Nearly-Free-Electron Approach to the Theory of Metallic Glass Alloys*

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A nearly-free-electron model for explaining the relative stability of some metallic alloys against crystallization is proposed. Arguments are presented which show that in an alloy the maximum stability corresponds to the composition for which the Fermi level lies at a minimum of the density of states. In this case any small enough perturbation around this configuration will increase the total electron energy. This approach predicts the correct composition range of metal glasses.

Although, in general, it is difficult to produce metals in an amorphous form,[1] there are certain metallic alloys which are surprisingly good glass[2] formers and remain relatively stable in the amorphous state. These materials are usually found in alloys $M_{1-x}X_x$ (where M is a transition or noble metal, and X is an element of Group IV or V) with the concentration, x, near the eutectic.[3] Examples of such glass systems are $\mathrm{Pd}_{0.80}\mathrm{Si}_{0.20}$[4] and $\mathrm{Au}_{0.7690}\mathrm{Ge}_{0.1366}\mathrm{Si}_{0.0945}$.[5] The content of the metal in these glass formers is generally in the region 75–80%. That the glass-forming tendency and stability is dramatically increased near the eutectic has been viewed[6-8] as a consequence of a high reduced glass temperature, $T_{rg}=T_g/T_m$, where T_g and T_m are the glass and melting temperatures, respectively.

However, the microscopic reason for this high glass-forming tendency is not well understood. Two possibilities have been advanced to account for it. The first suggests that these glasses exist essentially in a Bernal structure of close-packed hard-sphere metal atoms with the smaller atoms stabilizing the system by filling the inherent voids in such a structure.[9] Among other accomplishments this explains why the metal content is roughly 80%. Serious objections to such an explanation have been raised based on detailed studies of the effects of alloying with elements of differing atomic radii.[10] The second model for these glasses suggests that it is chemical bonding that stabilizes the structure.[10] Recent x-ray-photoemission measurements[11] have found no evidence for such bonding in the particularly stable[12] metallic glass $\mathrm{Pd}_{0.775}\mathrm{Cu}_{0.06}\mathrm{Si}_{0.165}$. In this paper we present an alternative theory for understanding the stability of these glasses. In particular our model shows why increased stability should occur with the metal content around 80%, as well as elucidates one process by which the glass-forming tendency may be enhanced (nucleation rate suppressed) in metal alloys.

This model takes a completely different approach from those mentioned above. It treats the alloy, which is after all a metal, as a nearly-free-electron gas and employs many of the concepts used in Ziman's theory of liquid metals to describe the system. For simplicity throughout our discussion we will treat these glasses as if they were still in the liquid state which is a good approximation since the glass has been obtained from the liquid by cooling and has a structure factor, $S(q)$, similar to that of the liquid. There are three important concepts which must be introduced for the liquid metal. These are (a) the Fermi momentum, k_F, where in the amorphous liquid state the Fermi surface is assumed to be spherical; (b) the pseudo potential, $v(q)$, which gives the interaction of the free electrons with the ionic cores; and (c) the structure factor, $S(\vec{q})$, which gives necessary information about the correlation between the ionic positions. In a crystal $S(\vec{q})$ depends on the direction as well as the magnitude of $\vec{q}$ since it is nonzero only when $\vec{q}$ is a reciprocal-lattice vector. In an amorphous solid or liquid, on the other hand, $S(q)$ is spherically symmetric. Of crucial importance in the liquid is the relationship between $2k_\mathrm{F}$ and q_p [the value of q for the first peak in $S(q)$]. For atoms with valence $z=1$, $2k_\mathrm{F}$ is less than q_p while it is generally accepted that for atoms with $z=2$, $2k_\mathrm{F}$ lies slightly higher than q_p. A schematic diagram of a typical structure factor with lines indicating the value of $2k_\mathrm{F}$ for a monovalent and divalent atom is shown in Fig. 1(a).

To solve for the energy levels or the density of states of this system we start with the free-electron states and use perturbation theory to arrive at an expression very similar to that for a crystal[13]:

$$E=E_k{}^0+v(0)+\frac{\Omega}{8\pi^3}\int\frac{|v(q)|^2S(q)}{E_{\vec{k}}{}^0-E_{\vec{k}+\vec{q}}{}^0}\,d^3q, \qquad (1)$$

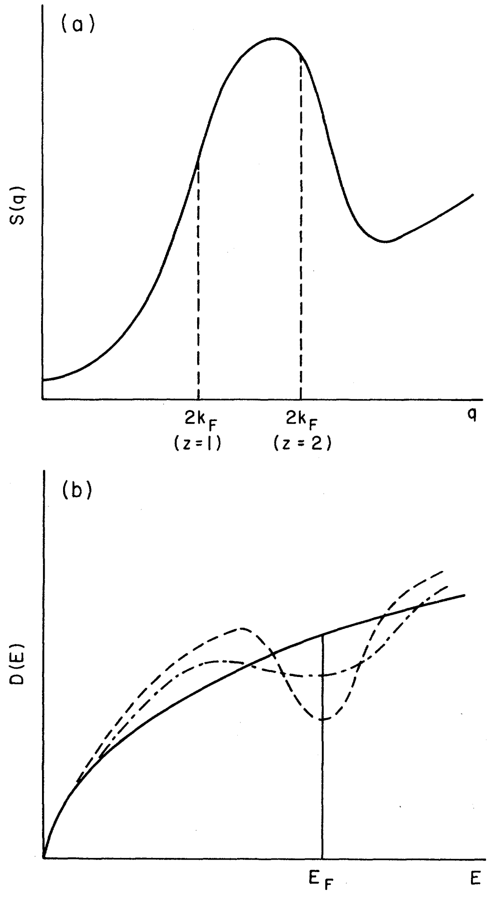

FIG. 1. (a) Schematic diagram of the structure factor as a function of wave number. The dashed vertical lines represent the values of $2k_F$ for monovalent and divalent metals. (After Mott and Davis, Ref. 13.) (b) Schematic diagram of the density of states, $D(E)$, for three cases: Solid line is for a totally-free-electron model; dashed line is for the glass in the nearly-free-electron model discussed in the text; dash-dotted line is for the perturbed glass with a nonspherically symmetric structure factor.

where $E_k{}^0=\hbar^2k^2/2m$ and Ω is the volume. This expression fails when $|\vec{k}+\vec{q}_p|=|\vec{k}|$ just as it does in the crystal where a gap opens up in the energy band at the zone boundary.[14] Although for the liquid we do not expect a gap, we do expect a similar decrease in the density of states at the energy $E=(\hbar^2/2m)|\frac{1}{2}q_p|^2$. We expect a substantial change since in the liquid or glass $S(q)$ is spherically symmetric so that *all* the states at $|k|=\frac{1}{2}q_p$ (which also all correspond to the same unperturbed energy) are affected. This is to be contrasted to the case in the crystal where $S(\vec{q})$ depends on the direction of $\vec{q}$ and thus affects only a fraction of the states with a particular magnitude $|\vec{q}|$. In addition the larger the value of $S(q)$ at q_p is, the larger the perturbation will be and the deeper we expect the minimum in the density of states to be.

One effect of alloying a monovalent metal with an element with higher valence is to shift the effective valence, $z_{\mathrm{eff}}=z_1(1-x)+z_2x$. This in turn shifts the value of $2k_F$ through q_p for some value of x. That this shift is a valid picture of what happens upon alloying is well substantiated as will be discussed later. To get an idea of what concentrations are needed for the situation $2k_F=q_p$ we take as a typical value $z_{\mathrm{eff}}=1.7$. If we alloy Au ($z_1=1$) with Si ($z_2=4$) we get a value for x of 0.23 ($\mathrm{Au}_{0.77}\mathrm{Si}_{0.23}$). If we alloy Au with P ($z_2=5$) we get a value for x of 0.18 ($\mathrm{Au}_{0.82}\mathrm{P}_{0.18}$). It is just at these concentrations when $2k_F=q_p$ that the Fermi energy, E_F, will lie at a minimum of the density-of-states curve, $D(E)$.

We shall now argue why such a system should be more stable against crystallization than a system for which $2k_F\neq q_p$. Our argument will be based on the fact that, even though the electronic energy of the glass may be higher than that of the crystal, the glass is still at a metastable minimum of energy. If the system starts to crystallize, as a result of a fluctuation in which the system develops long-range order, $S(q)$ is perturbed and is no longer spherically symmetric. The argument that all the states with a given magnitude of $|q|=\frac{1}{2}q_p$ are affected is no longer valid. The value of q_p will now depend on direction and will consequently act to lower the density of states at a different value of the energy for each direction. The deep minimum at $D(E_F)$ is no longer expected [see Fig. 1(b)]. Thus, as $S(q)$ is perturbed we find that the total energy of the system increases as more electron states are moved up to E_F where they have higher energy. The glass is in a metastable state since any perturbation will destroy the spherical symmetry of $S(q)$.

We have so far presented a model for the stability of certain metallic alloys in the glass form. This model predicts stability for the system $M_{1-x}X_x$ in the region $x\approx0.20$. The choice of $z_{\mathrm{eff}}=1.7$ is somewhat arbitrary but it is a reasonable estimate (cf. Fig. 1). Using this value we find that we can indeed predict increased stability in the same concentration range as that observed experimentally. Of course depending on the details of $S(q)$ in each instance, q_p will coincide with $2k_F$ at different values of z_{eff}. However, for an alloy where the interatomic distances do not significantly change with concentration the position of the first peak in $S(q)$ should remain unchanged as well.

Although we have so far concentrated on the importance of $S(q)$ to the glass formation, the behavior of the pseudo potential is also important. In the alkali metals $v(q_p)$ is small whereas for transition metals, like copper, it is much larger.[14] This increase is at least partially due to the influence of the d bands which thus do play a central role in the glass formation. For example calculations of $D(E)$ for Hg show a pronounced minimum whereas for Al they show none at all.[15]

We have made a number of other assumptions in the course of constructing our model which should be examined in the light of available experimental evidence. The two main ones are (1) that the effect of alloying can be treated as a rigid shift of E_F and k_F and (2) that the Group-VIII transition metals as well as the noble metals can be treated as if they had only one free electron per atom in the liquid. The two main conclusions of the model that also would be considerably strengthened by experimental support are (i) there is a decrease in $D(E_F)$ at the concentration where $2k_F = q_p$, and (ii) the glass transition temperature does scale with the height of the structure factor at q_p. We will now present evidence to support each one of these points.

The data on the resistivity of liquid metals and alloys amply justify the first two assumptions. In normal metals, according to Ziman,[16] the resistivity is

$$\rho \propto \int_0^{2k_F} S(q)|v(q)|^2 q^3 dq. \tag{2}$$

As two elements are alloyed, one with valence 1 and the other with higher valence, Faber and Ziman[17] predict that the resistivity will reach a maximum when $2k_F$ passes through q_p. The factor q^3 in the integrand weights this integral toward somewhat higher values of q, giving a larger value for z_{eff} at the maximum resistivity than the values of z_{eff} considered above. The data for many noble-metal alloys bear out this prediction[18] and the idea of a rigid shift of the Fermi level with alloying seems well founded. Busch and Güntherodt[18] also find that the transition metals can be treated as if they had one free electron per atom. Fe-Ge and Ni-Ge alloy systems have a maximum of their resistivity at a concentration of germanium in the 30% range, indicating, as expected, that this concentration corresponds to $2k_F = q_p$.

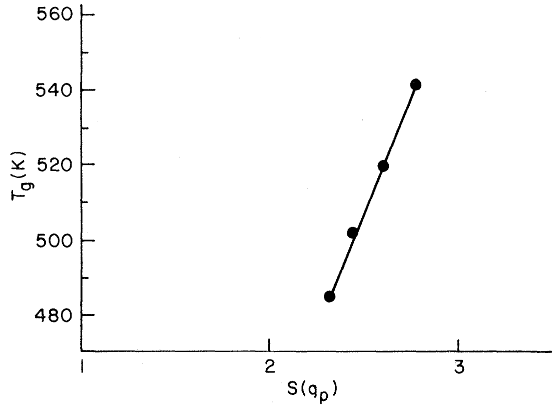

FIG. 2. Height of the structure factor at its first peak, $S(q_p)$, versus the glass temperture, T_g, for various alloys $(Pt_{1-x}Ni_x)_{0.75}P_{0.25}$. The values of x range from $x = 0.20$ to $x = 0.60$. The data are taken from Refs. 7 and 19.

From other experiments we can find evidence for the validity of the conclusions of the model. The paramagnetic susceptibility is proportional to $D(E_F)$ and we expect that if the density of states decreases so will the susceptibility. In fact a large decrease in magnetic susceptibility is reported[18] for AgIn and related alloy systems at the concentration where $2k_F = q_p$. Finally there is one piece of evidence that the stability of the system does increase with an increase in the peak height of the structure factor. Sinha and Duwez[19] measured the structure factor for the glass $(Pt_{1-x}Ni_x)_{0.75}P_{0.25}$ for various concentrations, x, of Ni. In another study Chen[7] measured the glass temperature, T_g, for the same series of alloys. In Fig. 2 we plot the values of T_g versus $S(q_p)$ for various concentrations x. We find that the glass temperature does indeed scale with the height of $S(q_p)$, and in the range studied, the variation is linear.

The evidence for the validity of this model has come from a wide variety of measurements. Perhaps its most attractive feature is that it starts from a free-electron framework and does not rely on chemical bonding to produce stability. It is thus thorougly consistent with the photoemission measurements made on these glasses. It also suggests that one should concentrate on the measurements of liquid alloys in order to gain insight into what makes these particular alloys comparatively good glass formers.

For an understanding of the properties of metallic glasses we benefitted from discussions with

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Theoretical Magnon Dispersion Curves for Gd[†]

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The magnon dispersion curve of Gd metal has been determined from first principles by use of augmented-plane–wave energy bands and wave functions. The exchange matrix elements $I(\vec{k},\vec{k}')$ between the $4f$ electrons and the conduction electrons from the first six energy bands were calculated under the assumption of an unscreened Coulomb interaction. The results are in good overall agreement with experiment provided the $I(\vec{k},\vec{k}')$ are diminished by a constant scale factor of about 2 which may be caused by screening.

The s-d (or s-f in the rare earths) interaction model has had great success in describing a variety of phenomena ranging from conduction-electron polarization effects to properties of localized magnetic moments. The s-f exchange interaction $I_{s\text{-}f}(\vec{k},\vec{k}')$ between the localized $4f$ and the conduction electrons in the rare-earth metals is the basis of the indirect exchange mechanism of