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Thermodynamic properties of tungsten

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Tungsten has several unusual thermodynamic properties, e.g., very high values of the melting point, the entropy of fusion, the expansion on melting and the lattice anharmonicity. These features are given a semiquantitative explanation, based on the electron density of states $N(E)$. Our treatment includes a numerical calculation of the electronic heat capacity from $N(E)$ and a calculation of the entropy Debye temperature $\Theta^S(T)$ from the vibrational part of the experimental heat capacity. $\Theta^S(T)$ decreases by 36% from 300 K to the melting temperature 3695 K, the largest drop in Θ^S for elemental metals. Recent quantum-mechanical *ab initio* calculations of the difference, $H^{\beta/\alpha}$, in Gibbs energy at $T=0$ K between the metastable fcc tungsten and the stable bcc phase yield $H^{\beta/\alpha}=50\pm5$ kJ/mol, which is much larger than the "experimental" values $H^{\beta/\alpha}=10$ and 19 kJ/mol derived from previous semiempirical analyses [the so-called calculation of phase diagrams ("CALPHAD") method] of binary phase diagrams containing tungsten. We have reanalyzed CALPHAD data, using the results of the first part of this paper. Because of the shapes of $N(E)$ of α-W and β-W, some usually acceptable CALPHAD procedures give misleading results. We give several estimates of $H^{\beta/\alpha}$, using different assumptions about the hypothetical melting temperature T_f^β of fcc W. The more realistic of our estimates gives $H^{\beta/\alpha}=30$ kJ/mol or larger, thus reducing considerably the previous discrepancy between CALPHAD and *ab initio* results. The physical picture emerging from this work should be of importance in refinements of the CALPHAD method.

I. INTRODUCTION

In thermodynamic modeling of alloy phase diagrams one often needs the difference in Gibbs energy for a pure element in two crystalline structures. That quantity is usually called the lattice stability. In view of the increasing importance of computer calculations of phase diagrams based on so-called CALPHAD assessments (an acronym for the "calculation of phase diagrams" method), the methods of evaluating lattice stabilities have been a matter of considerable interest. The CALPHAD approach to lattice stabilities is semiempirical and has its roots in chemical thermodynamics and early attempts to rationalize and describe the observed structural trends in the Periodic Table. An accurate representation of the macroscopic thermodynamic functions then is more important than a deeper understanding of their microscopic origin based on quantum mechanics. This method is described, e.g., in a monograph by Kaufman and Bernstein[1] and in the CALPHAD journal (Computer Coupling of Phase Diagrams and Thermochemistry).

Quantum-mechanical calculations of electron states represent a nonempirical approach to the phase stability. The first versions[2] could account for structural trends among transition metals, but were not accurate enough to be used in CALPHAD work. However, recent *ab initio* calculations for tungsten by Jansen and Freeman,[3] Skriver,[4] Davenport *et al.*,[5] Mattheiss and Hamann,[6] and Chan *et al.*[7] predict an enthalpy difference, $H^\beta - H^\alpha$, ranging from 44 to 55 kJ/mol, while Kaufman and Bernstein[1] estimated $H^{\beta/\alpha}=10$ kJ/mol. The latter value would be increased if the melting temperature T_f^β of fcc W is assumed to be considerably lower (e.g., by a factor of 2) than the value $T_f^\alpha=3695$ K of the stable bcc phase. Such a low melting temperature of fcc W is at variance with the general rule that elements in the middle of the transition-metal series in the Periodic Table have high cohesive energies and melting temperatures. Further, the CALPHAD method has proven to give very useful and quite reliable results for a large number of alloy systems. On the other hand, the *ab initio* calculations have reached such a sophistication that their results must be taken very seriously. The present investigation was primarily motivated by the significant discrepancy between the CALPHAD and the *ab initio* results for the lattice stability of tungsten.

CALPHAD assessments are based essentially on high-temperature data while the *ab initio* calculations refer to the absolute zero. A comparison of the two approaches to the lattice stability therefore must include a discussion of the heat capacity C_P of stable and metastable phases. The thermodynamics of the (stable) bcc phase of tungsten also is of considerable interest in itself because of the exceptionally large values for the melting temperature, the entropy of fusion, and the volume expansion on melting. Like several other transition metals which melt at high temperatures, tungsten has a rapidly increasing heat capacity at high temperatures, which is not due to the usual electronic term.[8] An explanation of these properties is a second important purpose of our paper, in particular since tungsten has been chosen a CODATA (Committee on Data for Science and Technology) key material.[9] We also wish to present a thermodynamic analysis of a metal in some detail, in order to provide a reference work to later discussions of other systems.

The outline of the paper is as follows. We first review experimental macroscopic thermodynamic data and the CALPHAD approach for tungsten. Next, we consider microscopic aspects of the heat capacity and some related properties of transition metals. We proceed to explain the unusual thermodynamics of bcc tungsten, and finally discuss the discrepancy between the CALPHAD and the *ab initio* results for the phase stability of fcc tungsten.

II. MACROSCOPIC THERMODYNAMICS

A. CALPHAD estimates

Pure tungsten has a bcc structure (α-W) from the absolute zero to the melting point T_f^α. We follow Gurvich *et al.*[10] and Gustafson[11] and take $T_f^\alpha = 3695$ K. Some tungsten alloys (e.g., W-Co, W-Ir, W-Ni, W-Pd, W-Pt, and W-Rh) have a concentration range with fcc structure; see Fig. 1. In the CALPHAD method,[1] the Gibbs energy difference between a stable (α) and a metastable phase (β) is usually derived from estimated values of the metastable melting point T_f^β, and the entropy difference between the liquid and the β phase, $S^l - S^\beta$. The melting point is obtained from a more or less arbitrary extrapolation of the liquidus curve, whereas the entropy difference is treated as a constant and estimated from available correlations for the entropy of fusion of various structures. For tungsten, Kaufman and Bernstein[1] in this way obtained $T_f^\beta = 2230$ K and $H_0^\beta - H_0^\alpha = 10$ kJ mol^{-1}. (Subscripts 0 denote $T = 0$ K.) Their value for T_f^β is very low, only 60% of T_f^α, and the enthalpy difference is considerably lower than that of *ab initio* calculations.

It is obvious that CALPHAD estimates may be quite uncertain. First, the metastable melting point T_f^β cannot be obtained from an extrapolation of the liquidus curve if that curve has a minimum in the metastable concentration range. About half of 70 phase diagrams in Hansen and Anderko's[12] compilation show, or suggest the existence of, a minimum. Even in the case where a linear extrapolation of the liquidus line does not seem unreasonable, different results may be obtained from different alloy systems. For instance, the value 2230 K estimated by Kaufman and Bernstein is consistent with an extrapolation from the Ir-W system.[13] However, an extrapolation from the Pt-W system[13] would give a larger value, say 3000 K, whereas extrapolations from the Co-W and Ni-W systems, which show maxima in the liquidus, would give very low values. Secondly, the assumption of a constant entropy difference between the solid and the liquid is not justified. It is generally accepted that a supercooled liquid, if prevented from crystallizing, will solidify by a glass transition. There are strong indications[14] that the metallic glass has an entro-

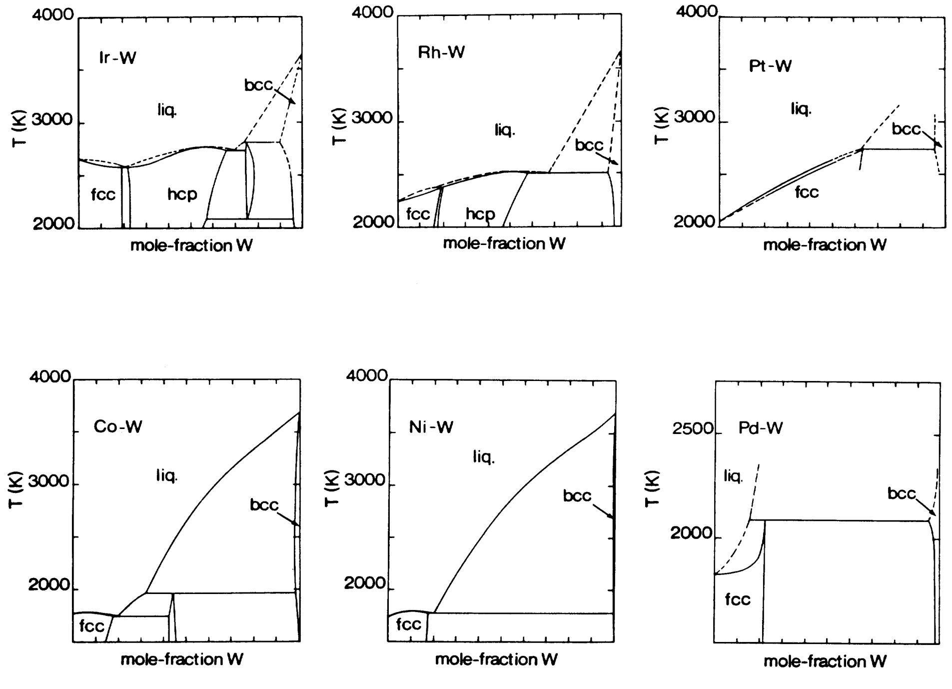

FIG. 1. Binary phase diagrams (Refs. 12 and 13) in which tungsten appears in the fcc structure.

py close to that of the solid phase. Thirdly, even if the existence of the glass transition is ignored, the estimated $H_0^\beta - H_0^\alpha$ will depend upon the experimental entropy of fusion S_f^α and the assumed properties of the liquid below the melting point. For instance, by accepting the values $T_f^\beta = 2230$, $S_f^\alpha = 14\ \mathrm{J\,mol^{-1}\,K^{-1}}$ and with a different extrapolation of the properties of the liquid phase below T_f^α, Gustafson[11] obtained $H_0^\beta - H_0^\alpha = 19\ \mathrm{kJ\,mol^{-1}}$ at the absolute zero; cf. Table I.

B. Heat capacity

Figure 2 shows the heat capacity C_P of tungsten according to various sources. From C_P we get the entropy S as

$$S(T) = \int_0^T \frac{C_P(T')}{T'} dT' . \tag{1}$$

In this paper, C_P, S, etc. are given per mole. The classical (Dulong-Petit) value of the heat capacity is $3R$ where $R = Lk_B$ is the gas constant, L is Avogadro's constant, and k_B is Boltzmann's constant. The solid line is C_P derived by Gustafson[11] in his assessment of experimental data. Those results are very close to the values selected by the CODATA group[9] and by Gurvich *et al.*,[10] whereas the values recommended in the JANAF Tables[15] show a larger increase with temperature when the melting point is approached.

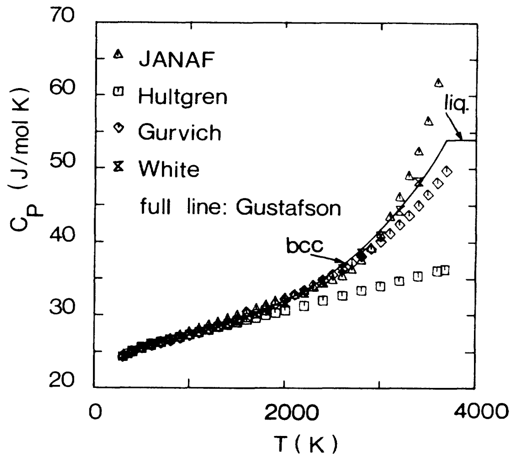

FIG. 2. The heat capacity of tungsten, from assessments of experimental data by Gustafson (Ref. 11) (solid line), Gurvich *et al.* (Ref. 10) (symbols), White and Collocott (Ref. 9) (symbols), and Hultgren *et al.* (Ref. 16) (symbols), and the JANAF Tables (Ref. 15) (symbols).

TABLE I. Enthalpy differences, kJ/mol. The enthalpy difference $H^\beta - H^\alpha$ between the fcc (β-W) and bcc (α-W) phases of tungsten. Values by Jansen and Freeman (Ref. 3) Skriver (Ref. 4), Davenport *et al.* (Ref. 5) Mattheiss and Hamann (Ref. 6), and Chan *et al.* (Ref. 7) for $T = 0$ K are the results of these authors from quantum-mechanical *ab initio* calculations. The corresponding entries for 2500 K are the *ab initio* values we corrected to 2500 K. The enthalpy differences of this paper refer to three different assumptions for the melting temperature of the metastable β-W. Values by Kaufman and Bernstein (Ref. 1) and by Gustafson (Ref. 11) are previous estimates using CALPHAD methods.

	$H^\beta - H^\alpha$	Comment
Jansen and Freeman	44	$T = 0$ K
	45±2	$T = 2500$ K
Skriver	54	$T = 0$ K
	54±2	$T = 2500$ K
Davenport *et al.*	55	$T = 0$ K
	55±2	$T = 2500$ K
Mattheiss and Hamann	48	$T = 0$ K
	48±2	$T = 2500$ K
Chan *et al.*	53	$T = 0$ K
	53±2	$T = 2500$ K
This paper	$< 16 \pm 11$	$T_f^\beta = 3500$ K
	$< 23 \pm 9$	$T_f^\beta = 2500$ K
	$< 31 \pm 6$	$T_f^\beta = 1500$ K
Kaufman and Bernstein	10	
Gustafson	19	

The heat capacity of the liquid is somewhat uncertain. Gustafson[11] and Gurvich *et al.*[10] suggest a temperature-independent C_P for $T > T_f^\alpha$, but of different magnitude. We accept the value of Gustafson, $C_P^l = 54\ \mathrm{J\,mol^{-1}\,K^{-1}}$. For liquids of nontransition metals, $C_P(T)$ is often almost independent of T in the range $T_f < T < 2T_f$.[17] Much less is known about $C_P(T)$ in transition metals, but we do not expect $C_P(T)$ to increase significantly faster than $C_P(T)$ of a (metastable) solid phase between T_f and $2T_f$. Later, we shall argue that in the absence of a stabilizing electronic contribution, T_f^α could have been about 2000 K or less (Sec. VII and Appendix). It therefore seems natural to assume that the glass transition of tungsten is well below 2000 K and let the vibrational part of C_P for liquid tungsten be a constant from 2000 K to $T_f^\alpha = 3695$ K.

C. Entropy of fusion

Figure 3 shows the measured entropy of fusion,[18,19] S_f, plotted versus T_f for the bcc and fcc structures of various metals. The average S_f of all bcc metals is $(0.92 \pm 0.3)R$ and that of all fcc metals is $(1.26 \pm 0.2)R$, in line with Richard's rule, which says that $S_f \approx R$. The increase of S_f with T_f poses a problem, because a large S_f tends to lower the Gibbs energy $G = H - TS$, thus leading to a low T_f if other factors are unchanged. If, however, the reason for a large S_f also implies a large enthalpy difference between the liquid and the solid (bcc) phase, the apparent inconsistency could be resolved.

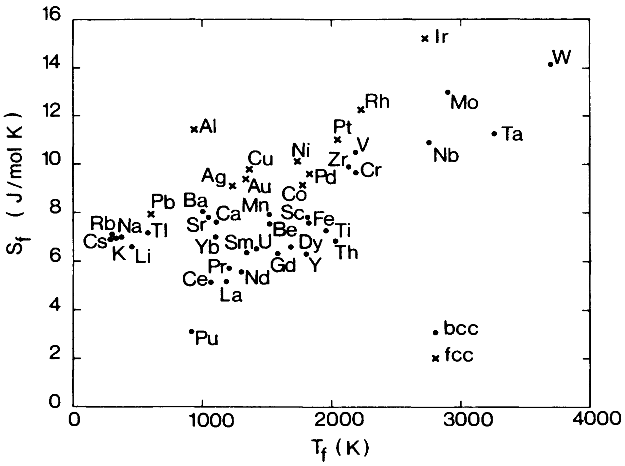

FIG. 3. Experimental values (Refs. 18 and 19) for the entropy of fusion S_f of bcc and fcc metals, plotted vs the melting temperature T_f.

D. Molar volume

From the slope of the liquidus curve of the (P,T) phase diagram of tungsten,[20] Gustafson[11] inferred that the molar volume $V^{\alpha}(T)$ increases by 8% on melting. This is the largest expansion observed for any bcc metal; the average volume increase for 35 bcc metals is $(3.4\pm2)\%$, whereas data for fcc metals give $(5.3\pm1)\%$.[19,21] The molar volume is (indirectly) related to the electronic band structure. In view of our subsequent discussion (Sec. VII), there is no reason to assume that β-W has an unusual atomic volume relative to the liquid, i.e., its volume change on melting might be estimated as about 5%. Accordingly, the volume difference between fcc and bcc W might be estimated as $8\%-5\%=3\%$, which is supported by recent *ab initio* calculations.[3,6,7,22]

III. *AB INITIO* CALCULATIONS OF PHASE STABILITIES

There are several recent *ab initio* calculations of the phase stability of tungsten, using different forms of the local-density scheme to calculate the electronic structure. Jansen and Freeman[3] used the full-potential linearized augmented-plane-wave (FLAPW) method, Skriver[4] used a linear muffin-tin orbital (LMTO) method, Davenport *et al.*[5] used the linear augmented Slater-type orbital (LASTO) method, and Mattheiss and Hamann[6] used procedures similar to those of Jansen and Freeman while Chan *et al.*[7] employed self-consistent pseudopotential linear combination of atomic orbitals. They all give essentially the same result (Table I).

Some early *ab initio* calculations are performed at a fixed atomic volume, taken from experiments on the stable phase. Suppose that V^{α} is the volume that minimizes $G_0^{\alpha}(V)$ and let V^{β} be the volume that minimizes the corresponding $G_0^{\beta}(V)$. If one, incorrectly, uses V^{α} for both structures, $G_0^{\beta}-G_0^{\alpha}$ is overestimated by an amount

$$G_0'=\frac{K^{\beta}(V^{\beta}-V^{\alpha})^2}{2V^{\alpha}} . \qquad (2)$$

Take[23] $K^{\beta}=310$ GPa (the observed bulk modulus of α-W), $V^{\alpha}=9.5\times10^{-6}$ $\mathrm{m^3\,mol^{-1}}$, and let V^{β} be 3% larger than V^{α} (cf. Sec. II D). Then $G_0'=1.3$ $\mathrm{kJ\,mol^{-1}}$, i.e., an insignificant correction to the *ab initio* values of $G_0^{\beta}-G_0^{\alpha}$ (≈ 50 $\mathrm{kJ\,mol^{-1}}$) in Table I.

IV. MICROSCOPIC THERMODYNAMICS

This section briefly presents results based on a quantum-mechanical description of electrons and lattice vibrations in transition metals. Details on the theory used in Sec. IV can be found, e.g., in a monograph by Grimvall.[24]

A. Electronic energy

The standard expression for the electronic heat capacity C_{el} at low temperatures is

$$C_{\mathrm{el}}=\gamma_b(1+\lambda)T=\gamma T . \qquad (3)$$

Here $1+\lambda$ is an electron-phonon enhancement factor and $\gamma_b T$ is what would result from a consideration of only the electron band-structure density of states $N(E)$ taken at the Fermi level E_F,

$$\gamma_b=(2\pi^2/3)k_B R N(E_F) . \qquad (4)$$

The corresponding entropy is

$$S_{\mathrm{el}}=\gamma_b(1+\lambda)T . \qquad (5)$$

Equation (5) is valid at low temperatures ($T \ll \Theta_D$ where Θ_D is a Debye temperature) while at high temperatures the factor $(1+\lambda)$ in the entropy should be absent. Moreover, S_{el} probes the electron density of states $N(E)$ in an "energy window," approximately limited by $E_F\pm3k_BT$. If $N(E)$ varies strongly with E near E_F, as is often the case for transition metals, the high-temperature electronic entropy must be found from a numerical integration involving $N(E)$. There is also a smearing effect on $N(E)$ due to the finite lifetime of electron states at high temperatures.[25] Figure 4 gives $S_{\mathrm{el}}(T)$, as we obtain it from $N(E)$ in Fig. 5. For comparison we also give $S_{\mathrm{el}}'=\gamma T$ that results from an extrapolation of the low-temperature data for α-W.[9] For tungsten, we take $\lambda=0.4$.[26]

B. Vibrational entropy

In a real solid, the heat capacity has anharmonic corrections to the Dulong-Petit value $3R$ of strictly harmonic lattice vibrations. It is convenient to represent the vibrational entropy S_{vib} by an "entropy Debye temperature" $\Theta^S(T)$.[27] This is just a parametrization of entropy data, which allows for anharmonic effects and does not imply the limitations inherent in the Debye model of introductory textbooks. We get $\Theta^S(T)$ by an iterative solution of the implicit equation

$$S_{\mathrm{vib}}(T)=S_D(T/\Theta^S)\ . \tag{6}$$

S_{vib} is the actual vibrational entropy, related to the vibrational heat capacity C_{vib} by Eq. (1). S_D is the entropy of a standard Debye model. Due to anharmonicity, the vibrational frequencies ω change with temperature. Hence $\Theta^S(T)$ from Eq. (6) is temperature dependent.

Before $\Theta^S(T)$ can be calculated from the experimental heat capacity, by Eqs. (1) and (6), nonvibrational contributions to C_P must be subtracted. We take $S_{\mathrm{vib}}=S_P-S_{\mathrm{el}}$, with S_{el} as in the solid line of Fig. 4. Figure 6 shows the resulting $\Theta^S(T/T_f)$, based on C_P from Gustafson[11] and Hultgren *et al.*[16] A similar analysis for nontransition metals[27] and transition metals[28] showed that $\Theta^S(T)$ typically decreases by 10–20 % when T increases from 300 K (or, rather, from Θ^S) to T_f. This is much less than the drop by 36% now obtained in tungsten. We note that a large drop in Θ^S requires a vibrational contribution to C_P which is much larger than the classical Dulong-Petit value.

$\Theta^S(T)$ generally has a smooth downward curvature when plotted versus T. The shape of $\Theta^S(T)$ derived from C_P of Hultgren *et al.*[16] is a sign of warning that the C_P data may be incorrect at high temperatures. [Cf. a critical discussion of C_P in Ca based on $\Theta^S(T)$.[29]] Gustafson[11] and White and Collocott,[9] in their assessments of C_P for tungsten, neglected the high-temperature values recommended by Hultgren *et al.*, which differ significantly from those of other sources.

Part of the shift in $\Theta^S(T)$ with T is due to the thermal expansion. From $T=300$ K to T_f^{α} (3695 K), $\Delta V/V=0.07$.[30] Gustafson[11] has evaluated C_V and C_{V_0}, i.e., the heat capacity at constant volume $V(T)$ and at fixed volume $V_0=V$(300 K). Using his result we find that the drop in Θ^S at T_f, relative to Θ^S(300 K), is 12% (from C_V), Fig. 6, and 11% (from C_{V_0}), to be compared with the 36% drop at the condition of constant pressure. Thus about $\frac{1}{3}$ of the shift of Θ^S is due to the "explicit" anharmonic effects which are present even at the condition of constant volume, and are caused by the increased vibrational amplitude with increasing T. In the bcc alkali metals, the explicit anharmonic part also is about $\frac{1}{3}$ of the total shift.[27]

The "frozen-phonon" method is a way to derive phonon frequencies from *ab initio* energy calculations in which one compares the perfect lattice with the lattice modulated by a single phonon mode. In this way, some phonon modes with anomalous temperature dependence have been investigated for Cr, Mo, and W.[31–33] Explicit anharmonicity (and not thermal expansion) is shown to dominate the frequency shift. However, these calcula-

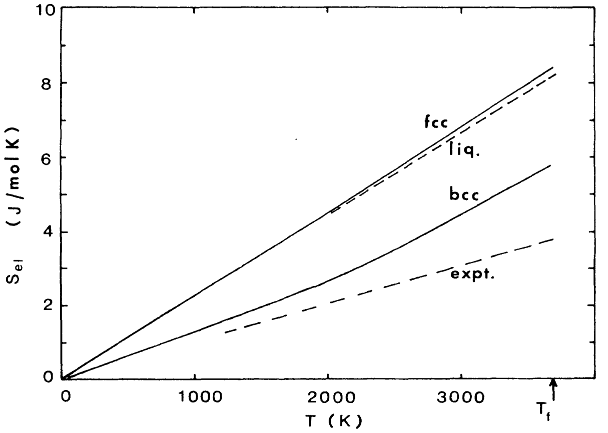

FIG. 4. The electronic entropy S_{el} of bcc W, fcc W, and liquid W, calculated from $N(E)$ in Fig. 5. The dashed line is an extrapolation of the low-temperature experimental results (Ref. 9).

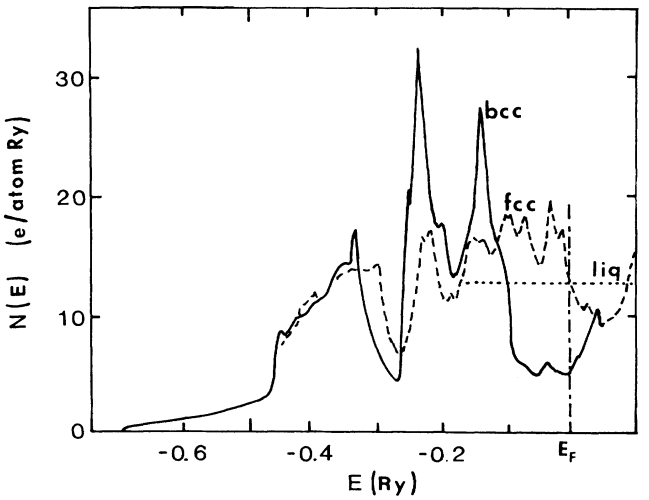

FIG. 5. The calculated (Refs. 3 and 47) electron density of states for bcc W (solid line), fcc W (dashed line), and our tentative curve for liquid W (dotted line).

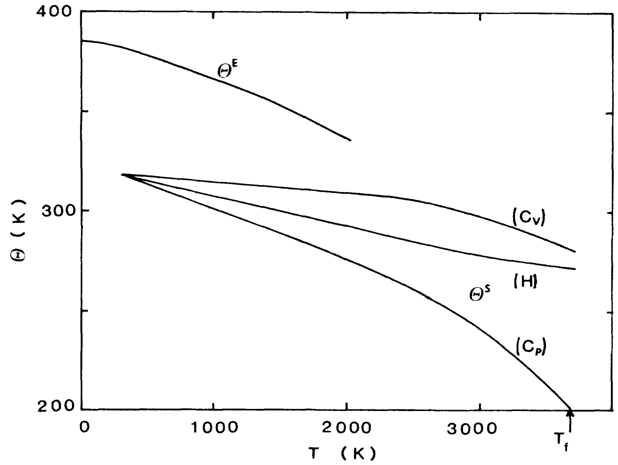

FIG. 6. The entropy Debye temperature $\Theta^S(T)$ derived from the vibrational heat capacity C_P of Gustafson (Ref. 11) (curve marked C_P), $\Theta^S(T)$ derived from $C_V(T)$ of Gustafson (Ref. 11) (C_V), and $\Theta^S(T)$ from the vibrational C_P of Hultgren *et al.* (Ref. 16) (*H*). $\Theta^E(T)$ is the elastic limit Debye temperature, derived from measured (Ref. 35) elastic constants.

tions only deal with a few exceptional modes, which are not characteristic of the entire phonon spectrum that is of interest to us.

In a derivation of Θ^S from C_P and C_V, S_{el} should be given a volume dependence. One can introduce an "electronic Grüneisen parameter" γ_{el},[24] which is usually not well known, but of the order of 2. Then $\Delta S_{\mathrm{el}}/S_{\mathrm{el}}=\gamma_{\mathrm{el}}(\Delta V/V)$. Close to T_f^α, we have $S_{\mathrm{el}}=0.7R$ (Fig. 4). Then, if we do not correct for the volume dependence of S_{el}, Θ^S is too low by approximately 3% [estimated from S_D in Eq. (6) by $\Delta\Theta^S/\Theta^S=\Delta S_{\mathrm{el}}/(3R)$ $\approx 0.07\times 2\times 0.7R/3R=0.03$]. We shall neglect this correction.

C. Defect-related entropy

Let the vacancy concentration at T_f be n_0. The entropy due to thermally generated vacancies, calculated as for two-level systems, is

$$S_{\mathrm{vac}}(T)=R\,[\ln(1/n_0)](T_f/T)(n_0)^{T_f/T}\ . \tag{7}$$

Even with n_0 as large as 10^{-2}, we get $S_{\mathrm{vac}}<0.02R$ at $T/T_f=\frac{3}{4}$. But a change in Θ^S by 1% implies a change in S by $0.03R$ [cf. Eq. (6) at high T]. Thus vacancies (or other thermally generated defects) cannot explain the decrease in $\Theta^S(T)$ with T, which is also unusually large well below T_f. On this matter we differ from MacDonald and Shukla,[34] who also noted the steep rise in C_P but suggest that it is due to creation of lattice defects.

D. Elastic properties

In the elementary Debye model, one introduces a Debye temperature Θ^E related to the elastic properties through the sound velocities. Θ^E samples only the low-frequency limit of the vibrational density of states $F(\omega)$. However, if all vibrational frequencies undergo the same relative shift as a function of temperature, $\Theta^S(T)/\Theta^E(T)$ would be independent of T. $\Theta^E(T)$ is calculated from the temperature-dependent elastic coefficients $c_{11}(T)$, $c_{12}(T)$, and $c_{44}(T)$. This means the solution of a third-order algebraic equation to get the longitudinal and transverse sound velocities C in different crystallographic directions, and then forming the average C^{-3} from which Θ^E follows by a standard textbook formula. Experimental data on c_{ij} are available up to $T/T_f=0.54$.[35] The resulting $\Theta^E(T)$, Fig. 6, is similar to $\Theta^S(T)$. The two Debye temperatures cannot be identical since they refer to different averages over $F(\omega)$.

E. Electrical resistivity

The temperature dependence of the electrical resistivity ρ sometimes is used to get information about the Debye temperature Θ^R (superscript R for "resistivity") of a metallic element.[23] In the simplest theory, ρ varies linearly with $T/(\Theta^R)^2$ at high temperatures. In some metals ρ/T increases with T, mainly because anharmonicity causes $\Theta^R(T)$ to decrease with T. A study of ρ/T therefore may shed light on the anharmonic properties. From the strong temperature dependence of Θ^S we might expect that $\rho/T\sim 1/[\Theta^R(T)]^2$ would increase at high T, but this is not seen in experiments[36] (Fig. 7). The reason is a "saturation" in $\rho(T)$ which appears almost universally in metals and alloys with large resistivities, typically when $\rho>100\ \mu\Omega\,\mathrm{cm}$.[37,38] The thermal conductivity κ has a similar saturation,[24,39] so that the Lorenz number $L_e=\kappa\rho/T$ shows no high-temperature anomaly for tungsten.[40] Thus, $\rho(T)$ gives no useful correlation to high-temperature thermodynamic properties of α-W, such as the temperature dependence of phonon frequencies or the presence of thermally created lattice defects.

V. EMPIRICAL RULES RELATED TO T_f

In this section we investigate whether the observed melting point of α-W can be reconciled with empirical rules related to the melting temperature.

A. The Lindemann melting rule

Lindemann[41] suggested that at T_f the root-mean-square vibrational atomic displacement u is a certain fraction $p=u/2a$ of the nearest-neighbor distance $2a$. We take $(4\pi/3)a^3=V/L$ where V is the molar volume. For several metals, $p=0.11\pm0.01$.[24] With $T_f=3695$ K and u calculated in a Debye model, i.e., $u^2=(9\hbar^2T_f/Mk_B)[\Theta^2(T_f)]^{-2}$, we get $p=0.13$ for tungsten. At $T=2500$ K, we would get $p=0.09$. Thus Lindemann's empirical melting rule is not of much help to elucidate the observed value of $T_f^\alpha=3695$ K. Note also that Lindemann's rule makes no reference to the Gibbs energies and therefore is expected to fail if the solid or liquid has anomalous Gibbs energy contributions.

B. Activation energy for self-diffusion

There is a well-known empirical rule (see, e.g., Grimvall and Sjödin[42]) that states

$$Q_d=CRT_f\ . \tag{8}$$

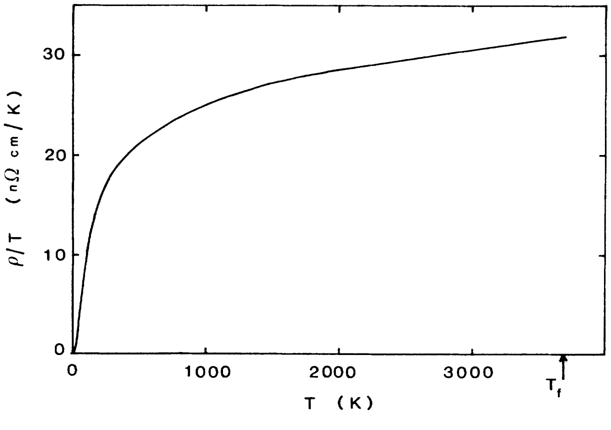

FIG. 7. The measured (Ref. 36) electrical resistivity, plotted as ρ/T vs T.

Q_d is the activation energy (per mole) for self-diffusion. A large number of metallic elements have $C=18\pm3$, while $C=20$ for α-W, which suggests that $T_f^\alpha=3695$ K is "normal." However, electronic band-structure effects increase T_f^α by stabilizing the bcc phase (Sec. VI), and it is conceivable that such effects also give rise to a large Q_d. Therefore one cannot decide directly from Eq. (8) whether T_f^α is anomalous.

VI. EXPLANATION OF THERMODYNAMIC ANOMALIES IN α-W

We shall now argue that the high melting temperature, the high entropy of fusion, the pronounced anharmonic effects at high temperatures, and the large increase in molar volume on melting observed for α-W all have natural explanations, directly or indirectly related to the electron density of states of $N_\alpha(E)$; cf. the model calculation in the Appendix. No other anomalous features in the bcc and liquid phases have to be invoked. The following picture emerges. The structural dependence of the d-electron states gives α-W an unusually high cohesive energy relative to the liquid phase. This pushes up T_f^α, and as a consequence anharmonic effects near T_f will be more pronounced than is usually the case in metals. This explains the large drop in $\Theta^S(T)$ and the large vibrational heat capacity when T approaches T_f. The large entropy of fusion is partly explained by the low electronic heat capacity of α-W relative to the liquid and partly by a volume dependence of Θ^S combined with the large volume difference between the bcc and liquid phase. That volume difference is also a consequence of the form of the d-electron band structure in α-W. These qualitative ideas will now be partly quantified. A numerically accurate treatment is not feasible, because we lack a detailed understanding of the liquid state. (Not even for a simple metal like aluminum is there a good quantitative understanding of the thermodynamics of the liquid.[43])

Figure 5 shows the calculated $N_\alpha(E)$ and $N_\beta(E)$. $N_l(E)$ (index l for liquid) is not known, but since the sharp peaks in $N_\alpha(E)$ originate mainly from the periodicity of the lattice, we expect $N_l(E)$ to be almost structureless, and suggest an $N_l(E)$ given by the dashed line in Fig. 5. The difference $N_l(E_F)-N_\alpha(E_F)$ contributes to the entropy of fusion an amount $S_{f,\mathrm{el}}^{l/\alpha}=2.4$ J mol^{-1} K^{-1}$=0.3R$; cf. Fig. 4.

The volume increase on melting for α-W is 8% while the normal value for bcc metals is 3.4% (Sec. II D). From the difference, 4.6% we can estimate an entropy shift

$$3R\,(\Delta\Theta^S/\Theta^S)=3R\gamma_G(\Delta V/V)=3R\,(1.7)(0.046)=0.23R\ .$$

Here we have used $S_D(\Theta^S)$ as in Eq. (6) and the Grüneisen parameter $\gamma_G=1.7$.[9] When this term and the entropy $0.3R$ of the preceding paragraph are subtracted from the measured $S_f^\alpha=1.7R$, one obtains $1.17R$, which is compatible with the average $(0.92\pm0.3)R$ for bcc metals (Sec. II C), i.e., the entropy of fusion no longer is anomalously high.

The argument given in the Appendix for the high cohesive energy of α-W is further corroborated by the phase diagram of tungsten alloyed with Ti or V. If these elements are added to α-W, the number of d electrons per atom, and hence the Fermi level E_F, is pushed down towards the steep increase in $N(E)$ at the left side of the trough in $N(E)$. This lowers the lattice stability of the bcc phase relative to the liquid, and the solidus temperatures decrease rapidly for a low concentration of the alloying element; see Fig. 8. In particular, Fig. 8 shows that about 70% of the total decrease in the solidus temperatures in the Ti-W system takes place in the composition range 0–30 at. % Ti. Although the effect seems to be less important in the V-W system, Fig. 8 suggests that an extrapolation of the solidus data from the Ti- or V-rich end to pure W would yield a T_f^α of the order of 2700 K, i.e., much lower than the actual T_f^α. In this discussion, we have relied on the rigid-band model, which is adequate for our qualitative arguments.

VII. PHASE STABILITY OF fcc TUNGSTEN

Table I summarizes the enthalpy difference

$$H^{\beta/\alpha}=H^\beta-H^\alpha \tag{9}$$

between the (metastable) fcc and the bcc phase of tungsten, as obtained in *ab initio* calculations by Jansen and Freeman,[3] Skriver,[4] Davenport *et al.*,[5] Mattheiss and Hamann,[6] and Chan *et al.*,[7] and as obtained from CALPHAD methods by Kaufman and Bernstein[1] and Gustafson.[11] The *ab initio* enthalpies refer to zero temperature while the CALPHAD estimates are based on high-temperature data and simple rules for their extrapolation to lower temperatures. We shall now reanalyze CALPHAD data, relying on the account of the heat capacity of tungsten developed in previous sections of this paper, and compare our result for the lattice stability with that of *ab initio* calculations.

At the melting temperature T_f^α of α-W

$$G^\alpha(T_f^\alpha)=G^l(T_f^\alpha)\ . \tag{10}$$

The experimental enthalpy of fusion is[44]

$$H^{l/\alpha}(T_f^\alpha)=T_f^\alpha S_f^\alpha=52\ \mathrm{kJ\,mol^{-1}}\ . \tag{11}$$

Suppose that the metastable β-W would melt at T_f^β, i.e.,

$$G^\beta(T_f^\beta)=G^l(T_f^\beta)\ . \tag{12}$$

Subtracting (10) from (12) gives

$$H^{\beta/\alpha}(T_f^\beta)=T_f^\alpha S_f^\alpha-T_f^\beta S_f^\beta-\int_{T_f^\beta}^{T_f^\alpha}[C_P^l(T)-C_P^\alpha(T)]dT\ . \tag{13}$$

The first term on the right-hand side of (13) is $H^{l/\alpha}=52$ kJ mol^{-1}. $N_\beta(E)$ does not have the minimum around E_F that caused S_f^α to be anomalously large, through a direct electronic contribution and an indirect volume-related term (Sec. VI). We therefore expect the "normal" entropy of fusion for fcc metals and take $S_f^\beta=(1.26\pm0.2)R=10\pm3$ J mol^{-1} K^{-1} (cf. Sec. II C). In

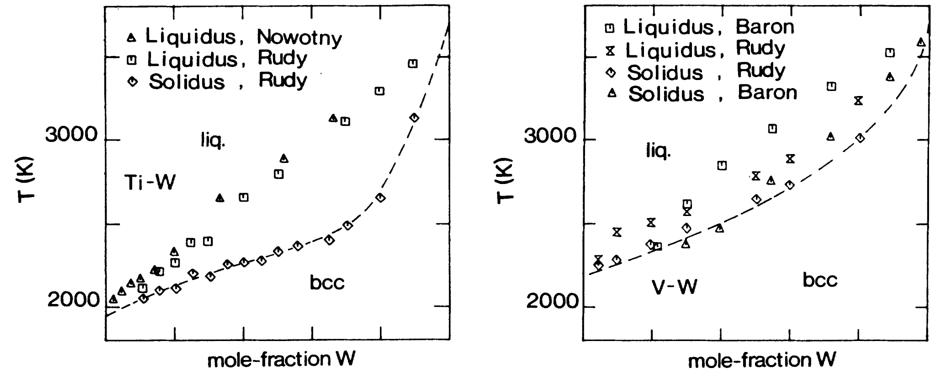

FIG. 8. The solid-liquid equilibrium in the Ti-W and V-W systems. Experimental data for the Ti-W systems according to Nowotny *et al.* (Ref. 51) and Rudy and Windisch (Ref. 52), and for the V-W system from Rudy (Ref. 53) and Baron *et al.* (Ref. 54). A dotted line has been drawn in the present work through the data points on the solidus line.

the last term of Eq. (13), $C_P^{l/\alpha}=C_P^l-C_P^\alpha$ has a vibrational and an electronic part. From Fig. 4, we estimate for the electronic part that $C_P^{l/\alpha}/T=(1\pm0.5)\times10^{-3}$ $\mathrm{J\,mol^{-1}\,K^{-1}}$. In Sec. II B we argued that the vibrational part of C_p^l may be approximately independent of T for $0.5T_f^\alpha<T<T_f^\alpha$. It therefore seems safe to assume that the vibrational contribution I to the integral in Eq. (13) is positive. We now put

$$T_f^\beta=\lambda T_f^\alpha\ . \tag{14}$$

Equation (13) and the estimates above, with the lower limit $I=0$, give the inequality

$$H^{\beta/\alpha}(T_f^\beta)<52-(37\pm11)\lambda-(7\pm2)(1-\lambda^2)\ \mathrm{kJ\,mol^{-1}}\ . \tag{15}$$

For $T_f^\beta=3500$, 2500, and 1500 K (i.e., $\lambda=0.95$, 0.68, 0.41), the right-hand side of (15) becomes 16 ± 11, 23 ± 9, and 31 ± 6 $\mathrm{kJ\,mol^{-1}}$, respectively. Before this is compared with an *ab initio* result $G_0^{\beta/\alpha}$, we should allow for a small correction, and write

$$H^{\beta/\alpha}(T_f^\beta)=H_0^{\beta/\alpha}+\int_0^{T_f^\beta}(C_P^\beta-C_P^\alpha)dT\ . \tag{16}$$

If $T_f^\beta>\Theta_D$, the contributions from harmonic lattice vibrations cancel in the integral in (16). There remain anharmonic and electronic contributions to C_P. They are, to a reasonable approximation, linear in T at the temperatures of interest. Then we can express the integral in (16), $H_C(T)$, as

$$H_C(T)=(T_f^\beta/2)C_P^{\beta/\alpha}(T_f^\beta)\ . \tag{17}$$

From the difference in $N(E_F)$ between α-W and β-W (Fig. 5), and the reasonable assumption that the anharmonic contribution to heat capacity of β-W differs at most by ±50% from that of α-W, we get

$$H_C(T)=(2\pm4)\lambda^2\ \mathrm{kJ\,mol^{-1}}\ . \tag{18}$$

At $T=2500$ K this amounts to only 1 ± 2 $\mathrm{kJ\,mol^{-1}}$. In Sec. III we estimated another correction, -1.3 $\mathrm{kJ\,mol^{-1}}$, due to volume effects. Table I gives *ab initio* results, corrected to 2500 K, the uncorrected *ab initio* results and our upper limit to $H^{\beta/\alpha}$, as derived if the metastable β-W would melt at 1500, 2500, and 3500 K, respectively. (Taken together, the phase diagrams in Fig. 1 suggest that the melting point of fcc W is of the order of 2500±1000 K.) The enthalpy differences obtained by Kaufman and Bernstein[1] and Gustafson[11] are also given in Table I. With $T_f^\beta=2500$ K, we find that the lattice stability of fcc W is lower than the value from *ab initio* calculations by approximately a factor of 2. Further, relation (15) indicates that in order for the CALPHAD stability to reproduce the value of about 55 $\mathrm{kJ\,mol^{-1}}$ from *ab initio* calculations, λ must be negative, i.e., fcc W must be less stable than the liquid phase at all temperatures. Thus there seem to remain only two alternatives: Either *ab initio* calculations of $H^{\beta/\alpha}$ give too large a value, or the extrapolation of the (metastable) liquidus line in W-Rh and W-Pt, to pure W, has a curvature such that it does not intersect the vertical axis (or does so at very low temperatures).[45]

These alternatives are now further discussed. Concerning the *ab initio* calculation, one notes that when the *ab initio* $H^{\beta/\alpha}$ is plotted versus the group number in the Periodic Table,[5] tungsten falls at a sharp maximum. A slight shift of the theoretical $H^{\beta/\alpha}$ along the group number axis can give good agreement with the CALPHAD-type estimate of this paper without any significant changes in $H^{\beta/\alpha}$ of the other 5*d* transition metals. There may also be structure-dependent many-body corrections to the one-electron description that is the basis for the quoted *ab initio* work.

At the end of Sec. VI we explained the rapid variation of the solidus line with the composition of W-Ti and W-V alloys, referring to the shape of $N_\alpha(E)$. We note in Fig. 4 that E_F of β-W falls at the low-energy edge of a trough in $N_\beta(E)$, and that E_F moves into the trough if W is alloyed with elements having a larger number of *d* electrons. As a consequence, the fcc phase will be rapidly stabilized relative to the liquid with the addition of, e.g., Pt. Then the solidus temperatures of the fcc structure in the Pt-W system are expected to increase rapidly when moving away from pure W, i.e., the solidus line in the Pt-W phase diagram shown in Fig. 1 is expected to bend downwards above 70 at. % W, giving a T_f^β much lower than the value from a smooth extrapolation, 2500 K. A value of, e.g., $T_f^\beta = 1500$ might be a better estimate. A more detailed analysis than ours, which may reconcile completely the experimental and the *ab initio* results, does not seem feasible until one has an *ab initio* treatment of the liquid phase and with about the same accuracy as one now has for solids.

VIII. MOLYBDENUM AND CHROMIUM

The thermodynamic properties of molybdenum[46] are similar to those of tungsten, but the anomalies are less pronounced. Molybdenum has a bcc structure up to $T_f = 2896$ K, with $S_f = 1.6R$ ($H^{l/\alpha} = 37$ kJ mol^{-1}) and a volume expansion on melting by 5%. The drop in $\Theta^S(T)$ between 300 K and T_f is 24%, i.e., the second largest drop observed for a metal (cf. Rosén and Grimvall,[27] Thiessen[28]). Band-structure calculations[47] show a minimum in $N(E)$ near E_F, similar to that in α-W. Chromium has a bcc structure with $T_f = 2180 \pm 20$ K, $S_f = 1.16R$, an increase in volume by 6.1% on melting,[48] and a minimum in $N(E)$.[49] Magnetic effects make an analysis of the thermodynamics of chromium complicated.

IX. CONCLUSIONS

Body-centered-cubic tungsten (α-W) has several unusual thermodynamic properties, e.g., very high values of the melting point, the entropy of fusion, the expansion on melting, and the lattice anharmonicity. These features are given a qualitative explanation only referring to the *d*-electron states of bcc W, in particular a minimum in $N_\alpha(E)$ around the Fermi level.

Previous[1,11] work, using so-called CALPHAD methods, yielded a lattice stability for bcc W relative to fcc W which was significantly smaller than that derived from *ab initio* electron band-structure calculations by Jansen and Freeman,[3] Skriver,[4] Davenport *et al.*,[5] Mattheiss and Hamann,[6] and Chan *et al.*[7]

We have reanalyzed CALPHAD data, relying on our account of the thermal properties of tungsten and characteristic features in the electron density of states. Then the magnitude of the discrepancy is considerably reduced. The reasons for the previously found disagreement can be understood in terms or $N(E)$ for bcc and fcc tungsten and the resulting influence on the phase equilibria of tungsten alloys. The CALPHAD approach expresses the thermodynamic functions by low-order polynomials in the temperature *T*, concentrations *c*, etc. In systems for which the free energy varies slowly with these variables, the CALPHAD method therefore gives reliable results. In the case of tungsten, however, the form of the electron density of states causes a rapid variation with *c* in tungsten-based alloys. We want to stress that both the *ab initio* calculations and the CALPHAD approach give considerable insight in the phase stabilities. The CALPHAD approach is, in most cases, more useful in practical work since its parameters are fitted to experimental data. The case of tungsten is an example where *ab initio* calculations are needed to clarify the situation. The physical picture emerging from this paper should be of importance in further attempts to refine the CALPHAD method.

Finally it should be noted that we have not achieved complete agreement in our attempts to reconcile the two methods. Although we believe that we have identified the most essential points, there is still a need for further work. In particular, it would be very interesting if *ab initio* calculations could be extended to liquids, so that the phase stability of bcc W relative to the liquid could be accurately determined without recourse to phase diagram fitting.

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APPENDIX

This appendix presents a model calculation of thermal properties of conduction electrons. The purpose is to show qualitatively how a metal may develop the unusual properties of tungsten, but the model should not be considered as a quantitative description of that metal.

Consider two different shapes, $N_a(E)$ and $N_b(E)$, of the electron density of states; see Fig. 9. If the electron states in the shaded part of N_a were all given an energy increase by *W*, they would fill the "trough" in N_a below E_F, and the total electronic energy would be equal to that of case *b*. The number of electron states given the energy increase would be $n = N_0 W/2$ per atom. Thus the cohesive energy (per mole) of case *a* is larger than that of case *b* by

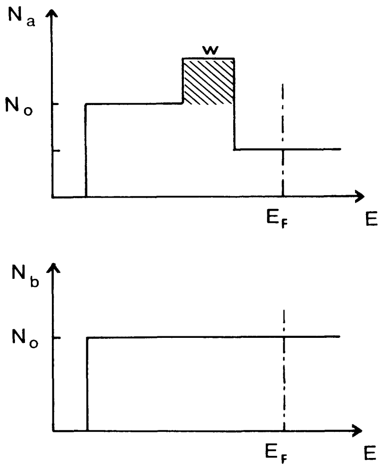

FIG. 9. The electron density of states in two models.

$$U = LnW = LN_0W^2/2 \ . \tag{A1}$$

We next consider the Gibbs energy and entropy of electronic excitations. For our purposes we may assume that $\Theta^S < T \ll T_W$, where $k_B T_W = W$, and take

$$S_{\text{el}} = \gamma_b T = (\pi^2/6) R k_B T N_0 \ . \tag{A2}$$

The corresponding Gibbs energy is $G_{\text{el}} = -\gamma_b T^2/2$ and the total Gibbs energy difference is

$$\Delta G = nRT_W - (\pi^2/6) nRT^2/T_W \ . \tag{A3}$$

We shall now see how ΔG may affect the melting temperature of a solid. Consider a "normal" solid with melting temperature $T_f = T'$ and an entropy of fusion $S' = R$ (Richard's rule). Let S' be due to the spatial atomic disorder of the liquid, and assume that the energy difference E' between the liquid and the solid phases has no significant temperature dependence. Then $E' = T_f S' = T'R$. We have considered a hypothetical liquid for which the glass transition is neglected. Now we add to the liquid phase the term ΔG, Eq. (A3). With numerical values $T_W = 5T'$ and $n = 0.3$, the melting temperature becomes $T_f \approx 2T'$. Thus the addition of a term ΔG due to d electrons increases the melting temperature in our model by a factor of 2. The entropy of fusion increases from $S' = R$ to $S_f \approx 1.4R$.

The molar volume of a transition metal is determined essentially by an attractive force from the d electrons and a repulsive force from s and p electrons overlapping with ion core electrons.[50] The attractive force arises because the width of the d band increases, while the "center of gravity" of $N(E)$ is not much changed, as the molar volume is decreased. That lowers the total energy, and more so in case a than in case b. The attractive forces thus are stronger in case a and give that structure a lower molar volume, since the repulsive forces do not depend on $N(E)$.

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