Solid Solution Strengthening and Fundamental Design of Titanium Alloys

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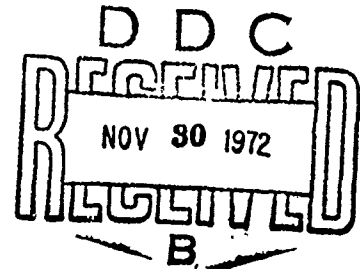
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E. W. COLLINS, H. L. GEGEL, AND J. C. HO

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13. ABSTRACT

Phase stabilization and solid solution strengthening in titanium alloys are discussed from an electronic viewpoint. Based on the structure dependence of cohesive energy, we rationalize the alpha and beta-stabilization of titanium as produced by alloying with nontransition and transition metals, respectively; and point out that only the addition of alpha-stabilizers will yield significant strengthening effect. The preference of multicomponent alloying, i.e., adding several nontransition metal solutes to titanium or otherwise beta-stabilized alloys, can also be justified from the concept to be described. Correlations between physical and mechanical properties of prototype systems (Ti-Al, Ti-Ga, Ti-Sn, Ti-Al-Ga, Ti-Mo, and Ti-Mo-Fe-Al) are presented to demonstrate the validity of the fundamental approach, which should eventually develop into useful alloy design criteria.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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E. W. COLLINS, H. L. GEGEL, AND J. C. HO

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FOREWORD

This program was initiated under Project 7353, "Characterization of Solid Phase and Interphase Phenomena in Crystalline Substances," and Task No. 735302, "Correlation of Physical and Mechanical Properties of Metals and Ceramics," during the period July 1970 through August 1972.

This research was done in the Advanced Metallurgical Studies Branch of the Metals and Ceramics Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433 and at the Battelle-Columbus Laboratories, Columbus, Ohio 43215. The principal investigators were Dr. H. L. Gegel (AFML/LLS), Dr. J. C. Ho of Wichita State University and Dr. E. W. Collings of Battelle-Columbus Laboratories.

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This technical report has been reviewed and is approved.

C. T. LYNCH
Chief, Advanced Metallurgical Studies Branch
Metals and Ceramics Division
Air Force Materials Laboratory

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I. INTRODUCTION

Development of useful titanium alloys has been worked on consistently for many years, and a series of materials for practical application have become available. They are designed primarily for the aerospace industry, even though their potential to be used in other types of industry such as food, chemical, heavy machine construction, is also feasible and should be explored.[1] By examining the alloys-in-service developed in the United States so far, however, it is interesting to note two points: First, alloy development programs generally emphasize the microstructural effects on mechanical properties, but pay relatively little attention to the base alloy selection. In other words, there is a lack of systematic study of fundamental (physical and thermodynamic) properties of various titanium alloys, such that one can formulate a first-principle guideline for choosing alloy elements and compositions. Such a guideline is undoubtedly needed for an economic and efficient alloy design. Second, multicomponent alloying of titanium is somewhat underestimated in the United States.[2] This contrasts to the Russian literature [3] which clearly indicates that even in the early 1960's enough information based on fundamental property studies was available for them to derive a 'physico-chemical' theory concerning solid solution strengthening. During the last several years, similar effort has been made in our laboratories. The results lead to certain alloy design criteria, and also justify the importance of multicomponent alloying.

In this paper the electronic bonding mechanism, which plays an important role in determining the mechanical properties of metals and alloys is briefly discussed. The experimental techniques used to quantitatively measure the bond strength are outlined. Prototype α- and β-stabilized systems are described to demonstrate this approach. The emphasis here is to find a way for formulating base alloys with inherent or electronic solid solution strengthening. After a base alloy is chosen, one can and should always optimize appropriate microstructures for specific applications.

II. CONSIDERATIONS ON SOLID SOLUTION STRENGTHENING --
WHY AN ELECTRONIC PROPERTY APPROACH IS NEEDED

Several theoretical models have been proposed to explain the phenomenon of solid solution strengthening in alloys. Mott and Nabarro [4] first pointed out the significance of atomic size misfit. The work was later extended by Li.[5] Fleischer [6,7] added another parameter based on the shear modulus misfit. Takeuchi [8] and Labusch [9] have essentially the same parameters in their models. However, experimental results from systematic studies on lead-base alloys by van der Planken and Deruyttere [10] and on iron-base alloys by Leslie [11] indicated that there is actually no simple relation between the size and modulus misfit and the solid solution component of strengthening that can be applied to all the alloys. Van der Planken and Deruyttere [10] attempted to account for the discrepancy by including an electronic contribution expressed in terms of the _sum_ of electronegativities of solute and solvent. Unfortunately, their model is fundamentally invalid for two reasons: (1) Only a large _difference_ in electronegativities implies a tendency of ionic bonding formation, but the sum has no physical meaning. (2) Their model involves a linear combination of a dimensionless size misfit parameter and an electronegativity term having a unit of $(eV)^{1/2}$. In this respect, it is interesting to note a 'physico-chemical' theory, derived by Russian investigators, [3] which is partly based on the electronegativity difference and is used in developing heat resistant titanium alloys.

From a physics viewpoint, one simply does not expect to have an adequate understanding of solid solution strengthening unless an electronic bonding mechanism is taken into consideration. The significance of such a mechanism is also demonstrated by the experimental force-activation distance curves determined by Conrad and coworkers [12,13,14] for both alpha and beta titanium alloys: The largest area under these curves occurs over a distance of about 1.5b, a region where elasticity theory breaks down. The activation energy for this region of the force-activation distance curve is about 1.3 eV for both crystallographic forms of titanium, but the portion of each curve which can

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be attributed to elastic interactions accounts for only 0.1 eV. It is felt that this order of magnitude difference in activation energy, independent of crystal structure, must also arise from an electronic boning effect. In order to check the idea and derive relevant parameters, one needs to determine certain fundamental properties of prototype systems. Such a program has been carried out from which one can correlate to a great extent the physical, thermodynamic, and mechanical properties through an electronic bonding mechanism. The strength of electronic bonding in dilute alloys can either be measured directly (electrical resistivity and thermodynamic interaction strength parameter) or be deduced from the observation that ordered compounds form at higher concentrations in α-stabilized but not in most β-stabilized Ti alloy systems. There tends to be a strong interaction between Ti and α-stabilizers, leading to solid solution strengthening, whereas a weak interaction exists between Ti and β-stabilizers. (One finds a similarity between Ti and Fe alloy systems along this line: Based on Leslie's work [11], the Fe alloy systems with enhanced elastic and shear modulus in the dilute region behave analogously to α-stabilized Ti systems in the phase diagram, i.e., the alloying effect stabilizes the low temperature α-phase of Fe.)

Like most of the models mentioned above, one also expects an athermal strengthening due to the electronic effect, which persists to reasonably high temperatures. Another important feature of such an electronic strengthening approach is that one can rationalize the importance of multicomponent alloying.

III. ROLES OF PHYSICAL PROPERTY STUDIES
ON SOLID SOLUTION STRENGTHENING

III-1. The Cohesive Energy of Pure Metals

A proper description of a metal, as an assembly of positive ions in equilibrium with the conduction electrons, must eventually lead to an understanding of the principal interactions which control ionic motion during deformation, and hence the mechanical properties. Such interactions can be expressed in terms of the cohesive energy (E_{COH}), a component of the internal energy (E), where

$$E = E_{COH} + TS, \tag{1}$$

with S and T representing entropy and absolute temperature respectively. If constant volume conditions prevail, E_{COH} may be identified as the Helmholtz free energy.

The key statement in this approach to an understanding of electronic-property/mechanical-property interrelationships takes the form of a series expansion of E_{COH} into components representing the contributions by (a) the electron gas itself, and (b) n-body (n = 1, 2 ...) ionic interactions;

$$E_{COH} = \sum_{i=1}^{n} E_i \tag{2}$$

Such an expression might well be used axiomatically [15], but has also been derived formally by Cohen [16] who showed that the free energy could in this way be resolved into structure-independent and structure-dependent components. The expansion for E_{COH} is dominated by E_1, which represents the contribution by the electron gas plus the self-energy of the ions embedded in it. Being structure-independent, it is this term which confers on metals and alloys their characteristic ductility. E_2 depends on pairwise (central-force) interactions, E_3 on triplet interactions, and so on. These are all structure-dependent, and therefore control the metal's resistance to

deformation. The convergence of Equation 2 depends on the strengths of the atomic potentials expressed in some suitable form.

For very weak potentials (such as pseudopotentials) the series may be terminated at n = 2.[17] Such a truncated form has been derived by Harrison [18] and by Blandin [19] using second-order perturbation theory. Under these conditions E_{COH} is only weakly structure-dependent. A second-order perturbation expression of E_{COH} is valid, for example, for the monovalent[20] pseudopotential metals Na and K, which are plastic at all temperatures.

If the atomic potentials are strong, perturbation theory may no longer be used and one returns to the full expression for E_{COH}, entering the regime of interest here, in which third- and higher-order terms become significant. The resistance to deformation of a pure metal may thus be related to the strength of its atomic potential; one measure of which, as Cohen has suggested[16], being E_g/Δ, the ratio of a low-lying band gap to the width of the unperturbed energy band.

III-2. Electronic Structures of Alloys

As the above discussion indicates, strengthening in metals is accompanied by a breakdown of perturbation theory. This clue leads to an understanding of solid-solution strengthening in alloys. Stern[21] has pointed out that perturbation theory may be used in describing the electronic structures of alloys formed between two simple metals only if V_{12}/Δ is small. V_{12} is the difference in the atomic potentials of the alloy components, and plays the same role as E_g for a pure metal. By selecting solute elements whose potentials differ considerably from that of the host the convergence of Equation 2, and consequently the degree of solid-solution strengthening, can be controlled.

Unfortunately, there is not enough information at present to assign a meaningful atomic potential value to a transition metal such as titanium. It can only be expected that 'low perturbation' occurs in titanium-rich alloys with nearby transition elements (β-stabilized systems). However, it would

be more appropriate to discuss the 'strong perturbation' of electron states in titanium-nontransition metal alloys (σ-stabilized systems) based on the 'charging' effect.

The atoms of a pure simple metal (metal-1) of valence Z each contribute Z electrons to the conduction band; similarly for a pure simple metal (metal-2) of valence Z + 1. But this is no longer true when metal-2 is dissolved in metal-1, since screening or charge-neutrality considerations require the extra valence electron to be partially localized in the vicinity of the metal-2 atoms. This was discussed initially by Mott[22], and developed into theories of metallic virtual bound states by Friedel[23] and into the theory of 'charging' through the work of Stern.[21, 24, 25] It shows that the perturbation approach and the rigid-band model are inapplicable to alloys of simple metals differi. in valence. The theory of charging implies more than a cell-by-cell neutralization of net charge by screening If charging is 'large'[24] the theory requires a drastic alteration in band shape as the electrons are redistributed in energy. For example, the screening electrons of atom-1 may be assigned mostly to low-lying states in the band, and conversely for atom-2. Such an arrangement would imply the existence of a minimum in the n(E) (density-of-states versus energy) curve. In contrast to the motion of 'neutral pseudo-atoms'[26] which carry their 'own' screening electrons with them, the movements of atoms under conditions of large charging are resisted by the energy barriers associated with redistribution cf the screening charge in space and energy with each change of local environment. This strong structure-dependence of electron states which accompanies large charging is expressive of solid-solution strengthening.

It is reasonable to view such a strengthening effect as due to directional bonding formation between atom-1 and atom-2. A significant consequence of this is that, when atomic ratios become suitable, a partially covalent (directional-metallic) bonded, long range ordered intermetallic compound will be formed.

III-3.   Physical and Mechanical Property Measurements

Listed below are several physical and mechanical property measurements on prototype titanium alloy systems. From these measurements solid solution strengthening is investigated from a fundamental viewpoint. Most of these measurements are carried out with standard techniques. Therefore only brief description is given.

Homogeneous alloys in the form of 40-gram buttons were prepared by repeated arc-melting high purity Ti and alloying elements with nonconsumable electrodes under a partial pressure of argon. Specimens for the various measurements were then prepared from these buttons.

III-3-1. Low temperature specific heat measurements were carried out between 1.5 and 4.2°K in a He^4 cryostat.[27] The total specific heat can be resolved into an electronic and a lattice contribution, yielding the electronic specific heat coefficient (γ) and the Debye temperature (Θ_D), respectively. The electronic specific heat coefficient is a direct measure of the electronic density of states at the Fermi level [$n(E_F)$].

III-3-2. Magnetic susceptibilities (χ) were measured with the Curie technique[28] over appropriate temperature ranges. The measurements serve for two purposes: to complement the low temperature calorimetry in estimating $n(E_F)$ and to trace the structural changes with temperature in certain alloys.

III-3-3. Hall coefficients (R_H) were determined with reasonable accuracy by using a constant current source and a magnet with precision current-regulated power supply.[29] The data are useful in estimating the density of charge carriers.

III-3-4. Electrical resistivity (ρ) values, obtained by the four-probe dc method[29], were used to scale the interaction strength among the alloying elements (see next section).

III-3-5. High temperature specific heat data in the temperature range above room temperature to about 1000°C were obtained by drop calorimetry.[30,31]

The specimen transfer from the furnace to the calorimeter was done rapidly so that the calorimeter did not pick up heat from the furnace and that the heat loss from the specimen during the drop was negligible. Drop calorimetry gives the heat content, from which the specific heat is obtained by differentiation and is used for analyzing the lattice vibrational anharmonicity.

III-3-6. Thermodynamic interaction strength parameters (I) were calculated from the thermodynamic activities of alloy components (see next section), which were first determined through the use of a triple Knudsen cell and a time-of-flight mass spectrometer.[32, 33] The technique employs the regular solution model in order to treat the vaporization data in terms of ion current ratios obtained from the mass spectrometer.

III-3-7. Tensile testing studies were made at room temperature in air, using an Instron tester. The strain rate was approximately 4×10^{-5} sec^{-1}. The results were then correlated to the physical and thermodynamic properties.

III-4. Electronic and Thermodynamic Bonding Parameters

Based on either the perturbation theory or the theory of charging, an effective control of solid solution strengthening is hinged on a reliable measure of the atomic 'dissimilarity'. The difference between the well-depths of a pair of atomic pseudopotentials has been suggested as an appropriate quantity.[15] Another extremely useful parameter is, of course, the Pauling electronegativity difference[34] which has been used by Kubaschewski and Sloman[35] in their studies of bonding mechanisms in intermetallic compounds. They were able to make good estimates of the proportions of metallic, covalent, and polar character of the bonds of binary phases. Unfortunately, the chemically derived quantities from heats of formation are not always appropriate to be used in metallic systems, particularly in systems involving transition metals. For example, the tabulated electronegativities for Ti and Al are either equal[34] or approximately equal[36], yet a strong interaction exists between Ti and Al atoms, which leads to the tightly bonded intermetallic compound Ti_3Al. For this reason, other physical and thermodynamic

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properties, which might be used as bonding parameters for gauging the interaction strength, are considered.

III-4-1. Electrical resistivity: It is possible to relate the solid solution strengthening capacity of a nontransition metal (designated B-metal), in Ti to the scattering potential presented by B-ions to d-wavefunctions. The relative magnitudes of the specific resistivities* of various metals, when dissolved in Ti, can be used as indicators of the degrees of charging, and consequently of solid-solution strengthening. The composition-dependencies of resistivity of ρ ʳal Ti alloys with either transition metal solutes or B-metal solutes a ʹn in Figure 1. It is seen that the specific resistivity common to various tɪar .ition metal ions in Ti[37] is approximately an order of magnitude smaller than those for B-metals; a result consistent with Section III-2. The resistivity data also suggest that the interaction strengths between various B-metals and Ti, and hence the solid-solution-strengthening abilities of the B-metals in Ti-B alloys, increase in the sequence Al → Ga → Sn. This has indeed proved to be the case for Al and Ga additions to Ti, as indicated in Figure 2.

III-4-2. Thermodynamic interaction strength parameter: It would be most interesting to develop a new scale appropriate for metallic systems including transition metals, to measure or to predict the interaction strength among the constituent elements in an alloy or intermetallic compound. Some success has been realized in deriving such a scale from thermodynamic studies.[38] Basically, one applies the regular solution model of Fowler and Guggenheim[39] and of Hardy[40] to Ti base solid solutions. In this model a pairwise interaction parameter is defined as,

$$\Omega_{ij} = Z\left[E_{ij} - (E_{ii} + E_{jj})/2\right],\qquad(3)$$

where Z is the coordination number and E_{ij}'s are the interaction energies between atom i and atom j. Experimentally, the Ω_{ij} values were determined

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*Specific resistivity is defined as the incremental change in resistivity per atomic percent solute.

by conducting a standard Knudsen cell experiment in a mass spectrom-
eter.[32,33,41] This was done by using the definition of thermodynamic
activities of alloying components and relating the ion current in the mass
spectrometer to partial pressures.

A thermodynamic interaction strength parameter I is introduced as,

$$I = \sqrt{\Omega_{ij}} \tag{4}$$

with a unit of $(eV)^{1/2}$, such that I can be considered as analogous to the
Pauling electronegativity difference.[38] However, it is suggested to be
more useful for metallic systems, because it is directly derived from
metallic systems. The I values for several Ti-based systems are presented
in Table I. There are noted agreement and disagreement between them
and the electronegativity differences based on the scales given by Pauling[34]
and by Astakhov.[42] The applicability of these values will be demonstrated
in Section IV.

IV. RESULTS AND DISCUSSION

IV-1. Alpha-Stabilized Alloys

IV-1-1. Alpha-stabilization: For isolated transition metal ions dissolved in nontransition metals, the amplitudes of the d-wavefunctions are large in the vicinity of the impurity. These are referred to as virtual bound states.[23] Together with some extra broadening of the d-states this applies to concentrated alloys, with the result that maximal d-wavefunction amplitudes are found at the transition metal ion sites. Accordingly, one can approximately represent the alloy as a 'diluted' or 'expanded' transition metal lattice. This model is substantiated by several pieces of experimental evidence. As a result of NMR studies of the V-Al system, Van Ostenburg et al.[43] were able to demonstrate that the d-band electrons tended to avoid the Al cells. This can be interpreted as showing a strong scattering of the d-wavefunctions by the Al ions. Van Ostenburg et al. also concluded that the valence electrons of the Al contributed to a low-lying band; a suggestion which later appeared[24] in Stern's tight-binding theory of disordered alloys. Although somewhat more refined, the conclusions reached by Lye[44] with regard to the electronic structures of intermetallic compounds of Ti with the nonmetallic 's-p' elements C, N, and O, from band-structure calculations for TiC, are in general agreement.

By 'diluting' the Ti lattice in the manner outlined above, the 's-p' elements (particularly the B metals) addition leads to solid solutions which remain 'Ti-like'. This is the mechanism of alpha-stabilization.

For an alpha-stabilized alloy, therefore, the concept that emerges is one of strong noncentral interactions between the ions, resulting in a pronounced structure-dependence of the corresponding E_{COH}. As alloying proceeds, the formation of an intermetallic compound is expected.

Phase diagrams of the prototype binary systems selected for this study, viz., Ti-Al[45] and Ti-Ga[46], are presented for reference in

Figures 3(a) and (b).

IV-1-2. Solid solution strengthening in binary alloys: Readjustment
of the energy states of a solute B in Ti can be designated as a strong inter-
action or directional bonding between B and its Ti neighbors. This has
been demonstrated by electrical resistivity measurements (Figure 1).

Further evidence of the directional bonding in Ti-Al alloys can be
found in the χ and γ data in Figures 4(a) and (b) and in the R_H data in
Figure 5. Accompanying the strong bonding formation, localization of a
large fraction of conduction electrons (of pure metals) would be expected.
Experimentally, the effect can be most easily observed by extending
measurements to the high concentration range where a long-range-ordered
intermetallic compound forms. Indeed, Figures 4(a) and (b) indicate that
although the density of states at the Fermi level $[n(E_F) \propto \gamma$ or $\chi]$ changes
little with alloying in the dilute solid solution range, it drops markedly on
entering the α_2 region. Similarly, Figure 5 shows the Hall coefficient to
increase, therefore the conduction electron density $(n \propto 1/R_H)$ to decrease,
drastically near stoichiometry. The little change in $n(E_F)$ in the dilute
alloy region, where appreciable solid solution strengthening is expected,
can be rationalized: As the Ti-lattice becomes diluted or 'expands', the
influence on $n(E_F)$ of a decreasing d-band width tends to be compensated for
by a decrease in the average volume-density of d-states.

Visualization of the influence of directional bonding has been made
possible by Gehlen [47] who deduced, from the results of X-ray diffraction
experiments on the stoichiometric Ti_3Al, the existence of effectively long
chains of partially covalent-bonded Ti_3Al groupings. This is illustrated
in Figure 6.

As mentioned in Section III-3-1, the low temperature specific heat
measurements also yield values for the Debye temperature. By applying
this experimental technique to an alloy series, it is therefore possible
to make direct comparison, in a restricted sense, of a physical with a

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mechanical property. Figure 7 compares the low-temperature calorimetric properties of the Ti-Al system with the Young's modulus (E) data.[48] The stiffening of the lattice in the vicinity of the composition Ti_3Al is reflected as a pronounced local increase in Θ_D. A corresponding increase in Young's modulus is also seen. In addition, the Young's modulus curve demonstrates solid-solution strengthening effects in the α-regime, followed by additional strengthening in the two-phase $(\alpha+\alpha_2)$ field. E and Θ_D represent what can be termed 'equilibrium' (i.e., elastic) mechanical properties. Figure 7 seems to indicate a monotonic increase in strength with additions of Al of up to 25 atomic percent. As will be discussed later, however, because of the embrittling effect of α_2 the ultimate tensile strength passes through a maximum, situated approximately at the limit of the α-phase field.

In order to discuss solid solution strengthening without being complicated by the α_2 precipitates effect[49], one has to stay in the low concentration, single phase region. The electronic solid solution strengthening effect in titanium alloys appears to occur over a solute concentration (c) range up to 4 at. %. This is based on the tensile test data as shown in Figure 8, in which the increase in tensile strength due to various substitutional solutes can be considered to be proportional to the square root of the atomic fraction of the solute content in this range. In addition, Figure 4(a) shows that the magnetic susceptibility falls rapidly between 0 and 4 at. % Al.

The questions now arise as to why Ga is so effective a strengthener and whether an adequate scale of relative strengthening for different solute elements can be developed. To answer these questions, one certainly has to know their respective atomic potentials. In practice, however, a correlation generated from thermodynamic studies can be used. It is found that the effectiveness of strengthening, as measured by $d\sigma/dc^{1/2}$ (i.e., the slopes of the straight lines in Figure 8), is proportional to the thermodynamic interaction strength parameter I as defined in Section III-4-2. Figure 9 shows such a relation. Conrad[50] suggests that the athermal component of the flow

stress in α-Ti alloys is proportional to (Ic$^{1/2}$). It is important to note that we actually achieve the same conclusion, concerning the relative effectiveness of different elements (Al, Ga, Sn) on solid solution strengthening, based on either the thermodynamic studies (I) or the physical property measurements (ρ, Figure 1).

To further illustrate the usefulness of the (dσ/dc$^{1/2}$)-I relation, one can estimate the interaction strength parameter between Ti and O by using the value of dσ/dc$^{1/2}$ = 550 KSI for Ti-O alloys with up to 1 at. % O content.[14] The I value of 2.4 (eV/atom)$^{1/2}$ obtained is identical with the electronegativity difference between Ti and O given by Astakhov.[42] Similarly, using the dσ/dc$^{1/2}$ data [51] of 720 KSI for Ti-N alloys, one obtains an I value of 3.0 (eV/atom)$^{1/2}$. This implies that N is actually a more effective strengthener than O. Szkopiak [52] reported similar observations in his study on Nb-O and Nb-N alloys. The fact that the same relation can be used for both substitutional (Al, Ga, Sn) and interstitial (O, N) solutes is another support of the electronically controlled strengthening mechanism.

IV-1-3. Solid solution strengthening in multicomponent alloys: In comparison to binary Ti based alloys, Glazunov [2] discussed a significant improvement of tensile strength by multiple element additions of equivalent total solute concentration. This is actually nothing new, almost every alloy of technical importance contains two or more solute elements for one reason or another. However, there seems to be no unified theory to explain why multicomponent alloying is preferred. Most models on solid solution strengthening include a solute concentration term in their formula, but do not distinguish the different cases involving only one or several kinds of solute elements.

It is instructive to compare a ternary Ti-xAl-xGa system with the binary Ti-Al and Ti-Ga systems. In Figure 2, the ultimate tensile strength data reveal that the curve corresponding to the ternary system lies above the two curves corresponding to Ti-Al and Ti-Ga, instead of between them as

one would expect for an 'averaging' effect. The picture is even more pro-
nounced in the dilute region with up to 4 at. % Al, Ga, or (Al+Ga), where no
α_2 precipitate is expected. An interpretation based on electronic strengthening
can be made. From the cohesive energy argument, the more alloying elements
are present, the higher order terms in Equation 2 have to be taken into con-
sideration. From the thermodynamic interaction approach, on the other hand,
one simply has to deal with all possible combinations of interaction strength
parameters, I(Ti-Al), I(Ti-Ga), and I(Al-Ga).

An additive effect has been assumed to operate here as a first approxi-
mation, which has also been suggested by the work of Kornilov and Nartova [53]
and of Glazunov. [2] The sum of the interaction parameters is therefore used
in Figure 9 for multicomponent alloys. It can be seen that the point corre-
sponding to Ti-xAl-xGa also falls on the straight line defined by those for Ti-
Al and Ti-Ga.

Using the values for $d\sigma/dc^{1/2}$ taken from the straight line in Figure 9
for Ti-xAl-xSn, the $\sigma-c^{1/2}$ relation for this system is presented as broken
lines in Figure 8. From general experience with the commercial alloy
Ti-5Al-2.5Sn, Ti-xAl-xSn should be somewhat stronger than Ti-xAl-xGa.
It is difficult, however, to directly compare this work with experimental
results previously published on the Ti-Sn or the Ti-Al-Sn system, since the
strength level obtained depends strongly on the oxygen content of the base
metal. As shown in the last section, oxygen is much more effective than a
B-metal in the α-phase strengthening.

IV-1-4. Discussions on the Ti$_3$X type intermetallic compounds: In the
previous sections the formation of long-range-ordered intermetallic com-
pounds, when an appropriate amount of α-stabilizing elements is added to
titanium, was mentioned. This paper concerns mainly the solid solution
strengthening. However, some consideration must be given to the
additional strengthening achievable through an ordered particle effect.
The Ti$_3$X type (X being Al, Ga, Sn, or a combination of them) is chosen for

two reasons. First, they are closely related to the dilute alloys considered in this paper. Second, they have been shown to be important in the technical alloy development.

The structure and properties of Ti_3Al, Ti_3Ga, and Ti_3Sn have been well documented in the literature. Figure 6 shows the ordered α_2 structure of Ti_3Al.

The ordered particle effect has been theoretically discussed by Gleiter and Hornbogen[54, 55], and by Lütjering and Hornbogen.[56] Experimentally it has been verified by Lütjering and Weissman[49] for the Ti-Al binary system in alloys containing 14-18 at. % Al and having $(\alpha+\alpha_2)$ microstructures. They demonstrated that the dislocation distribution can be drastically changed by the addition of either zirconium or silicon. Zirconium partitions chiefly to the α-phase (matrix) and produces a change in its lattice parameter, and it subsequently changes the misfit between the matrix and the α_2 particle. This effect changes the dislocation mechanism from a particle cutting to a particle by-pass mechanism. Silicon produces the same effect by partitioning to the α_2 precipitates. When both zirconium and silicon are simultaneously added, along with a β-stabilizer such as Mo, a stable zirconium silicide forms and a particle ductilizing effect occurs. Gegel and Fujishiro[57] have demonstrated these two effects for the Ti-xAl-xGa base system.

For a given binary system, the maximum tensile strength generally occurs at the $\alpha/(\alpha+\alpha_2)$ solubility limit, e.g., at about 12 at. % Al in the Ti-Al system. This has been described by Nartova.[58] Figure 10 shows such a feature also to occur in the ternary system Ti-xAl-xGa: The room temperature ultimate tensile strength increases rapidly with solute concentration in the single-phase solid solution range. A leveling off occurs as solid solution strengthening competes with the presence of an increasing fraction of the brittle α_2 phase. Finally, strength decreases with solute concentration in the α_2 phase field as the composition Ti-12.5Al-12.5Ga is approached. The observed general decrease in strength with increasing temperature is normal, and various

reasons can be offered for it. The higher temperature isothermals tend to level off at higher solute concentrations, due to the increasing α-solubility range at higher temperatures. The maximum tensile strength at room temperature in this ternary system corresponds to 12 at. % (Al+Ga). This suggests that replacing half of the Al in Ti-Al by Ga does not alter the gross picture of the strength-concentration relation, provided that the concentration refers to the total α-stabilizing elements in the alloy. Similar results are obtained by comparing the magnetic susceptibility data for Ti-xAl-xGa with that for Ti-Al in Figure 11. The common solid line indicates: (a) that both systems have practically the same $n(E_F)$ in the dilute, disordered region; and (b) that the α-phase fields terminate at the same total solute concentration. This plot makes the derivation of χ-values for 'disordered' binary and pseudobinary compounds possible by linearly extrapolating the locus of the disordered-alloy susceptibilities.

In Figure 12 the percentage elongation prior to rupture of Ti-12.5Al-12.5Ga plotted against test temperature is shown. There is a rapid increase in ductility which occurs near 600°C. More work is clearly needed, but the evidence suggests that the observed ductility is due to the onset of structural disordering near that temperature. The susceptibility temperature-dependence curves for Ti$_3$Al and Ti-12.5Al-12.5Ga, as shown in Figure 13, appear to support this view. In that figure, the break-point on the Ti$_3$Al curve can be identified as the order-disorder transformation point; since the higher-temperature line segment extrapolates back to a susceptibility value which is estimated, from the procedure summarized in Figure 11, to be equal to that of disordered Ti$_3$Al at room temperature. Similarly the break in slope, occurring near 640°C on the curve for Ti-12.5Al-12.5Ga, is probably due to an order-disorder transformation. A disordering reaction could be the origin of the observed brittle-ductile transition in Ti-12.5Al-12.5Ga (Figure 12). As noted earlier, the brittle character of the α_2 phase is a result of lattice rigidity associated with the directional bonding of the ordered atomic arrangement;

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consequently, with the introduction of lattice disorder, the resultant 'smearing-out' of bond directionality would be expected to have a ductilizing effect.

Another type of information related to bond strength and lattice dynamics is available, derived from the results of high temperature calorimetry. Hoch [30,31] has shown that the specific heat, in the temperature range $\Theta_D <$ T < melting point, can be expressed by an equation of the form

$$C_p = 3R\ F(\Theta_D/T) + cT + dT^3, \tag{5}$$

where $F(\Theta_D/T)$ is the Debye function, c is identifiable with the electronic specific heat coefficient γ, and the coefficient d is a measure of the lattice vibrational anharmonicity. Approximately d should be inversely proportional to Θ_D, thus $[\Theta_{D,\ Ti}/ < \Theta_{D,\ compound} >_{av.}] \cong [< d_{compound} >_{av.} / d_{Ti}]$. From the data listed in Table 2 for Ti_3Al, $Ti_3(Al_{1/2}Ga_{1/2})$, and Ti_3Ga, this model suggests that a stiffening of the lattice occurs in all compounds, and the magnitude of this effect increases from Ti_3Ga to Ti_3Al.

IV-2. Beta-Stabilized Alloys

IV-2-1. Beta stabilization, lattice stability, and solid solution strengthening in binary alloys: Stabilization of the β-phase of titanium can be achieved by alloying with another transition element, which adds conduction electrons to titanium. In general, the charging effect is particularly small in alloys between adjacent transition elements near the middle of a long period. [25,59] Excellent agreement with the rigid-band model has in fact been demonstrated by McMillan [60] for binary alloys from the sequence Hf-Ta-W-Re. One would not expect to find such good adherence to rigid-band principles for Ti-rich alloys with transition elements, but nevertheless such alloys may still be classed as 'low perturbation'. This is consistent with the extensive solid solubility ranges of all transition elements in titanium, and in particular the unlimited solid solubility of the nearest neighbors. A remarkably good descriptor of structural, electronic, and some mechanical properties of various β-Ti alloys is the average number of valence (s+d)

electrons per atom (usually referred to as the electron-to-atom ratio, e/a)* For Ti-Mo, which is a prototype system to be described below, e/a ranges from 4 to 6.

Understanding the solid solution strengthening of β-Ti alloys is much more difficult than that of α-Ti alloys, because one is fundamentally involved with the problem of lattice stability. This will be discussed in detail subsequently. For the moment it can be rationalized that, based on the atomic 'similarity' or the thermodynamic interaction strength approach, only small strengthening would be expected from the addition of transition elements far away from Ti in the periodic table such as Fe; in the case of alloying with its near neighbors, a negative result should even be realized. The latter can be understood from the fact that low e/a values favor a hexagonal structure which, because of lower symmetry, implies a higher degree of directional metallic bonding and consequently a stiffer lattice. The β-stabilization is associated with an increase in conduction electron density, which makes the hexagonal structure less favorable. Indeed, Young's modulus measurements on selected members of the Ti-Mo system have shown [62] [c.f., Fedotov et al. [48]] that hcp-Ti is considerably stiffer than the 'nearest' single-phase bcc alloy with 20 at. % Mo.

The problem of lattice stability must now be considered. Figure 14 shows portions of the equilibrium and nonequilibrium phase diagrams of Ti-Mo, and also indicates the various microstructures which were observed to form as a result of quenching into iced brine from elevated temperatures. This figure aids in the interpretation of the composition-dependencies of the various physical

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*For α-Ti alloys such as Ti-Al, one usually calculates the e/a values by taking into account the d, s electrons of Ti and the s, p electrons of Al. However, the dilution concept referred to in Section III-2, together with the conclusions of other workers [61], suggest that a more physically meaningful e/a-type scale, valid for both α- and β-Ti alloys, might result if consideration is restricted to the average density of only the d-electrons.

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properties given in Figures 15 and 16.

The ω-phase appeared as a microscopic precipitate, hexagonal in struc-
ture, in Ti-Mo alloys with e/a values ranging from 4.1 to about 4.3. Since
the degree of development of the precipitate is quite sensitive to aging, the
e/a range for its appearance will also depend on the rapidity with which a
specimen is quenched prior to examination. The results of low-temperature
calorimetric and magnetic susceptibility measurements on this system are
summarized in Figure 15. The superconducting transition temperature, T_c,
electronic specific heat coefficient, γ, and magnetic susceptibility, χ, are
all $n(E_F)$-related quantities. The magnetic susceptibility data, which may be
taken at elevated temperatures, is central to an extrapolation procedure[63]
used to estimate values of γ for the single-phase bcc alloys. As the figure
illustrates, $n(E_F)$ for single phase bcc alloys would increase monotonically
as e/a decreases from 6 to 4. For the real alloys, the turning point in $n(E_F)$
which occurs near e/a = 4.4 is apparently induced by the presence of ω-phase
precipitation which increases in density in the quenched alloys as e/a decreases
below the threshold value.[63] The up-turn in the directly measured Θ_D
values for e/a $\lesssim$ 4.4 is indicative of the stiffening influence of the ω-phase.*
Θ_D can be regarded as being representative of a bulk elastic modulus. An
empirical procedure[64] yielded $\Theta_D \sim$ 200 K for bcc Ti at low temperatures.
Such relative lattice softness, which commences rather suddenly at e/a $\sim$ 4.3
[the limit of single-phase β (see Figure 14)] is a reflection of the instability
of single-phase β-Ti-Mo (e/a $\gtrsim$ 4.3) and β-Ti at ordinary temperatures.
Further support of this statement comes from Fisher and Dever's work[65]

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* The ω-phase itself must be a low-$n(E_F)$, high Θ_D structure. We speculate
that it might be a brittle, directionally bonded material, at least in its low
e/a limit. In this respect, possible similarities in the mechanical and
electronic properties between the ω and the α_2 phase are worthy of continued
study.

on elastic constant measurements of Ti-Cr single crystals. The elastic shear constants C_{44} and $C' = (C_{11} - C_{12})/2$ are summarized in Figure 16. Again, it is obvious that the Ti-rich ω-phase is responsible for a marked stiffening of the lattice. It is interesting to observe the elastic properties of the single-phase β-alloys. These become increasingly soft to shear stresses as e/a decreases in the β-regime. Finally for sufficiently low e/a values, for which the quenched alloys are ($\beta+\omega$), the virtual (extrapolated) single-phase β-alloys exhibit pronounced softening of their elastic shear constants. The vanishing of C' at e/a ~ 4.1 (i.e., Ti-5Cr, which is equivalent to Ti-5Mo) coincides with the absolute limit of stability of the bcc phase at ordinary temperatures in this class of alloy. For β-alloys, there is clearly a mutual relationship among electronic structure (as characterized by the e/a parameter), elastic properties, and phase stability. The continuous softening of the shear moduli in the β-lattice with decreasing e/a results initially in the instability which promotes ω-phase precipitation (hexagonal structure), and ultimately in the martensitic transformation which commences near e/a = 4.1 at ordinary temperatures.

IV-2-2. <u>Solid solution strengthening in multicomponent alloys</u>: As discussed in Section III, solid solution strengthening in titanium can be achieved through the addition of α-stabilizing elements. The significance of multicomponent alloying has also been pointed out. One expects similar effects to occur in β-stabilized systems. A set of alloys were prepared in which Fe and Al were added to Ti-Mo while maintaining the average e/a constant at 4.3. Aluminum was assumed not to contribute to e/a. The compositions in atomic percent of the four test alloys are indicated by a square diagram in Figure 17. In this diagram additions of Al and replacement of Mo by Fe are represented, respectively, by translations from left to right and from top to bottom. Also summarized in the same diagram are the results of low temperature specific heat measurements. The arrows indicate the directions of increase of the various parameters, Θ_D, γ, and T_c (super-conducting transition temperature). As usual (c.f., Figure 15) γ and T_c

follow the same trends, and Θ_D proceeds in the opposite direction. Because of the position that Fe occupies in the transition metal series, it was initially predicted that the partial replacement of Mo by Fe at constant e/a would result in some lattice stiffening. Figure 17 shows this procedure to result in very slight increases in Θ_D, with corresponding decreases in the $n(E_F)$-related quantities, γ and T_c. A much greater degree of strengthening was observed as expected, accompanying the admixture of Al. The Debye temperature increased by some 30-35 K upon addition of the 6 at. % Al. Maximal stiffness was achieved in the quaternary alloy whose composition in the present terminology is (Ti-10Mo-2.5Fe)-6Al. These experimental results tend to verify the approach taken to solid solution strengthening mechanisms in both α- and β-stabilized Ti alloys in so far as Θ_D is concerned. However, they have yet to be coupled to the results of direct measurement of mechanical and elastic properties.

V. CONCLUSION

The resistance to deformation of a metal is gauged by the extent to which the cohesive energy (E_{COH}) is structure-dependent. E_{COH} may be expanded in the form: $E_{COH} = \sum_{i=1}^{n} E_i$, in which E_n represents n-body interactions. The convergence of the expansion is controlled by the strengths of the atomic potentials in the case of pure metals; or the atomic potential differences between the constituents in the case of alloys -- in other words by the extent to which perturbation theory holds. These principles have been employed to provide a fundamental understanding of phase stability and solid solution strengthening in Ti-base alloys, and their validity has been demonstrated by correlating physical and mechanical properties of prototype systems. In practice, the pairwise interaction strength can be estimated in terms of the specific resistivity or the thermodynamic interaction strength parameter for a particular solute in Ti.

When Ti is alloyed with B-metals the lattice remains 'Ti-like' and consequently α-stable. Solid solution strengthening can also be achieved through a directional bonding formation between Ti and the solute ions with large atomic 'dissimilarity'. By alloying Ti with other transition elements, the increase in conduction electron density favors the bcc over the hcp structure of lower symmetry. This is the mechanism for β-stabilization with small or even negative solid solution strengthening. In order to strengthen the β-alloys, one has to add B-metals to form multicomponent systems. In fact, multicomponent alloying is always preferred, because of the solute strengthening additivity effect.

In conclusion, we would like to point out that this paper is intended to emphasize the importance of a not necessarily new but much ignored fundamental approach towards solid solution strengthening. Further studies based on this understanding are recommended as an integral part of Ti alloy development programs.

TABLE I
SPECIFIC HEAT PARAMETERS FOR Ti AND Ti$_3$X-TYPE
INTERMETALLIC COMPOUNDS

Specimen	Θ_D (K)	d (10^{-9} J/mole-K^4)
Ti	420	9.5±0.6
Ti$_3$Ga	430	8.5±1.3
Ti$_3$(Al$_{1/2}$Ga$_{1/2}$)	465	8.6±1.4
Ti$_3$Al	495	8.8±0.7
	$\langle\Theta_{D, \text{compound}}\rangle$av. = 463	$\langle d_{\text{compound}}\rangle$av. = 8.6

Note: The values of Θ_D and d are determined, respectively, from low-temperature and high-temperature calorimetric measurements.

TABLE II
SOME EXPERIMENTALLY DETERMINED VALUES OF
THERMODYNAMIC INTERACTION STRENGTH PARAMETERS

Systems	I, (eV)$^{1/2}$
Ti-Sn	0.96±0.01
Ti-Ga	0.75±0.02
Ti-Al	0.62±0.01
Ti-Mo	0.35±0.03
Ti-Cr	0.29±0.03
Ti-V	0.28±0.02
Ti-Cu	0.26±0.03
Al-Ga*	0.07±0.07

*Measured value based on ternary Ti-Al-Ga system
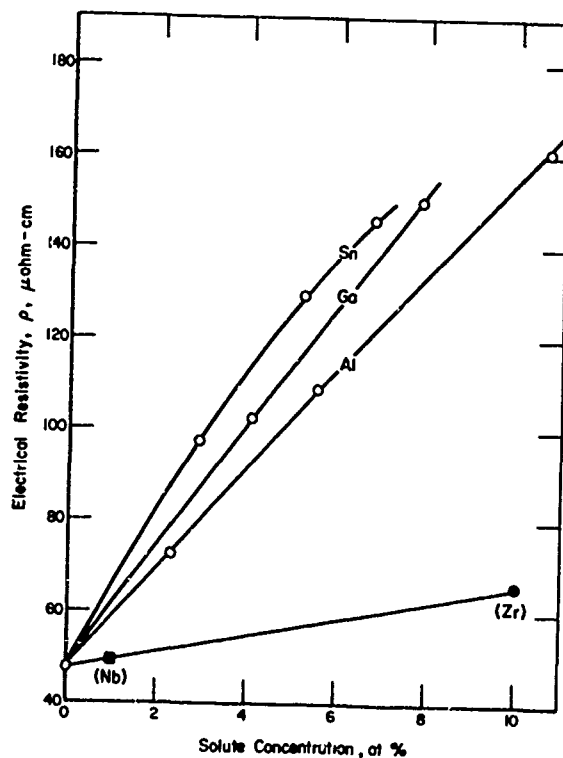
Figure 1. Influences on the resistivity of Ti of small additions of Al,
Ga, and Sn; compared with those of the transition metals
Nb and Zr.   The data for the nontransition metal elements
are from this work, while those for the other elements are
from Reference (37).   Significant in the present context is
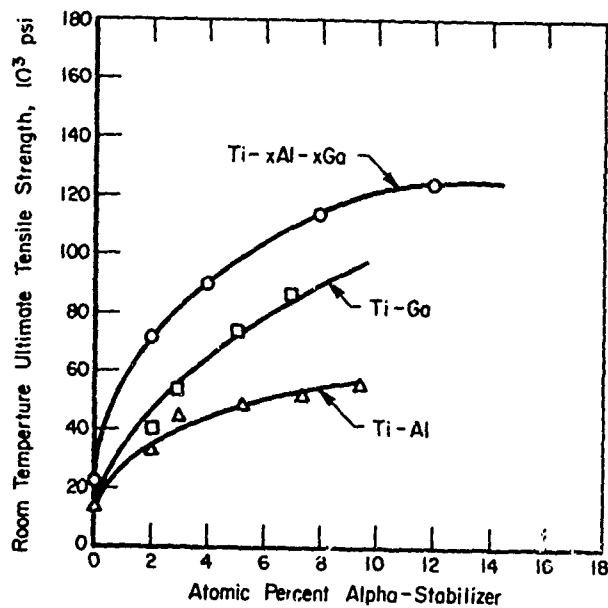the relatively large electron scattering for nontransitional
solutes.

Figure 2.   Influence of solute species and concentration on the room
temperature ultimate tensile strengths of α-stabilized alloys.
Ga is seen to be a more effective strengthener than Al; a
property which is consistent with (a) the larger Ti/Ga inter-
action strength parameter (Table 1) and (b) the larger electron
scattering cross section of the Ga ion (Figure 1).
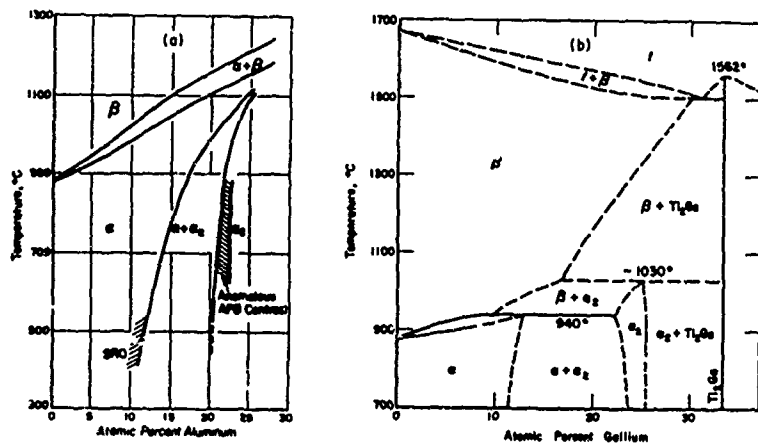
Figure 3   Portions of the phase diagrams of the systems (a) Ti-Al
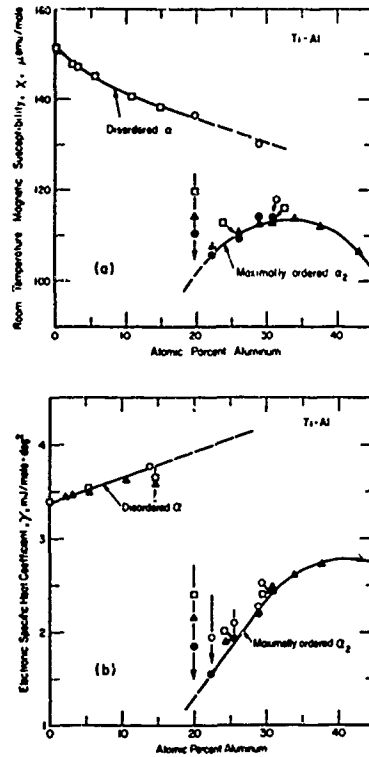[after Reference (45)], and (b) Ti-Ga [after Reference (46)].

Figure 4. (a) Total room-temperature magnetic susceptibility, χ, and
(b) low-temperature electronic specific-heat coefficient, γ,
for Ti-Al alloys. The arrows indicate the effect of im-
proving the degrees of long-range order by heat treatment.
☐ - annealed at 50°C below $\alpha/(\alpha+\beta)$ and quenched, except for
Ti-30Al which was heat treated as for Ti-20Al. ▲ - as-cast.
O - quenched into iced brine from β-field. ● - long step-
cooling anneal to promote maximal long-range ordering.
In curve (a), no account has been taken of χ_{orb} which we
expect to decrease more or less linearly with solute con-
centration. It is this component that is primarily responsible
for the negative slope of the line corresponding to the dis-
ordered alloys. Ordering, which for Ti_3Al cannot be
inhibited by quenching (as judged by density-of-states-
sensitive properties) results in a pronounced drop in $n(E_F)$.
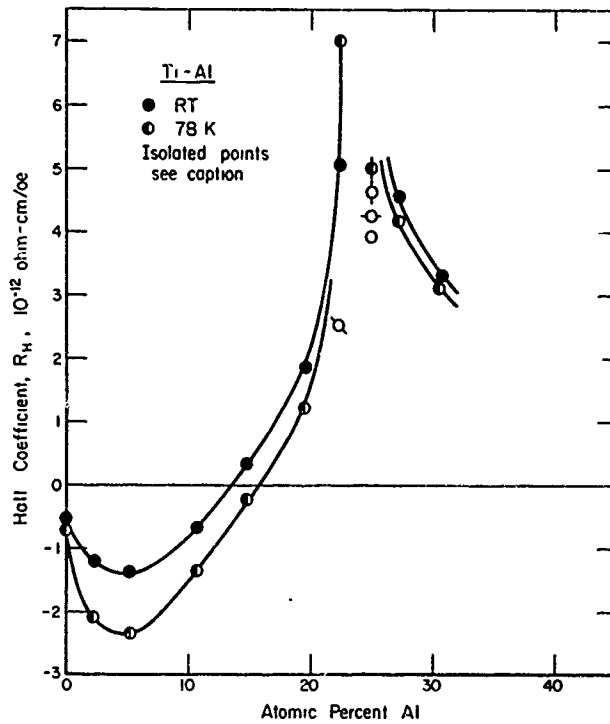
Figure 5.   Hall coefficient in Ti-Al. The relatively large value of
             R_H at Ti-25Al indicates hole conductivity with a relatively
             low density of charge carriers. The true value of R_H at
             stoichiometry has not been measured since microcracking
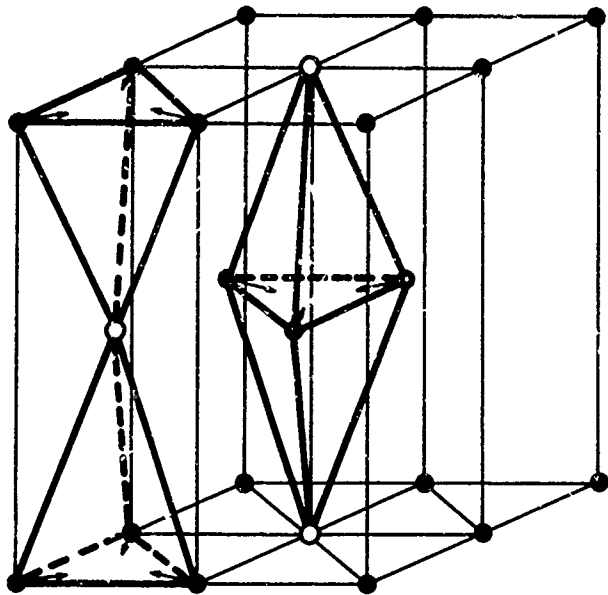   seems to be unavoidable in this brittle material.

Figure 6.   Structure of Ti_3Al. The Ti atoms (●) are drawn slightly
inwards and are bound to the Al atoms (O) in "tetrahedral"
chains, [after Reference (47)].
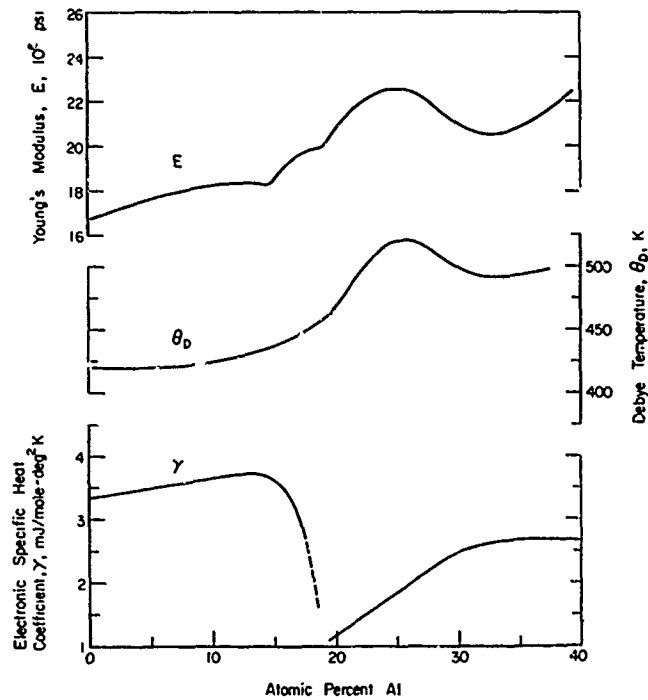
Figure 7.   Comparison of the low-temperature calorimetric properties
             of part of the Ti-Al-system with the Young's modulus data of
             Reference (48).   The lattice stiffenings present in $(\alpha+\alpha_2)$,
             and finally in the α_2 phase [for which $n(E_F) \stackrel{\sim}{\propto} \gamma$ is low] are
             reflected in both E and Θ_D.

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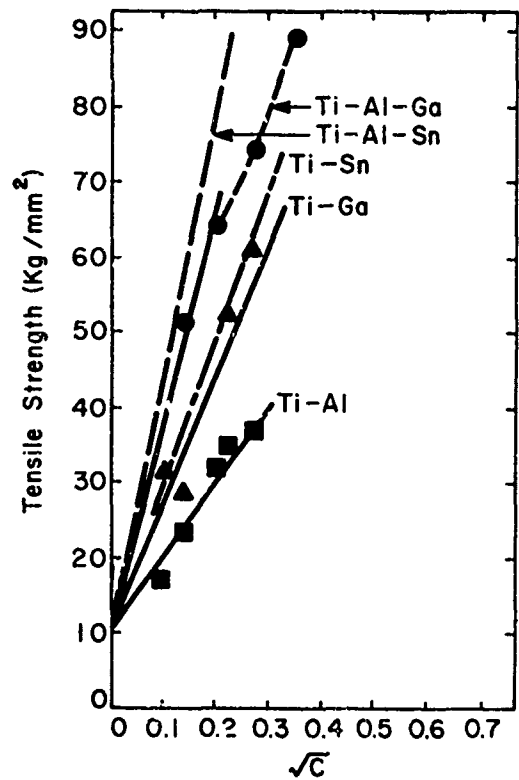
Figure 8.   Ultimate tensile strength at room temperature versus square
root of the atomic fraction of α-stabilizing solutes.   The
slopes of the lines representing Ti-Sn and Ti-Al-Sn are
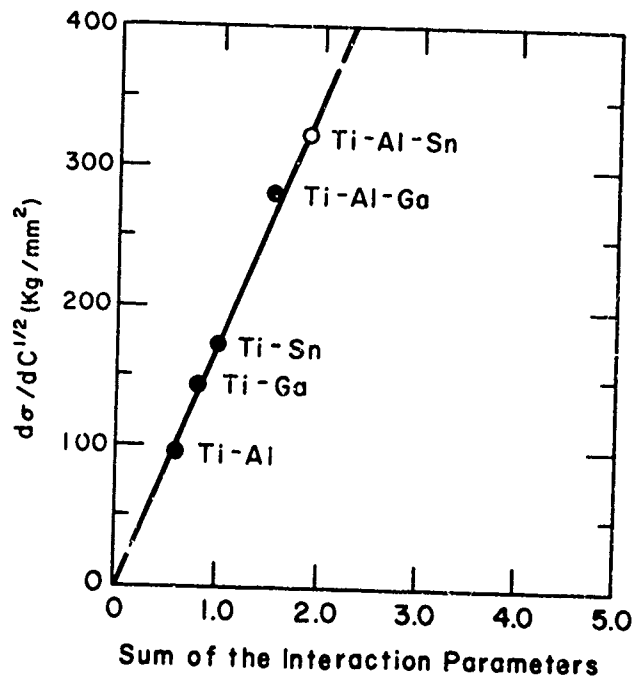estimated from Figure 9.

Figure 9. $d\sigma/dc^{1/2}$ versus the sum of thermodynamic interaction
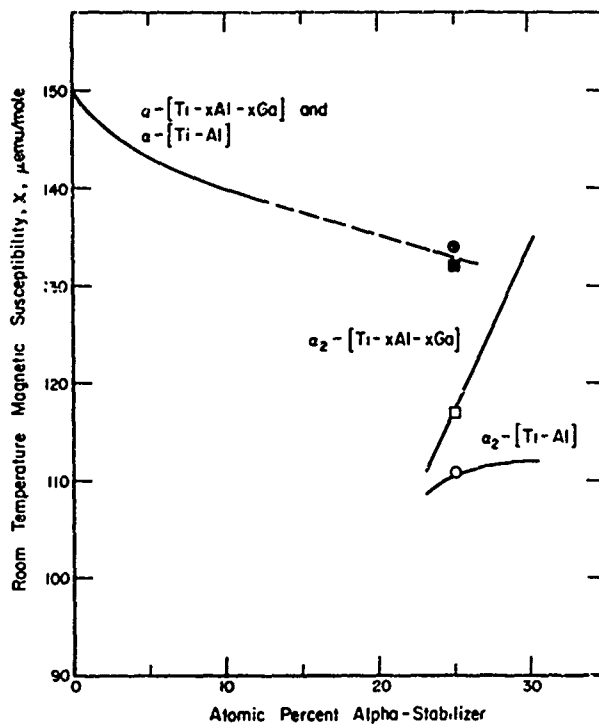strength parameters.   The Ti-Al-Sn point is estimated.

Figure 10.   Room-temperature magnetic susceptibilities of Ti-Al and
Ti-xAl-xGa (in which half of the original Al has been
replaced by Ga). In the α-phase field (upper full line) the
susceptibility data for the two systems coincide, within
experimental accuracy. This line has been produced
(dashed) for the purpose of estimating the susceptibility
of the disordered 25 at. % alloys at room temperature.
The points ● and ■ near this line are the extrapolated
values from Figure 13. Data for ordered (α_2) Ti-Al is
shown as well as that corresponding to as-cast Ti-xAl-xGa,
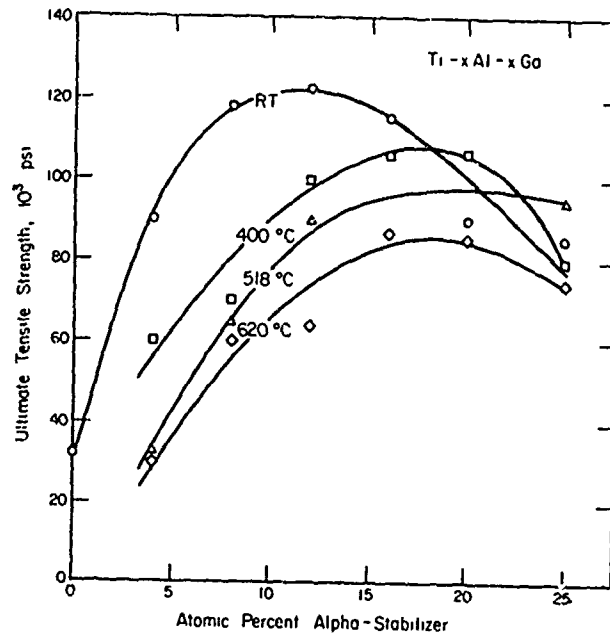the metallurgical state of which is not well understood.

Figure 11.   Ultimate tensile strength isothermals for Ti-xAl-xGa. A
pronounced reduction in strength occurs beyond the limits
of the α-phase field, which becomes more extensive as the
temperature increases [c. f. Figures 3(a) and (b)]. We
attribute the decrease in strength at higher concentrations
to the precipitation of α_2 particles. In the concentration
range 15-25 at. %, the measured strength at elevated tem-
peratures is a result of competition between α_2 precipitation
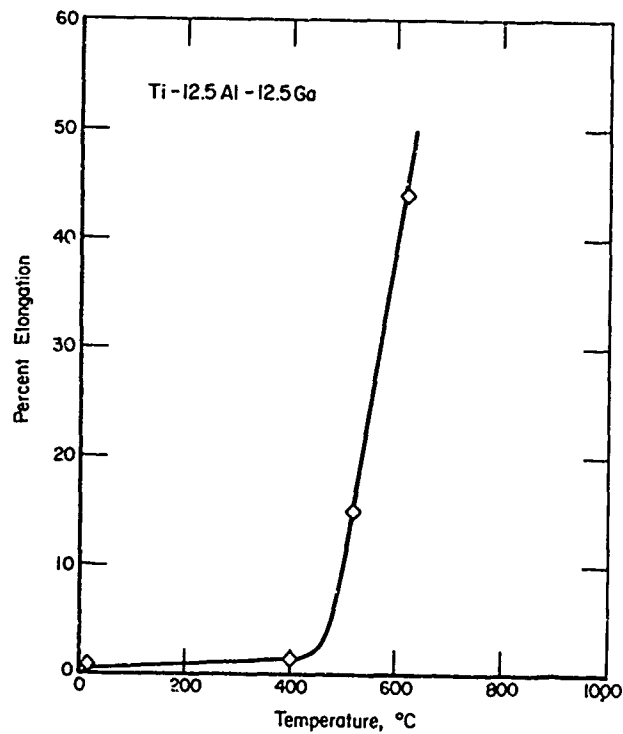and thermal disordering.

Figure 12. Influence of temperature on the elongation of Ti-12. 5Al-
12. 5Ga. We tentatively attribute the brittle-ductile
transition to the onset of an order-disorder transformation,
evidence for which is derived from the results of magnetic
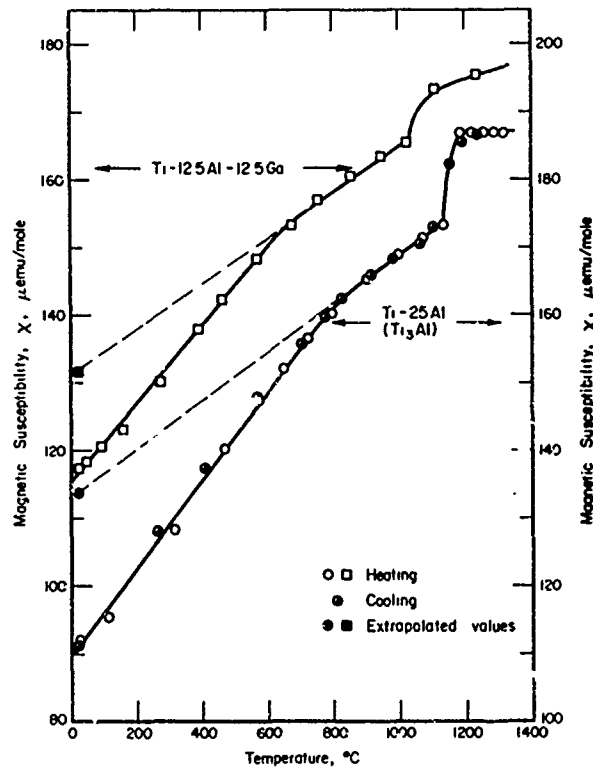susceptibility studies as summarized in Figures 11 and 13.

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Figure 13.   Temperature dependence of the magnetic susceptibilities of
Ti-25Al (Ti$_3$Al) and Ti-12.5Al-12.5Ga [Ti$_3$(Al$_{1/2}$Ga$_{1/2}$)].
The curves have been separated since the data points of the
α-phase alloys would otherwise interfere, as already indicated
in Figure 11.   Break-points occur at 850°C and 640°C respec-
tively, followed by line-segments which extrapolate back to
susceptibility values corresponding to the points ● and ■
of Figure 11.   The room-temperature starting points
correspond to O and □ of that figure.   Taken together, the
evidence of Figures 11 and 13 implies that the above-
mentioned temperatures are order-disorder transformation
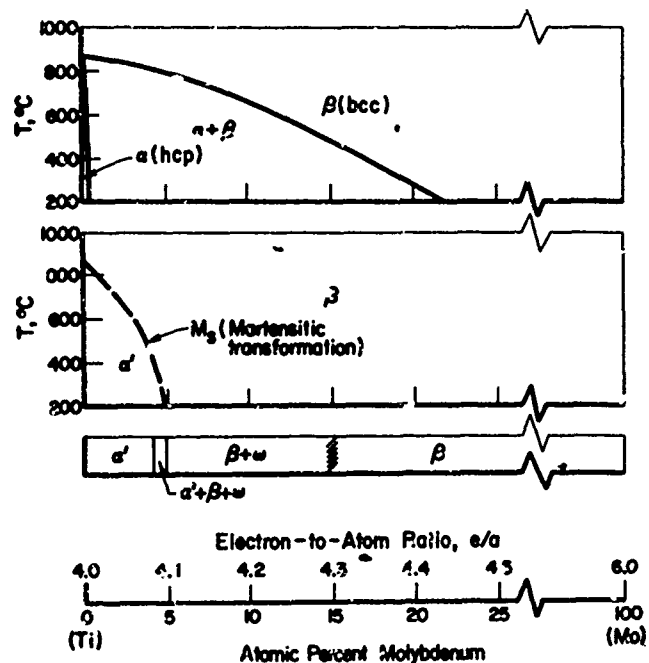temperatures.

Figure 14. The upper diagram is part of the usual equilibrium phase
diagram of Ti-Mo. The lower pair of diagrams represent
the non-equilibrium structures expected to be present after
quenching to the temperatures indicated from the single-
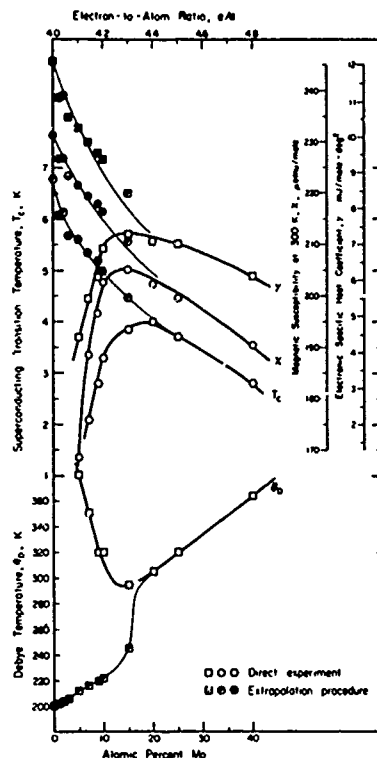phase β-field.

Figure 15.   Collected results of low-temperature specific heat measure-
ments of β and (β+ω) Ti-Mo alloys.   The upper branches of the
γ and χ curves represent values for single phase β alloys
derived according to Reference (63).   The extrapolation of
T_c is consistent with these; and that for Θ_D then follows
using an empirically derived tabulation of T_c/Θ_D - values
for virtual β-Ti-Mo (Reference 64).   The turning points are
induced by the presence of ω-phase; and the low values of
Θ_D (extrapolated) are consistent with the instability of
single-phase β at ordinary temperatures for e/a $\overset{\sim}{<}$ 4.3.
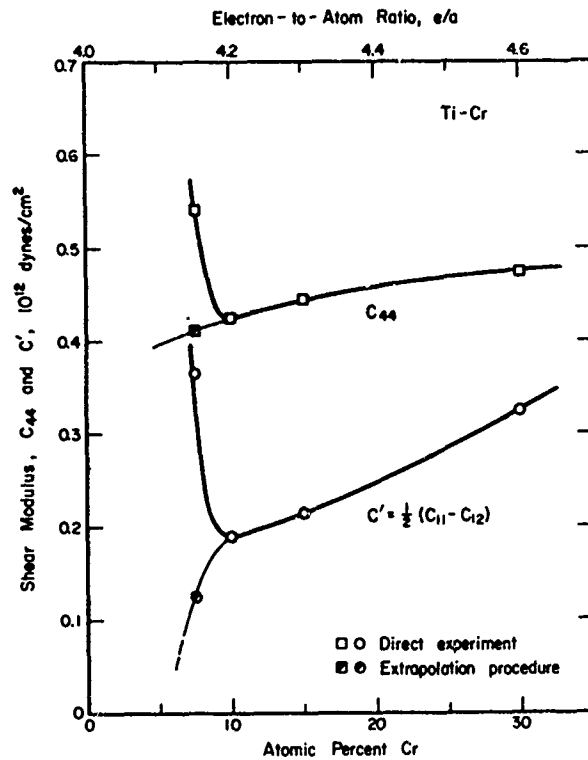
Figure 16. Plots of the elastic shear constants C_{44} and $C' = (C_{11} - C_{12})/2$ of Ti-Cr, redrawn from the data of Reference 65. The shaded points were obtained by extrapolating data from the high-temperature β field, and indicate extreme softening in C', consistent with martensitic transformation near $e/a \cong 4.1$ at ordinary temperatures.
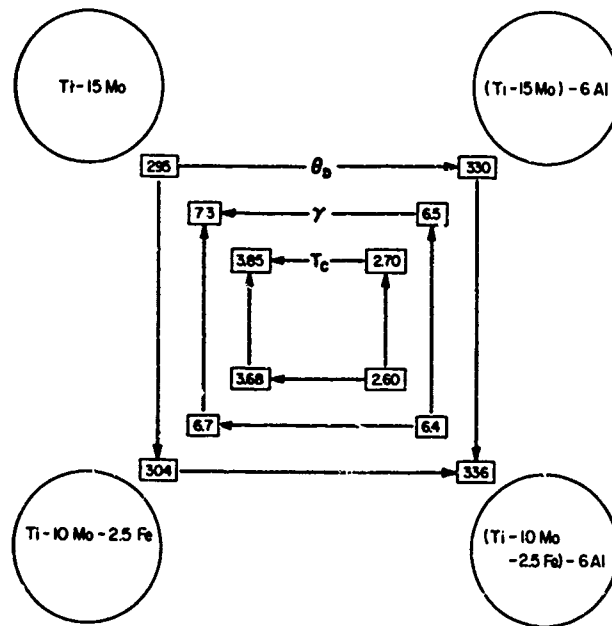
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Figure 17. Summary of the results of low-temperature calorimetry experiments on ternary alloys based on Ti-15Mo. When adding Al we proceed from left to right; and when substituting Fe for Mo, from top to bottom. The units for Θ_D, γ, and T_c are K, mJ/mole-K^2, and K, respectively.

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