PHYSICS OF TITANIUM ALLOYS*-II: FERMI DENSITY-OF-STATES PROPERTIES, AND PHASE STABILITY OF Ti-Al AND Ti-Mo

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The results of magnetic and calorimetric measurements leading to evaluations of the Fermi densities-of-states, $n(E_F)$ and Debye temperatures, Θ_D, of Ti-Al and Ti-Mo alloys in various structural states are presented. Phase stability in these systems is correlated with the observed variations of $n(E_F)$ and Θ_D with electron-to-atom ratio, $\bar{e}$; and the paper concludes with some general comments on the relationships between physical properties and phase stability in transition-metal binary alloys, and Ti-base alloys in particular.

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1. INTRODUCTION

1.1 Specimen Materials - Experimental Techniques

In an investigation of the electronic bases of phase stability and solid-solution strengthening in Ti alloys, physical property measurements were made on specimens of Ti-Al and Ti-Mo alloys as typical examples of "α-stabilized" and "β-stabilized" systems, respectively. Although a great deal of useful information was derived from measurements of a pair of electrical transport properties viz. resistivity[1], and Hall coefficient[2], the principal experimental techniques used in the study were low-temperature calorimetry augmented by magnetic susceptibility.

The low-temperature specific heat, $C = \gamma T + \beta T^3$, when plotted in the format C/T vs T^2 yields as intercept, the electronic specific heat coefficient γ [leading to $n(E_F)$, the Fermi density-of-states] and as slope ($\beta \propto \Theta_D^{-3}$) the Debye temperature Θ_D. Also, as discussed in the companion paper (henceforth I) if the specimens become superconducting within the temperature range of the calorimeter, the specific heat measurements yield a wealth of information regarding the superconducting transition. Magnetic susceptibility, χ, was used as adjunct to the low-temperature specific heat investigations. Since χ contains a separable component, χ_{spin}, which also depends on $n(E_F)$ the magnetic susceptibility technique was used to confirm and extend the results of the calorimetric measurements. Magnetic susceptibility is a simple, rapid, and economical measurement, requiring only relatively small specimens (100 mg compared with ~30g for specific heat). It can be employed advantageously when a detailed study is required of the response of $\langle n(E_F) \rangle_{av}$ to a wide range of alloy solute concentrations and heat treatments (such as quench temperatures and aging conditions). In addition the susceptibility technique can be used to investigate the $n(E_F)$ properties of alloy phases stable only at elevated temperatures and, therefore, inaccessible to low-temperature calorimetry.

1.2 Experimental Program

(a) The results of magnetic susceptibility and low-temperature specific heat measurements on "β-quenched" Ti-Mo alloys; and "α-quenched", and otherwise heat-treated, Ti-Al alloys were presented in the previous International Titanium Conference.[3] (b) In order to determine the $n(E_F)$ behavior of single-phase-bcc (i.e., β) Ti-Mo alloys in the electron-to-atom-ratio ($\mathcal{E}$) range below about 4.3, in which they are not stable at ordinary temperatures, use was made of elevated-temperature magnetic susceptibility data in the manner indicated in the companion paper (I). A comparison of the results with

those for the as-quenched alloys showed that $\langle n(E_F) \rangle_{av}$ was relatively low in the latter due to the presence of ω-phase precipitates. (c) As confirmation of this conclusion, and in order to determine some of the physical properties of ω-phase itself, magnetic and calorimetric measurements were made as a function of ω-phase development to "metastable equilibrium"[4] through moderate-temperature (350° C) aging.

1.3 Data Analysis

An aim of the analytical procedure was to determine $n(E_F)$, a fairly fundamental quantity, and one which may be compared with the results of band structure calculations when such information is available. In suitable units[5] $n(E_F) \cong 0.212\ \gamma/(1 + 0.212\ \gamma\ V_{app})$, where the denominator is the electronic-specific-heat electron-phonon enhancement factor. When dealing with a family of transition-metal alloy superconductors the calorimetric data itself may contain sufficient information which, if expressible in the form of a linear $\log (T_c/\Theta_D)$ vs $(0.212\ \gamma)^{-1}$ plot of slope $-1/V_{app}$, enables the electron-phonon correction to be readily applied.[6] Such was, in fact, the case for Ti-Mo alloys, including α-Ti, as has already been shown[7]. Values of $n(E_F)$ [$\cong 0.212\ \gamma/(1 + 0.212\ V_{app}\ \gamma)$], calculated by applying the electron-phonon correction with $V_{app} = 0.26$ eV-atom,

Table I. Debye Temperature, Θ_D, And Fermi Density-of-States, $n(E_F)$, For Alloys in Electron-to-Atom-Ratio ($\mathcal{Z}$) Ranges $3.63 \leq$ " $\mathcal{Z}$ " ≤ 4.08 And $6.05 \leq \mathcal{Z} \leq 6.76$

Alloy*	"$\mathcal{Z}$"	Phase	Θ_D	$n(E_F)$	Alloy	$\mathcal{Z}$	Phase	Θ_D	$n(E_F)$
HP-37	3.63	[α_2]	495	0.50_1	Pure Ti	4.00	α	420	0.60
HP-33.3	3.66	[α_2]	506	0.48_2	TM-4.3	4.08	ω	420	0.54_6
HP-30	3.70	[α_2]	485	0.45_6					
HP-28	3.72	[α_2]	518	0.41_6	MR-5	6.05	β	450	0.38_4
HP-25	3.75	α_2	495	0.36_8	MR-10	6.10	β	440	0.45_0
HP-23	3.77	α_2	485	0.30_3	MR-20	6.20	β	420	0.59_6
HP-20	3.80	α_2	485	0.35_4	MR-25	6.25	β	405	0.62_6
HP-15	3.85	α	442	0.64_4	MR-30	6.30	β	395	0.63_4
HP-13	3.87	α	445	0.66_0	MR-40	6.40	β	340	0.67_1
HP-10	3.90	α	413	0.64_0	MR-50	6.50	β	320	0.66_4
HP-5	3.95	α	427	1.62_8	MR-58	6.58	σ	351	0.54_0
HP-3	3.97	α	413	0.61_8					
HP-2	3.98	α	403	0.61_5	MO-38	6.76	σ	371	0.54_2

*HP, TM, MR, and MO-x represent Ti-Al, Ti-Mo, Mo-Re, and Mo-Os (x at.%) respectively.

to the measured γ's for β-phase and $(\beta+\omega)$-Ti-Mo alloys have been presented in Table I of I. Also tabulated there are the directly-measured values of Θ_D, together with a list of extrapolated Θ_D's for "unstable"[8] β-Ti-Mo ($4.0 < \bar{z} < 4.3$), derived from a set of T_c/Θ_D values[9]. The α-Ti-Al alloys on the other hand were "nonsuperconducting" (i.e., $T_c < 1.5$ K). But since pure α-Ti was represented by a point on the above-mentioned semilog plot, $V_{app} = 0.26$ eV-atom was also used in correcting γ_{Ti-Al} for electron-phonon effects. The values of $n(E_F)$ so obtained are listed (together with the directly-measured Θ_D's) in Table I of this paper.

2. RESULTS AND DISCUSSION

2.1 Physical Properties of α-, and α_2-Ti-Al and ω-, $(\beta+\omega)$-, and β-Ti-Mo Alloys

The experimental results, expressed in terms of the physical properties γ, χ, and Θ_D for α, α_2, ω, $(\beta+\omega)$, and β-phase alloys, are summarized in Figure 1.

2.1.1 Θ_D in Ti-Mo

Since as described in I, the Debye temperatures were separated out from a set of empirically-derived (T_c/Θ_D)-values, some confirmation of the validity of the form of the resulting composition-dependence of Θ_D was warranted.

Accordingly a comparison was made with Θ_D(Ti-Cr), calculated by applying Anderson's method[10], to Fisher and Dever's[11] measured elastic constants. The results of this procedure are summarized in Figure 2. Taking into consideration the fact that, in the fairly massive ingots measured, ω-phase seemed to make its appearance in Ti-Mo at a higher $\bar{z}$ than was the case for Ti-Cr[12] Figure 2(c) shows that the deduced Θ_D-composition-dependence for "virtual"[8] β-Ti-Mo was in good accord with that calculated for virtual β-Ti-Cr. Θ_D is sensitive to the shear modulus $C' = (c_{11}-c_{12})/2$ which as pointed out by Fisher and Dever[11] decreases relatively rapidly with decreasing $\bar{z}$ upon entering the virtual-β regime. This behavior is reflected in Figure 2(c). For Ti-Cr, martensitic transformation which has been observed within $4.10 < \bar{z} < 4.12$[13] seems to be related to the vanishing of C' which Figure 2(a) shows as occurring at Ti-Cr(5.03 at.%) or $\bar{z} = 4.1$. At the same time, Anderson's formula yields $\Theta_D = 208$ K; a value which tends to confirm the independently deduced behavior of Θ_D (Ti-Mo) which drops to 207 K at 5 at.% Mo, just prior to martensitic transformation at 4-1/2 at.% Mo[14]. Whereas the martensitic transformation is undoubtedly associated with $C' = 0$[4,11] (i.e., "softening"[15]), de Fontaine *et al*[4] have shown that the $\beta \rightarrow \omega$ transformation can be achieved formally by altering

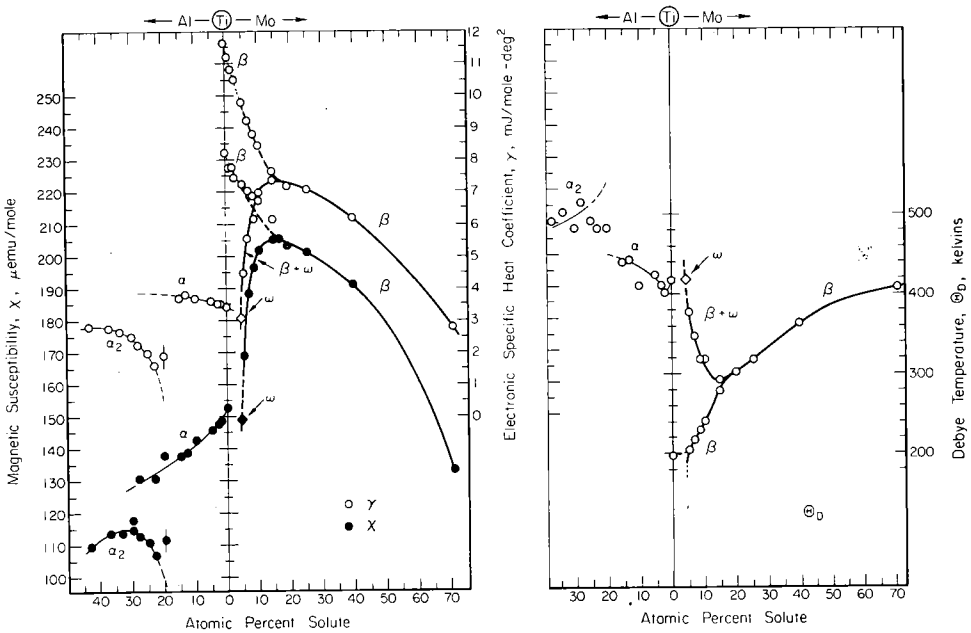

Figure 1. Composition-dependences of magnetic susceptibility (χ), low-temperature-specific-heat coefficient (γ), and Debye temperature (θ_D), for Ti-Al and Ti-Mo alloys in various structural states viz.: α_2, α (Ti-Al); and α, ω, $\omega+\beta$, and β (Ti-Mo).

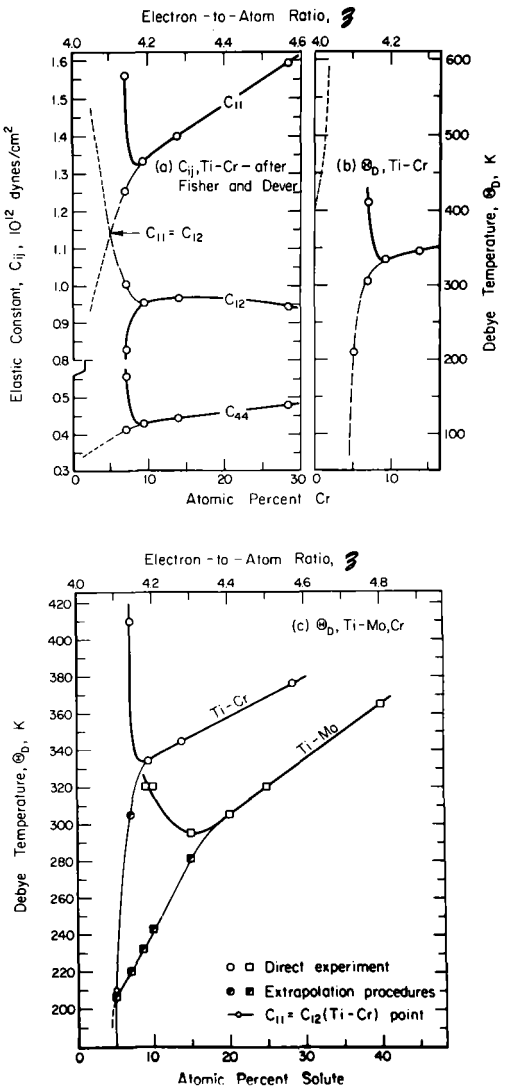

Figure 2. (a) Elastic constants c_{11}, c_{12} and c_{44} of Ti-Cr - after Fisher and Dever(11,16). (b) Θ_D for Ti-Cr calculated from the data of the previous figure, using Anderson's(10) method. (c) Comparison of the temperature-dependence of Θ_D for Ti-Cr and Ti-Mo. At the observed room-temperature threshold of martensitic transformation for Ti-Mo (viz. 4-1/2 at.%), and when $c_{11} = c_{12}$ for Ti-Cr, we find $\Theta_D]_{\text{Ti-Mo}} \tilde{\approx} \Theta_D]_{\text{Ti-Cr}} = 208$ K.

the atomic force constants at constant c_{ij}. In practice, however, it seems that it is in fact a "weakening" (16) of C' (as the softening-point, C' = 0, is approached) which leads to displacement fluctuations(4) of sufficient amplitude to excite the $\beta \rightarrow \omega$ diffusionless transformation.

2.2 Physical Properties of ω-Phase in Ti-Mo

In an aging study, Ti-Mo (10 at.%) (TM-10) was annealed at 350°C for 880 hours, by which time it was assumed that a condition approximating quasi-equilibrium had been attained as represented by the metastable phase diagram of Reference (4). The evaluation of f_ω, the mole-fraction of ω-phase present in the aged TM-10 has been discussed in I. If Φ is then taken to represent the physical properties χ, γ, and Θ_D in turn, the conservation equation:

$$\langle\Phi\rangle_{av} = f_\omega \Phi_\omega + (1-f_\omega)\ \Phi_\beta \ , \qquad (1)$$

together with the previously estimated values of Φ_β, may be used to determine χ_ω, γ_ω, and $\Theta_{D,\omega}$ for ω-TM-4.3. The values so obtained, plotted as special points in Figure 1, are seen to be in excellent agreement with the directly measured quantities for (β+ω)-Ti-Mo. These results serve to confirm that the decreases in χ and γ with decreasing $\bar{z}$ ($\lesssim 4.3$) as well as the corresponding stiffening of Θ_D are, in fact, due to the continuously increasing influence of ω-phase precipitation. The $n(E_F)$ for ω-TM-4.3, derived from γ_ω using V_{app} = 0.26 eV-atom as before, is listed in Table 1.

2.3 $n(E_F)$ and Θ_D in Ti-Al and Ti-Mo

The variations of $n(E_F)$ and Θ_D with $\bar{z}$, derived as a result of the magnetic and calorimetric experiments on the α and α_2 phases of Ti-Al, and the α, ω, β+ω, and β phases of Ti-Mo are shown in Figure 3. In this Figure, $\bar{z}$ is not intended to have a real physical meaning but is to be interpreted as an arbitrary horizontal scale, based on the average number of atomic s, p and d electrons in the case of Ti-Al, and s+d electrons in the case of Ti-Mo. Particularly noticeable are (a): that the more stable (at say, room temperature) of a pair of allotropes, possesses the lower $n(E_F)$ together with the higher Θ_D--tightly-bound α_2-Ti-Al compared to α-Ti-Al is a very good example of this--and (b): that discontinuities or turning points in the $\bar{z}$-dependence of $n(E_F)$ [or Θ_D, which scales inversely with it] occur at the limits of the various regimes of structural stability.

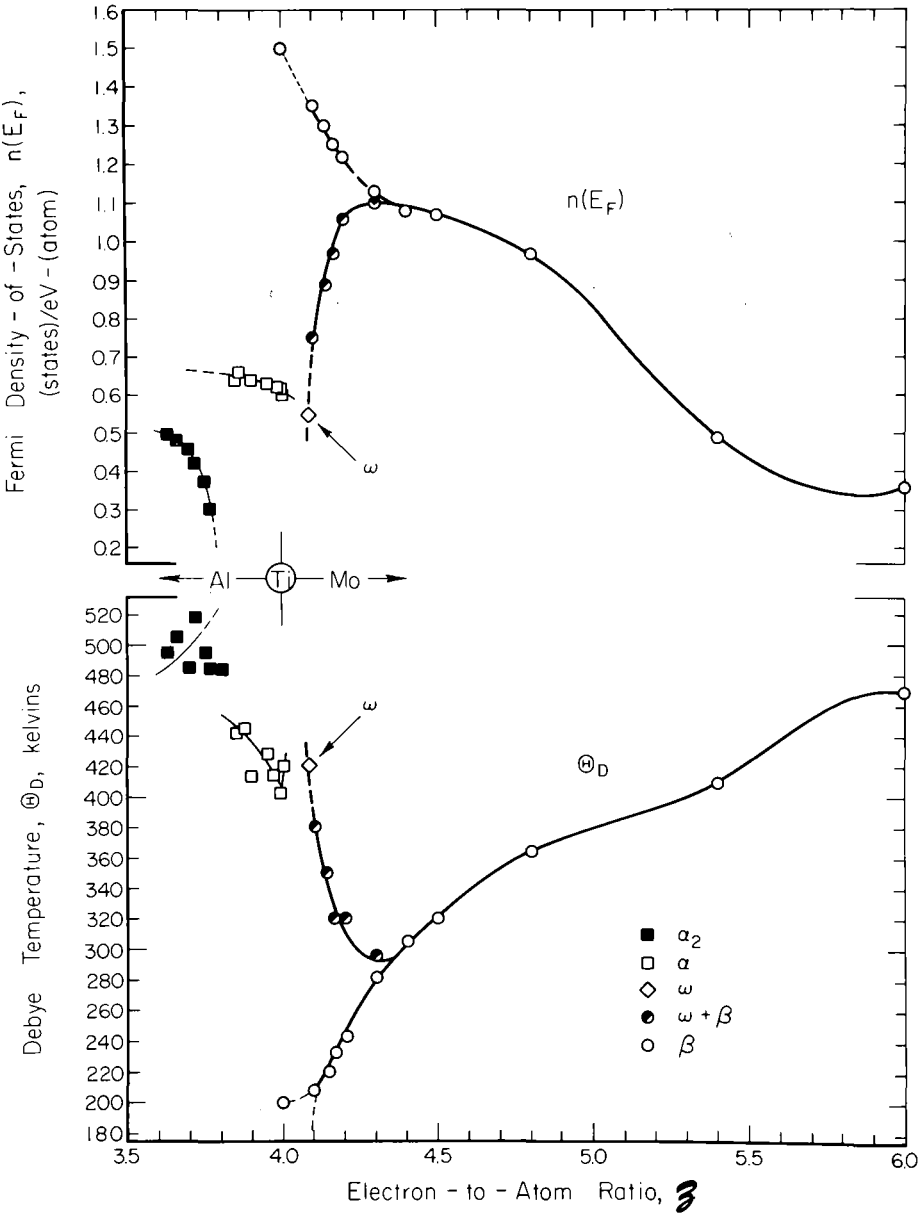

Figure 3. Empirically-derived Fermi density-of-states, $n(E_F)$, and Debye temperature, Θ_D, as functions of electron-to-atom ratio, z, in Ti-base alloys.

2.4 Phase Stability in Titanium Alloys

Figure 4 presents an experimentally-determined $n(E_F)$ curve for some binary transition-metal alloys within $4 \leq \mathfrak{z} \leq 7$. The $4 \leq \mathfrak{z} \leq 6$ regime was covered by Ti-Mo, as described above. In order to extend the range to $\mathfrak{z} = 7$, use was made of the calorimetrically determined data for Mo-Re, and Mo-Os from the work of Morin and Maita[17] and Bucher et al.[18]. In applying an electron-phonon correction in this range Morin and Maita's[17] $V_{app} = 0.42_6$ was employed. The experimentally-derived curve may be compared with a "calculated" $n(E_F)$-curve based on computed[19] values of $n(E_F)$ for bcc Ti, V, Cr, Mn, and Fe, and for the alloy system Ti-Mo[20]. Also included for comparison as an inset, are reproductions of Waber's[20] calculated n(E) profiles for the bcc 3d and 4d elements Cr and Mo. Such curves for all bcc 3d transition elements as well as some bcc 4d transition elements are characterized by a pair of dominant peaks[21]. At this stage it is appropriate to point out that, even within the context of rigid-band-type behavior [as discussed in (19)], the twin main peaks of the N(E) curves of pure bcc metals (see inset) are not to be confused with those apparent in the calorimetrically-derived $n(E_F)$ loci. The latter occur "closer in" and are induced by structural transformations of the β-phase, which take place both for $\mathfrak{z} \lesssim 4.3$ and $\mathfrak{z} \gtrsim 6.7$. Thus, the experimentally-determined maxima (e.g. that for $\mathfrak{z} \sim 4.3$) vanish when $n(E_F)$ is extrapolated semi-empirically into the unstable β regime.

De Fontaine[22] in studying the lattice dynamics of the bcc structure has computed with remarkable success the instability conditions leading to spontaneous ("athermal") ω-phase formation. Presumably the upper-$\mathfrak{z}$ limit of bcc stability could also be treated in terms of atomic force constants. The ions of course interest via the electrons[23], but so far a rigorous electronic interpretation of transition-metal-alloy phase stability, using modern theories of metals, has not yet appeared. Figures 3 and 4, however, contain some empirical results which could perhaps serve as a starting point viz.:

(a) For a given $\mathfrak{z}$ the more stable ($\lesssim$ room temperature) of a pair of allotropes is associated with the lower $n(E_F)$. Thus, for three specific single-phase situations (Figure 3):

$$n(E_F)_{\alpha_2\text{-}Ti_3Al} < n(E_F)_{\alpha\text{-}Ti_3Al} \quad (T \lesssim 830^\circ\ C)$$

$$n(E_F)_{\alpha\text{-}Ti} < n(E_F)_{\beta\text{-}Ti} \quad (T \lesssim 883^\circ\ C)$$

$$n(E_F)_{\omega\text{-}TM\text{-}4.3} < n(E_F)_{\beta\text{-}TM\text{-}4.3} \quad (T \lesssim 500^\circ\ C)$$

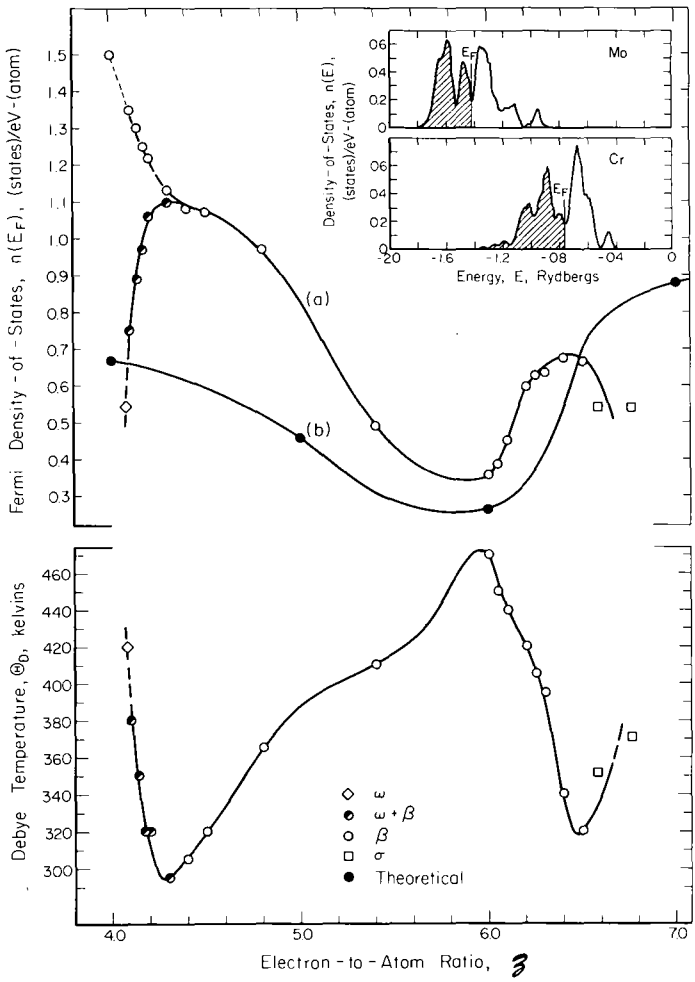

Figure 4. z-dependence of $n(E_F)$ for transition-metal-binary (i.e. T_1-T_2) alloys: (a) Empirically-derived curve for Ti-Mo-Re, based on the present data and those of References (17) and (18); (b) "calculated" $n(E_F)$ for bcc T_1-T_2 alloys based on published data points[19] for bcc Ti, V, Cr, Mn and Fe. For comparison, the z-dependence of Θ_D for Ti-Mo-Re is also shown. The remarkable inverse scaling exhibited by the $n(E_F)$ and Θ_D curves owes its origin to phase stability-considerations.

Inset are calculated n(E) curves for bcc Ti and Mo from the work of Waber and colleagues[20]. $n(E_F)$ is at a local minimum in n(E) for both bcc Ti and Mo; however, the latter shows an extra peak, which seems to be reflected in the calculated $n(E_F)$ for Ti-Mo[20] but not in the experimentally derived curve presented here.

(b) As $\mathcal{Z}$ is varied, maximal bcc stability is achieved with a half-filled d-band. The decrease in stability as $\mathcal{Z}$ either increases or decreases from this position is reflected in a decreasing Θ_D. This, in turn, is the result of a weakening in $C' = (c_{11}-c_{12})/2$ which has been shown to occur in each case[24,11, respectively], and which precedes structural transformation to σ-phase on one hand, and ω-phase on the other.

For Ti-base alloys, therefore, since the only way to increase the occupancy of the d-band is to add conduction electrons, transition elements tend to be β-stabilizers. On the other hand non-transition metals such as Al, Ga, and Sn reduce the occupancy of the Ti d-band, not only because they possess fewer conduction electrons but through the formation of bound states. These are, of course, α-stabilizers.

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7. See Figure 3 of Paper I.

8. Referring to single-phase-bcc (β) Ti-Mo we have designated several electron-to-atom-ratio ($\mathcal{Z}$) regimes as follows:
   $4.0 \leq \mathcal{Z} \leq 4.3$ - "unstable"; a regime which includes
   (i) $4.0 \leq \mathcal{Z} \leq 4.05$ - "absolutely unstable", and
   (ii) $4.05 \leq \mathcal{Z} \leq 4.3$ - "virtual".

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