

Stability in ordered and amorphous transition-metal compounds

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We present a comparison of measured and calculated state densities which suggest (1) that transition-metal glasses possess a short-range coordination similar to that of fcc crystals, (2) that the relative stability of different short-range atomic arrangements varies inversely with the state density at the Fermi level, (3) that transition-metal glasses tend to have large Fermi-level state densities, and therefore (4) that transition-metal glasses are characterized by the relative *instability* of their short-range atomic arrangements. We also argue that stoichiometry fluctuations are more effective in stabilizing the glass if the valence difference between the constituents is large. This effect is manifest in a correlation between the valence difference of the glass constituents and the width of the concentration range in which glasses form and the relative quenching rates required to form the glasses.

INTRODUCTION

Transition-metal glasses that can be prepared by conventional rapid quenching, using melt-spinning or splat-cooling techniques are known to share the following four properties: (1) They involve two or more constituents. (2) The valence difference of the constituents is usually large. (3) The smaller-valence constituent usually predominates. (4) The relative concentration of the constituents places the alloy near a deep eutectic in the phase diagram. The purpose of this work is to interpret these observations in terms of the underlying electronic structure and to add a fifth entry to the list.

Our new entry focuses on the state density at the Fermi level. Simple bonding arguments indicate that energetically favorable atomic arrangements will lead to a small Fermi-level state density. These arguments can be summarized by the statement that systems with energetically favorable short-range atomic configurations tend to have small Fermi-level state densities. We review the success with which these ideas account for the observed crystal structures of the transition-metal elements and show that the same considerations can be applied to ordered compounds. Transition-metal *glasses*, on the other hand, tend to have large Fermi-level state densities, suggesting that the chemical and structural arrangements of atoms in glasses are *not* particularly stable. This observation is consistent with the relative ease of glass formation in the vicinity of deep eutectics in the phase diagram because, a deep eutectic is a composition range in which the solid is not significantly more stable than the liquid. In other words, glasses tend to form when there is no atomic

arrangement available that is particularly stable. In our view, this is reflected in the relatively large Fermi-level state density observed in glasses.¹ Therefore, our fifth entry to the list is that transition-metal glasses have relatively high Fermi-level state densities.

ORDERED SYSTEMS

Let us first consider the transition-metal elements. Pettifor² and Andersen³ have shown that the observed variation of crystal structure across each transition series can be understood in terms of the general properties of transition-metal *d* bands. More specifically, they have shown that the sum of the single-particle energies, or equivalently the first moment of the occupied state density accounts for most of the structure-sensitive portion of the total energy. The connection between stability and the Fermi-level state density is easily understood in terms of the sum of the single-particle energies. The *d* states on different transition-metal atoms interact to form covalent bonds. Individual *d* states are strongly directional and are also quite localized, making the covalent-bond formation sensitive to the near-neighbor environment. In a structurally stable configuration the Fermi level will result in the occupation of the bonding hybrid states, with the antibonding states left empty. That is, the Fermi level falls in the "gap" between the bonding and antibonding states. In a solid such bonding and antibonding states broaden into bands, but the notion that stable configurations are characterized by a small Fermi-level state density retains its fundamental validity. It should be remembered in this context that the

short-range interatomic interactions dominated by d -electron covalent bonding determine the slow variations of the state density with energy, whereas long-range interactions tend to be responsible for the higher-frequency variations. Here we are primarily concerned with the low-frequency aspects of transition-metal state densities, those that reflect the near-neighbor coordination of each atom. For example, the bcc and fcc structures lead to two- and three-peaked d -band state densities, respectively. Therefore, midseries transition elements with half-filled d bands tend to have Fermi levels in the central fcc peak and in the gap between the two bcc peaks. Midseries transition elements like niobium and molybdenum, therefore, strongly prefer the bcc structure. Early and late transition-metal elements, on the other hand, tend to have Fermi levels in one of the bcc peaks and in an fcc minimum, making these elements tend to favor (except for the magnetic cases) the fcc form.

Consider now ordered compounds. We have performed energy-band calculations for transition-metal compounds in crystal structures characterized by both high and low nearest-neighbor coordination. (These calculations employ the local-density description^{4,5} of electronic exchange and correlation, and the augmented-spherical-wave method⁶ for self-consistently solving the effective single-particle equations. The atomic density was determined by

minimizing the calculated total energy.) The CuAu and Cu₃Au structures are fcc-like with twelve nearest neighbors, and the CsCl structure is bcc-like with eight neighbors. In Fig. 1 we show the state density of TiFe in the CsCl and CuAu structure to demonstrate the correlation between stability and Fermi-level state density. (The calculated equilibrium lattice constants are 2.933 and 2.620 Å, respectively, and the heats of formation are -0.66 and -0.06 eV/atom, respectively.) Near the center of the d -band state density, this compound exhibits a deep valley in the bcc-like CsCl structure and a sharp peak in the fcc-like CuAu structure. Since the valence average of Ti and Fe is 6, the Fermi level lies in the center of the band in the bcc valley and in the fcc peak. TiFe, therefore, forms a stable congruent melting compound in the CsCl structure.

In addition to the number of neighbors, the energy separation between the atomic d levels of the constituent transition-metal atoms is an important consideration in determining the shape of the state density. The energy separation is roughly proportional to the valence difference and leads to the gradual formation of a well defined gap for compounds with constituents with a large valence difference. In other words, constituents with large valence differences lead to compounds with "split-band" state densities. We show below that the constituent valence difference is also an important factor in glass formation.

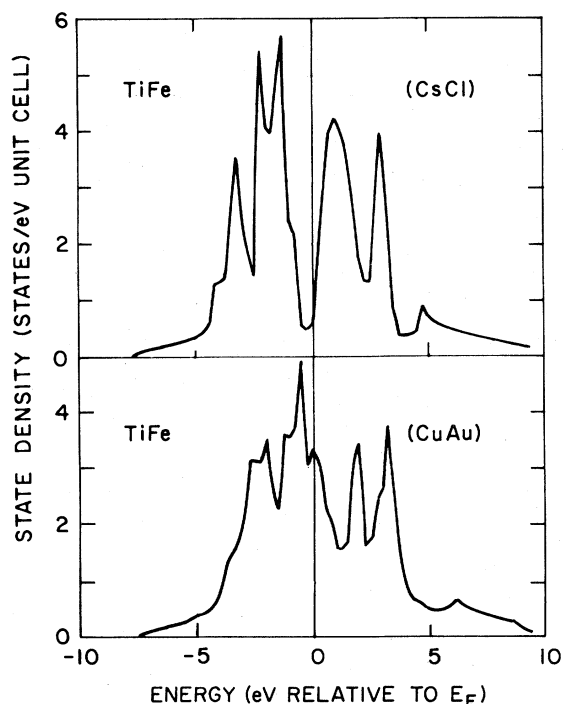


FIG. 1. Calculated state density for TiFe in the bcc-like CsCl and the fcc-like CuAu structures.

GLASSES

We now apply the correlation between stability and Fermi-level state density to transition-metal glasses. The first point we wish to make in this context is that the near-neighbor coordination found in glasses is high and therefore well approximated, for our present purposes, by the fcc crystal structure. Evidence for this contention is (1) direct estimates of the coordination number by extended x-ray absorption fine structure⁷ (EXAFS), (2) general agreement between valence-band state densities observed by photoemission and those given by our calculations for fcc-like ordered compounds,¹ and (3) the significantly *greater* similarity of measured state densities and those calculated for fcc-like structures. The last piece of evidence exists only for those few glasses that form near (50-50) at. % stoichiometry, where we can perform calculations for a variety of crystal structures, including the low-coordination bcc-like CsCl structure. The preceding discussion argues that we can focus on fcc-like structures. Accepting this argument, we now observe that our compound calculations indicate a rather large Fermi-level state density for those systems that form glasses, whereas systems that form ordered compounds tend to have

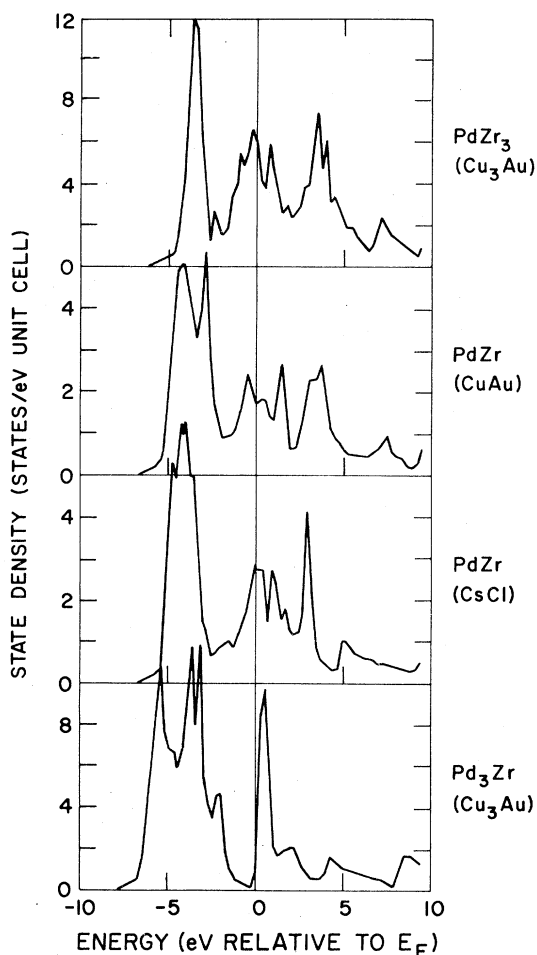


FIG. 2. Calculated state density for ordered palladium-zirconium compounds. Glass formation occurs in the zirconium-rich composition region, where the Fermi-level state density is high. Ordered compounds in this composition range are relatively unstable with the constituents exhibiting little preference for specific configurational arrangements. The ordered palladium-rich compound Pd_3Zr has a low Fermi-level state density and is relatively stable.

small Fermi-level state densities. Consider, as an example, the Pd-Zr alloy system. Shown in Fig. 2 are the state densities for fcc-like ordered structures corresponding to the three different stoichiometries: Zr_3Pd , ZrPd , and ZrPd_3 . We also include, for reference, the state density for ZrPd in the CsCl structure. The figure shows that ordered PdZr_3 , which is in the glass composition range, has a relatively large Fermi-level state density. As a function of Pd concentration, the Fermi-level density remains high through 50% Pd, but drops dramatically on going to Pd_3Zr . This behavior of the Fermi-level state density is consistent, in our view, with the fact that

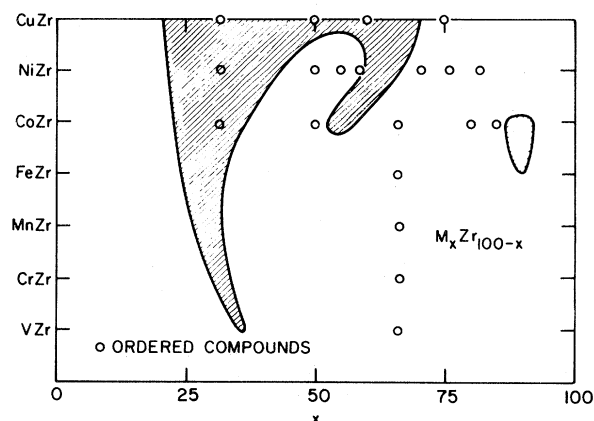


FIG. 3. Valence-difference dependence of glass-formation region. Materials considered ($M_x\text{Zr}_{100-x}$, where M is V, Cr, Mn, Fe, Co, or Cu) are characterized by monotonically increasing valence difference. The glass-forming range is shaded and is bounded by smooth curves drawn through available data (Ref. 8).

glasses form only in the Zr-rich alloys; it is also consistent with our calculated heats of formation which are -0.31 , -0.65 , and -0.87 eV/atom for Zr_3Pd , ZrPd , and ZrPd_3 , respectively. (The calculated equilibrium lattice constants for these compounds are 4.329, 2.953, and 4.033 Å, respectively. For ZrPd in the CsCl structure, the heat of formation is -0.50 eV/atom and the equilibrium lattice constant is 3.350 Å.)

Consider now the question of the importance of valence difference to glass formation. The first indication that a substantial valence difference is necessary is simply that single-constituent transition-metal glasses do not exist. Further evidence is provided by Fig. 3, where we show the glass-formation range⁸ as a function of valence difference for a series of zirconium-based systems; the correlation is striking. Systems with large valence differences form glasses over much wider concentration ranges than systems with small valence differences. Although not indicated on the figure, we note that quenching rates required to form the glasses are much lower for the larger valence difference systems than for the smaller valence difference systems, and that the quenching rates are consistent with phase-diagram melting points, in agreement with previous results.⁹ The relative stability of systems in which the Fermi level falls in a state-density valley leads us to speculate that the role of the valence difference is to create the possibility of stabilizing stoichiometry fluctuations, which permit the Fermi level to fall in a state-density valley locally in the glass. The effect of such fluctuations will be greater, the larger the valence difference of the constituents. It should be

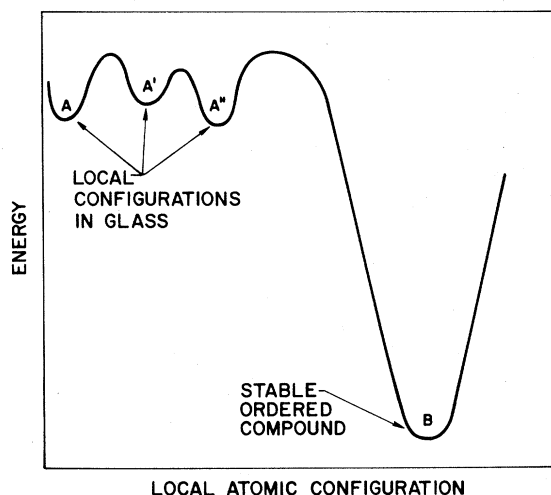


FIG. 4. Schematic local-configuration dependence of total energy. Local minima labeled A , A' , and A'' correspond to different configurations expected to be present in glasses. The deep minimum labeled B corresponds to a stable ordered compound.

noted, however, that such fluctuations must only involve a small fraction of atoms, since otherwise the Fermi-level state density would be smaller than that observed in photoemission measurements.¹

Our results indicate that zirconium-rich compositions in the palladium-zirconium system, with highly-coordinated structures characteristic of a glass, possess relatively large Fermi-level state densities, and are therefore not particularly stable. This absence of stable highly-coordinated configurations is a necessary, but not sufficient, condition for both the existence of a deep eutectic and the formation of a glass. (An additional requirement for both is the absence of stable configurations of either low coordination or complexity, like that of the Laves phases, that permit the system to exploit subtle atomic size differences or directional-bonding effects.) That is, our results show that there is an absence of ordered compounds in the glass-formation region and infers the presence of a eutectic in the same region. The depth of the eutectic, which is a measure of the glass-forming tendency, depends upon mixing and configurational entropic effects which are not accessible in our calculations. We can, therefore, expect the molten state to persist down to low temperatures and, indeed, we find a deep eutectic in the zirconium-rich region of the phase diagram. In the molten form, the system can possess stoichiometry fluctuations and can simultaneously contain a number of different configurations. Rapid quenching through the melting point freezes the system in a microscopically inhomogeneous

state. On the other hand, if the system is cooled through the melting point at a rate slow enough to permit atomic diffusion, the system can phase segregate and form a two-phase region; or, with proper annealing, can form a low-energy (noncongruently melting) ordered compound.

In our view, the glass-formation process can be discussed in terms of the schematic energy versus local configuration curve (local configuration includes both concentration and structure variation) shown in Fig. 4. We speculate that, in the concentration range in which glasses form, there is relatively little energy variation as a function of local atomic configuration. In this range, the function contains many local minima which correspond to different energetically favorable configurations. Although energetically favorable, these local configurations, labeled A , A' , and A'' in the figure, are much less favorable than configurations corresponding to stable ordered compounds and labeled B in the figure. That is, the deep minimum shown in Fig. 4 corresponds to an ordered compound. Glass formation is facilitated by the absence of such deep minima at the glass-formation concentration.

At a given concentration, we envision that the molten state supports a number of different configurations or stoichiometries. Quenching through the melting point simply freezes the system in a form corresponding to one or more stoichiometries. If the average concentration is in the glass-formation range, and if the quenching rate is sufficiently slow to allow for atomic diffusion, the configurations corresponding to deep minima can form, leading to macroscopic phase segregation. On the other hand, if the quenching rate is fast enough to prevent atomic diffusion, the persisting configurations will be those which are in the vicinity of the average concentration. That is, they will correspond to the local minima labeled A , A' , and A'' in the figure. In this case, the energy differences between various configurations will be very small so that many local configurations will be present, leading to microscopic regions of different stoichiometry and a disordered glassy form.

The Nagel-Tauc model¹⁰ proposes that glasses will have maximum stability for compositions with a low Fermi-level state density. Our energy-band calculations and experiments on transition-metal glasses both indicate that compositions with a low state density at the Fermi level will tend to form an ordered compound rather than a glass. Note that the apparent contradiction between the Nagel-Tauc model and our work can be resolved if the Nagel-Tauc criteria is applied on a local scale for the molten state. In our view, local application of the

Nagel-Tauc criteria is the basis for stabilizing the stoichiometry fluctuations which, in the final analysis, leads to the formation of the glass. The Nagel-Tauc criteria ensures that the configurations which persist are those which correspond to local energy minima.

An interesting aspect of transition-metal glasses is that they tend to form in composition ranges that favor the early transition element. From Fig. 3 we note conspicuous gaps near (50-50) at. % compositions and for compositions with the late transition element as the majority constituent. In other words, the glass-forming ability is unsymmetrical with respect to concentration. The origin of the asymmetry is the fact that the d levels fall in energy and become narrower as we traverse a transition series. This means that the d bands of early transition metals lie higher in energy and are broader. It is for this reason that, for composite systems, lower-energy states are always derived from the late transition-metal constituents, while higher-energy states are always derived from the early transition-metal constituents. If the late transition element is the majority constituent, the lower occupied states of the composite system come from the late majority constituent, which has a narrow band. Because of the width and position of the majority constituent bands, the states derived from the early constituent are shifted to higher energies and appear as a very narrow band split off from the majority bands. In this process a well-defined minimum usually appears between the states derived from the different constituents. If the Fermi level happens to fall in the vicinity of this minimum, the system will be stable and form the indicated ordered compound. Compositions rich in the early transition element, on

the other hand, usually do not show a well-developed minima because if the early transition element is the majority, its wider bands will extend throughout the energy range near the Fermi level. This, in our view, is the basic reason for the tendency for transition-metal glasses to form with the early transition element as the majority constituent.

CONCLUSIONS

We have noted an empirical correlation between glass-forming ability and large Fermi-level state density. This observation, when combined with the fact that in systems for which the atomic positions are known (crystalline elements and compounds), a high Fermi-level state density usually reflects the *absence* of short-range stability, suggests that metallic glasses are characterized by the absence of short-range stability. We find this to be consistent with the relative ease of glass formation near deep eutectics in the composition phase diagram. This point of view appears to be essentially opposite that of Nagel and Tauc. The Nagel-Tauc criterion for glass formation is based on the connection between short-range *stability* and *low* Fermi-level state density. Although this connection is valid for ordered compounds, metallic glasses appear to us to reflect the absence of short-range stability rather than its presence.

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