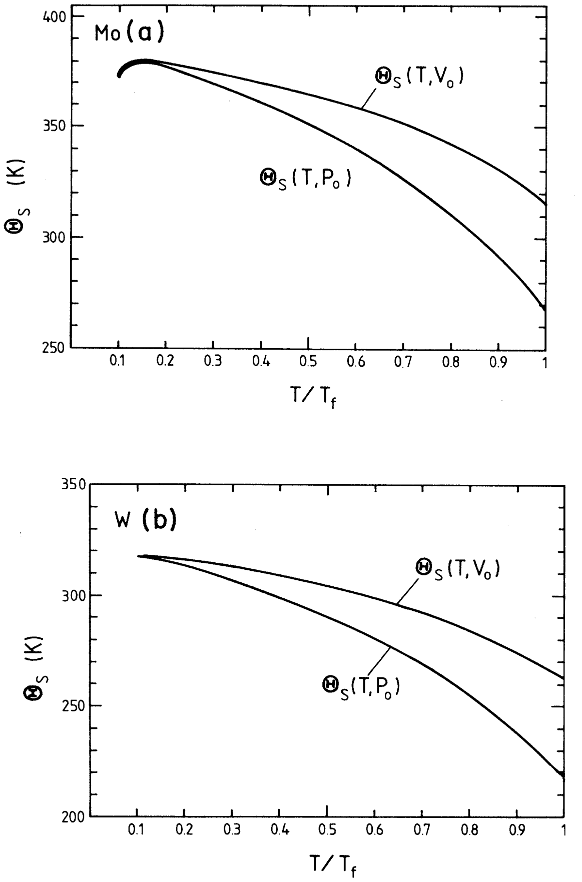

FIG. 7. The entropy Debye temperature at constant pressure, $\Theta_S(T,P_0)$, and at fixed volume, $\Theta_S(T,V_0)$, as a function of T/T_f for (a) Mo and (b) W.

parameter to use in a discussion of the thermodynamic properties of solids at high temperatures.

There are several theoretical approaches which, in principle, should be able to account for the results of this paper. For instance, Gong, Horton, and Cowley[57] performed Monte Carlo calculations to get the thermodynamic properties of NaCl up to its melting temperature. Shukla, Cowley, and Wilk[58] have considered high-order anharmonic terms in the Helmholtz energy of a vibrating lattice. However, these methods do not at present seem to be capable of giving quantitatively relevant results for solids with interactions as complicated as in the transition metals Mo and W. Another approach is that of "frozen phonons," in which one makes an *ab initio* calculation of the total energy of the lattice, modulated by a phonon mode. Most calculations, e.g., for bcc Zr, Nb, and Mo, have concentrated on a few high-symmetry modes which behave anomalously.[59] To extend the calculations to get the full phonon spectrum, as a function of temperature, is so demanding on the computing facilities that it is not yet feasible. In this context, we should also note that the phonon spectrum of Mo has been measured by neutron scattering, at 295 and 1203 K.[59] Most phonon modes soften with increasing temperature, but some zone-boundary modes stiffen. The variation between the modes is too large to allow for a comparison with our $\Theta_S(T)$.

Finally we comment on the contribution of vacancies to the thermodynamic quantities. It is sometimes assumed that the nonlinear increase in C_P with temperature is due to the formation of vacancies. The data we use show a small increase in the molar volume above $T/T_f=0.9$, which we interpret as due to vacancies with a concentration less than about 0.4% at T_f. The polynomial used here to fit to C_P does not pick up the rapid (exponential) increase just below T_f, and therefore effects of vacancies are not present, e.g., in $\Theta_S(T)$. Moreover, the vacancy concentration is much lowered under the condition of fixed volume.[60] It should be remarked that sometimes a second-degree polynomial can be accurately fitted to a linear plus an exponential term, and anharmonic effects can be mistaken for vacancy effects.[61]

VII. CONCLUSIONS

The recent availability of accurate thermodynamic information for Mo and W up to their melting temperatures has allowed us to make a detailed study of thermodynamic quantities such as the entropy at fixed volume and the Grüneisen parameter. The factors entering a reduction of thermodynamic properties at constant pressure to the condition of fixed volume are discussed in detail. When various quantities related directly or indirectly to anharmonic effects are plotted versus the reduced temperature T/T_f, there are striking similarities between molybdenum and tungsten. There are large anharmonic effects also at fixed volume, and their temperature dependence at high temperatures, cannot be accounted for by low-order perturbation theory.

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[1] G. K. White, Physica **149B**, 255 (1988); Int. J. Thermophys. **9**, 839 (1988).

[2] D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).

[3] G. Grimvall, M. Thiessen, and A. Fernández Guillermet, Phys. Rev. B **36**, 7816 (1987).

[4] J. Häglund (unpublished), from LMTO calculation as described, e.g., in G. Arbman and T. Jarlborg, Solid State Commun. **26**, 857 (1978).

[5] M. Thiessen, Int. J. Thermophys. **7**, 1183 (1986).

[6] T. H. K. Barron, in *Lattice Dynamics,* edited by R. F. Willis (Pergamon, Oxford, 1965), p. 247; E. R. Cowley and R. A. Cowley, Proc. R. Soc. London Ser. A **287**, 259 (1965).

[7] J. Rosén and G. Grimvall, Phys. Rev. B **27**, 7199 (1983).

[8] F. D. Murnaghan, Proc. Natl. Acad. Sci. (USA) **30**, 244 (1944).

[9] A. Fernández Guillermet, P. Gustafson, and M. Hillert, J. Phys. Chem. Solids **46**, 1427 (1985).

[10] B. Sundman, B. Jansson, and J.-O. Andersson, CALPHAD **9**, 153 (1985).

[11] O. L. Anderson, J. Geophys. Res. **72**, 3661 (1967).

[12] A. Fernández Guillermet and P. Gustafson, High Temp.—High Press. **16**, 591 (1985); A. Fernández Guillermet, High Temp.—High Press. **19**, 119 (1987).

[13] A. Fernández Guillermet, J. Phys. Chem. Solids **48**, 819 (1987).

[14] B. Jansson, Ph.D. thesis, Royal Institute of Technology, Stockholm, Sweden, 1984.

[15] W. C. Overton, Jr., J. Chem. Phys. **37**, 116 (1962).

[16] K. W. Katahara, Ph.D. thesis, University Hawaii, 1977; values quoted in Ref. 31.

[17] A. Fernández Guillermet, Int. J. Thermophys. **6**, 367 (1985).

[18] M. E. Straumanis and R. P. Shodhan, Trans. AIME **242**, 1185 (1968); Z. Metallk. **59**, 492 (1968).

[19] J. W. Edwards, R. Speiser, and H. L. Johnston, J. Appl. Phys. **22**, 424 (1951).

[20] Y. Waseda, K. Hirata, and M. Ohtani, High Temp.—High Press. **7**, 221 (1975).

[21] V. A. Petukhov and V. Ya. Chekhovskoi, High Temp.—High Press. **4**, 671 (1972).

[22] V. A. Petukhov, V. Ya. Chekhovskoi, and A. G. Mozgovoi, High Temp. **15**, 175 (1977).

[23] Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and P. D. Desai, *Thermophysical Properties of Matter* (Plenum, New York, 1975), Vol. 12, p. 208.

[24] A. N. Amatuni, T. I. Malyutina, V. Ya. Chekhovskoi, and V. A. Petukhov, High Temp.—High Press. **8**, 565 (1976).

[25] A. P. Miiller and A. Cezairliyan, Int. J. Thermophys. **6**, 695 (1985).

[26] V. Ya. Chekhovskoi, L. N. Latyev, V. A. Petukhov, E. N. Shestakov, S. V. Onufriev, and A. Z. Zhuk, High Temp.—High Press. **19**, 397 (1987).

[27] In-Kook Suh, H. Ohta, and Y. Waseda, J. Mater, Sci. **23**, 757 (1988).

[28] P. Bujard, R. Sanjines, E. Walker, J. Ashkenazi, and M. Peter, J. Phys. F **11**, 775 (1981).

[29] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **77**, 189 (1949); Values tabulated in Ref. 32.

[30] S. N. Vaidya and G. C. Kennedy, J. Phys. Chem. Solids **31**, 2329 (1970).

[31] L.-C. Ming and M. H. Manghnani, J. Appl. Phys. **49**, 208 (1978).

[32] G. C. Kennedy and R. N. Keeler, in *American Institute of Physics Handbook,* edited by D. E. Gray, 3rd ed. (McGraw-Hill, New York, 1972), Sec. 4d.

[33] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[34] P. Gustafson, Int. J. Thermophys. **6**, 395 (1985).

[35] L. V. Gurvich, I. V. Veits, and V. A. Medvedev, *Calculations of Thermodynamic Properties* (Nauka, Moscow, 1982).

[36] A. Cezairliyan and J. L. McClure, J. Res. Natl. Bur. Stand. **75A**, 283 (1971).

[37] E. Arpaci and M. G. Frohberg, Z. Metallk. **75**, 614 (1984).

[38] G. K. White and S. J. Collocott, J. Phys. Chem. Ref. Data **13**, 1251 (1984).

[39] G. K. White and R. B. Roberts, High Temp.—High Press. **15**, 321 (1983).

[40] A. P. Miiller and A. Cezairliyan, Int. J. Thermophys. **11**, 619 (1990).

[41] R. K. Kirby, High Temp.—High Press. **4**, 459 (1972).

[42] D. I. Bolef and J. de Klerk, J. Appl. Phys. **33**, 2311 (1962).

[43] F. H. Featherston and R. J. Neighbours, Phys. Rev. **130**, 1324 (1963).

[44] R. Lowrie and A. M. Gonas, J. Appl. Phys. **38**, 4505 (1967).

[45] G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook,* 2nd ed. (MIT Press, Cambridge, Mass., 1971).

[46] A. Fernández Guillermet (unpublished).

[47] R. G. McQueen, S. P. Marsh, J. W. Taylor, J. N. Fritz, and W. J. Carter, in *High Velocity Impact Phenomena,* edited by R. Kinslow (Academic, New York, 1970).

[48] G. H. Miller, T. J. Ahrens, and E. M. Stolper, J. Appl. Phys. **63**, 4469 (1988).

[49] A. Fernández Guillermet, Int. J. Thermophys. **8**, 751 (1987).

[50] G. Grimvall, *Thermophysical Properties of Materials* (North-Holland, Amsterdam, 1986).

[51] A. Fernández Guillermet and G. Grimvall, Phys. Rev. B **40**, 1521 (1989).

[52] A. Fernández Guillermet and G. Grimvall, J. Less-Common Metals **147**, 195 (1989).

[53] D. L. Martin, Can. J. Phys. **65**, 1104 (1987).

[54] A. J. Leadbetter, J. Phys. C **1**, 1489 (1968).

[55] D. Stroud and N. W. Ashcroft, Phys. Rev. B **5**, 371 (1972).

[56] H. J. Fecht and W. L. Johnson, Nature **334**, 50 (1988).

[57] Zhaoxin Gong, G. K. Horton, and E. R. Cowley, Phys. Rev. B **38**, 10 820 (1988).

[58] R. C. Shukla and E. R. Cowley, Phys. Rev. B **3**, 4055 (1971); R. C. Shukla and L. Wilk, *ibid.* **10**, 3660 (1974).

[59] J. Zarestky, C. Stassis, B. N. Harmon, K.-M. Ho, and C. L. Fu, Phys. Rev. B **28**, 697 (1983).

[60] P. Varotsos, K. Eftaxias, and V. Hadjicontis, Phys. Rev. B **38**, 4296 (1988).

[61] G. Grimvall, High Temp.—High Press. **15**, 245 (1983).