

Theoretical studies on structural models of metallic glass alloys

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Recently developed modeling techniques are applied to the study of binary metallic-glass-alloy systems. Computer-generated models of glass alloys in the families Pd-Si, Fe-P, Fe-B, and Pd-Ge have been analyzed, and compare favorably to the known properties of these glasses. New, and as yet unmeasured, structural features are predicted for the Fe-B system. Systematic variations of structural features in pair-correlation functions are predicted and are used to explain variations in pair-interaction energetics, which is offered as an explanation for the long-known trend of increasing hardness and glass-transition temperature with increasing metalloid content. Further analysis suggests that the structures are collections of well-defined molecular units. The existence of such units and their packing properties could be the source of the physics which causes the deepening of the eutectic in the phase diagram of glass-forming alloys.

I. INTRODUCTION

The glassy state of metallic alloys is known to exist near deep eutectics in their phase diagrams. In practice, there is a range of compositions about the eutectic minimum within which the glass state can be reached (by suitably rapid quenching); physical properties vary considerably, even discontinuously, across this range. It is the purpose of this paper to explore structural origins of physical-property variations by studying computationally simulated models of binary glass alloys.

It is fairly well accepted that the reason metallic glass alloys are fabricable near their eutectic composition is that the reduced glass-transition temperature is large¹; $T_{rg} = T_g/T_l$, T_g is the melt \rightarrow glass transition temperature and T_l the unconstrained liquidus temperature. Physically this corresponds to quenching across a relatively narrow thermal range. It is not clear, however, whether there is a direct structural origin of the eutectic behavior; this is one of the motivations of the present study.

Metallic glasses fall into two categories. The so-called metal-metal glass alloys consist of metal atoms exclusively; e.g., Gd-Co, Cu-Au, Ti-Zr, etc. The composition range over which the glass state is fabricable tends to be relatively wide, 40 at. % in some cases; and it is frequently near the point of equal atomic proportions. The transition-metal-metalloid (TM-M) glass alloys,² on the other hand, are found in rather narrow composition ranges, usually less than 10 at. % wide; the center of the composition range is almost universally found at 78-80-at. % TM. This paper focuses on the latter type glass where sharper variations in physical properties occur over rather narrow changes in alloy composition.

Chen and Jackson³ summarize measurements of glass-transition temperature, plastic flow and fracture, elastic constants and hardness, the ductile brittle transition, and thermal stability and magnetic properties of the TM-M class of metallic glasses. Guntherodt³ describes electrical resistivity and its temperature dependence as alloys composition is varied. The only comprehensive study of physical properties on a well-characterized series of samples from a binary system (Fe-B) is by Hasegawa and co-workers.⁴ They have measured mechanical, thermal, and magnetic properties; in addition, densities are reported for alloys of Fe-B, Fe-P, and Ni-P as metalloid content is varied. These studies support the general observations, important to this work, that hardness and glass-transition temperature T_g increase with metalloid content; also that density decreases with decreasing metalloid content and, in the case of Fe-B, shows a sharp break at 20-at. % B.

Direct probes of the structure in TM-M glass alloys have been made primarily by x-ray and neutron diffraction. Information is limited by the lack of long-range order to radial distributions of neighbors. Cargill⁵ has reviewed this field but there are some significant recent contributions. Suzuki *et al.*⁶ have used high-resolution neutron diffraction to resolve the near-neighbor radial distribution peaks for Pd-Pd and Pd-Si pairs in Pd₈₀Si₂₀. X-ray and neutron-diffraction results have been combined by Suzuki *et al.*⁶ and by Sadoc and Dixmier⁷ to yield partial pair correlations in Pd₈₀Si₂₀ and Co₈₀P₂₀, respectively. Waseda *et al.*⁸ used multiple sources of x radiation to extract partial pair correlations on Fe-P glass alloys from 20- to 25-at. % P; they observed no composition variation within the error bounds of their measurements. The most useful aspect of

these measurements is the availability of individual pair coordination numbers with which to compare structural models. More recently extended x-ray absorption fine structures (EXAFS) have been used to probe the short-range order in metallic glasses. Hayes *et al.*⁹ have studied the binary alloy Pd₈₀Ge₂₀ and find a very narrow (<0.1 Å) shell of 8.6 ± 0.5 Pd neighbors around each Ge; there are no Ge-Ge near-neighbor pairs. Wong *et al.*¹⁰ have used EXAFS to study more complex systems and are able to conclude that there are different dynamical interactions between different types of metal atoms with a given type metalloid. The interpretation of these interactions requires a more precise understanding of the structural short-range order.

Since detailed information from experimental sources is limited by the very nature of the material being investigated, much effort has gone into the development of models. The models are based on plausible physical principles and attempt to reproduce the known facts; they are useful for suggesting details of the structure which are not directly accessible experimentally. The most widely used models are based on a concept of dense random packings of spheres (DRPS). The idea was thrust into prominence by Polk¹¹ who recognized that the experimental one-size hard-sphere structures of Bernal¹² could accommodate 21-at. % metalloid with minimal distortion. Considerable effort went into computationally simulating these general ideas; Finney¹³ has written an excellent review. Only recently has it become possible to make satisfactory representations of binary systems.¹⁴ The present paper applies these successful modeling concepts to several series of binary metallic glass alloys: Pd-Si, Fe-P, Fe-B, and Pd-Ge. From these studies a number of specific explanations of observed phenomena are offered; a conceptual framework which goes beyond the simple idea of Polk¹¹ is developed.

In Sec. II the methods of simulation are described as well as the alloy compositions studied. Section III summarizes the diffraction data from the model structures. Section IV discusses coordination numbers and the conclusions drawn from them. Deductions from energetic relaxations of the models are presented in Sec. V. Conclusions are summarized in Sec. VI.

II. STRUCTURAL MODELS

All of the models studied in this paper were produced by a two-step process. First, a random packing of two different size hard spheres was produced using the algorithm originally sug-

gested by Bennett.¹⁵ The different size spheres represent different type atoms, the large spheres locate TM sites while the small ones locate *M* sites. The alloy composition is controlled by the algorithm described in a previous paper.¹⁴ Typically 2500 spheres are packed into a spherical cluster. To produce an acceptable model, 2000 "atoms" from the center of hard-sphere clusters are relaxed according to procedures described previously.¹⁴ Suitably modified¹⁴ Lennard-Jones, 6-12, potentials were used for all of the work reported here; the effect of less stiff potentials is simply to broaden the features of the various distribution functions.

Parameters for the interaction potentials used to describe Pd-Si alloys have been given earlier¹⁴; these same parameters were used in the models of Fe-P glasses by simply scaling the large atom diameter to the average Fe-Fe spacing of 2.72 Å. The potential parameters for the Fe-B glass structures were taken from the crystal structure data on Fe₃B: the Fe-Fe interaction minimum was set at 2.72 Å while that for the Fe-B interaction was at 2.07 Å. For the Pd-Ge model, the average atomic spacing of Pd and Ge sites was taken to agree with the result of Hayes.⁹ The Pd-Pd spacing was assumed to be the same as in Pd₃Si,⁶ since data on Pd₃Ge are not available. The ratios of metalloid "radius" to transition metal "radius" for these systems are then 0.8, 0.72, and 0.52 for Pd-Ge, Pd-Si (or Fe-P), and Fe-B, respectively.

The interaction strengths were adjusted so that the metal-metalloid interaction is twice as strong as that for metal-metal interaction; the factor of 2 is arbitrary, but intuitively satisfies chemical requirements. Considerable computation has gone into exploring the effect of this choice; in summary, the only significant variation in results occur when the TM-*M* interaction strength is weakened to equal that of the TM-TM interaction. The treatment of the *M-M* interaction is not as simple; a strength of 0.05% of the TM-TM interaction was used at a distance of twice the *M* "radius." This would seem to encourage *M-M* near neighbors contrary to both neutron-diffraction⁶ and EXAFS (Ref. 9) measurements. Indeed in the original hard-sphere packings, considerable care is taken to avoid *M-M* near-neighbor sites. Alternatives to the above scheme were explored and discarded: Ching and Lin¹⁶ suggested using four times the *M-M* "radius," but that results in a very unphysical collection of *M-M* pairs at rather large distances; a potential of zero strength was also tried but resulted in metalloids sharing the same site. The scheme adopted provides sufficient repulsion to avoid site sharing but is insufficiently strong an interac-

tion to cause M - M near-neighbor pairs to relax into the structure.

A number of structures were "built" corresponding to various compositions of the alloys above. Pd-Si (or Fe-P) was studied from 10- to 30-at. % metalloid. Fe-B was studied at three compositions: 85-15, 80-20, and 75-25. Only one model of $\text{Pd}_{80}\text{Ge}_{20}$ was examined to compare to the results of Hayes *et al.*

Each model was analyzed to yield radial distribution functions (RDF), reduced radial distribution functions (RRDF), and the various partial pair-correlation functions ρ_{ij} ; each of these is defined for multicomponent systems by Cargill.⁵ The radial distributions are composites of the ρ_{ij} for various components each weighted by the atomic numbers of the scattering species to stimulate their x-ray scattering factors (K dependence was ignored). All distributions are measured to 8 TM-atom diameters and are corrected for the finite size of the cluster.¹⁴ A Fourier transform of the RRDF produces the so-called reduced interference functions,⁵ conventionally labeled $F(K)$, where $K \equiv 4\pi\lambda/\sin\theta$ in the diffraction experiment. The results for $F(K)$ are accurate to at least 60 reciprocal diameters (of the TM atoms) which is approximately 20 \AA^{-1} for Pd-Si.

Near-neighbor coordination numbers of atom type i by atom type j are obtained by integrating ρ_{ij} ; the integrals are cut off at the first minimum beyond the first peak. Density is approximated by counting "atoms" inside a bounding sphere of known volume; this inevitably involves assigning a specific radius to each atom and leads to the possibility of errors which are difficult to estimate. This point is discussed further in Sec. V.

III. DIFFRACTION DATA

Selected portions of the diffraction data simulated from the computer models are presented in this section; if required for specific comparison, the remaining data are available directly from the author. Figure 1 shows the variation of the reduced interference function $F(K)$ with changes in the composition of the glass alloy Fe-P. As metalloid content increases, the position of the first peak moves to larger values of K and its amplitude decreases. In real space, this corresponds to a decrease in both amplitude and wave-length of the long-range oscillations in the RDF curves, and suggests a somewhat less ordered structure. Logan¹⁷ studied Fe-P glass alloys from 78- to 86-at. % Fe; he did not publish the interference data, but the long-range amplitudes of the RRDF's he measured do decrease monotonically with

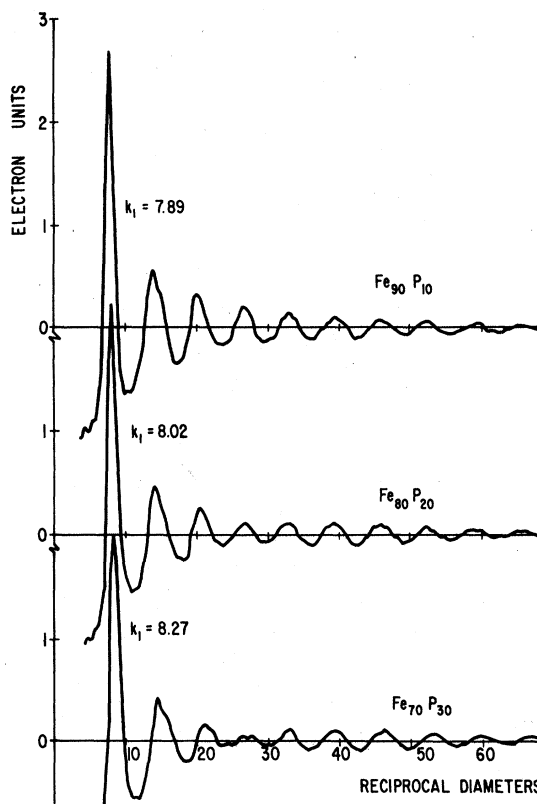


FIG. 1. Reduced interference functions of simulated x-ray diffraction from models of Fe-P glass.

increasing P content as expected. Waseda *et al.*⁸ were not able to resolve any reproducible shift in the partial structure factor; however, the composition range they investigated was only $\frac{1}{4}$ as wide as that considered here, and the effect is only expected to be 3% in peak position.

The reduced interference functions for three $\text{Fe}_{1-x}\text{B}_x$ structures have a first peak at 2.9 \AA^{-1} for all three structures; the height is 2.8 e.u. for $x = 20$ and 25, but jumps to 3.1 for $x = 15$. This implies an amplitude increase in the long-range correlations in low B content alloys and suggests a more ordered structure. The second peak has been cited by experimentalists as being characteristic of $\text{Fe}_{80}\text{B}_{20}$; it has an exceptionally low amplitude shoulder on the high-K side.¹⁸⁻²² Figure 2 shows the second peak as a function of composition and such a shoulder is indeed evident for $\text{Fe}_{80}\text{B}_{20}$ glass; the shoulder appears to dissolve, however, as the composition is varied. This is not inconsistent with the results of Cargill on Ni-P glasses where no shift in the first peak position is observed; while Ni-P glasses do not have a sphere size ratio (≈ 0.7) as small as Fe-B glasses, it is smaller than that used for the Fe-P models.

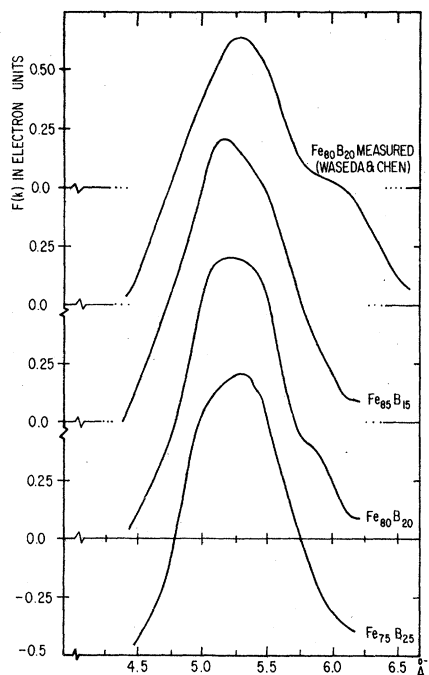


FIG. 2. Second peak of the x-ray reduced interference function shown in detail for three alloy compositions of Fe-B glass. In mid-range, the low-lying shoulder is characteristic of this glass system.

The suggestion is that the smaller the sphere size ratio, the smaller are any shifts in $F(K)$ peak positions. Finally, the reduced interference function for $\text{Pd}_{80}\text{Ge}_{20}$ is shown for reference in the inset of Fig. 3.

Figure 4 compares the RRDF and pair-correlation functions and PCF's of $\text{Fe}_{75}\text{P}_{25}$ with the results of Waseda *et al.*⁸ The experimental RRDF (top) does not resolve the Fe-P and Fe-Fe near-

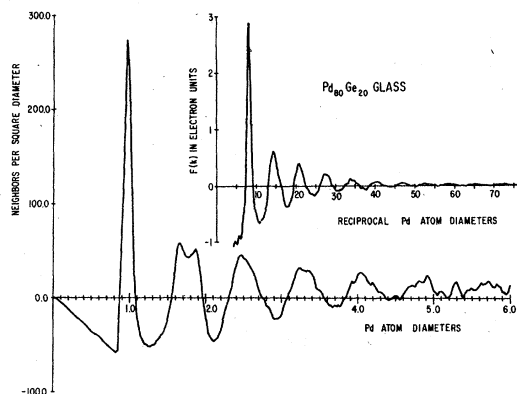


FIG. 3. Reduced radial distribution function (x-ray) for a model of $\text{Pd}_{80}\text{Ge}_{20}$. The inset shows its Fourier transform, the reduced interference function.

neighbor shells as does the theoretical curve, but the overall agreement is excellent. The lower half of Fig. 4 compares the correlation functions for individual types of pairs. The worst feature is the disagreement in the second peak of the Fe-P curve. In fact, this portion of the experimental curve is the most severe test of the data reduction procedures used by Waseda; the Fe-P pairs contribute only about 20% to the total scattering and there may be large truncation errors in their analysis.

The entire set of partial PCF's for the series of Fe-P structure is presented in Figs. 5 and 6. The first peaks are centered on the minimum in the potential energy curve describing the interaction of the type pair being considered. The area under the first peak supplies coordination number information to be discussed in Sec. IV. Note, however, that various features of the remainder of the curve move to smaller r values as P content increases; the exception is the outer half of the second peak which remains fixed. The movement of the inner half of the second-neighbor

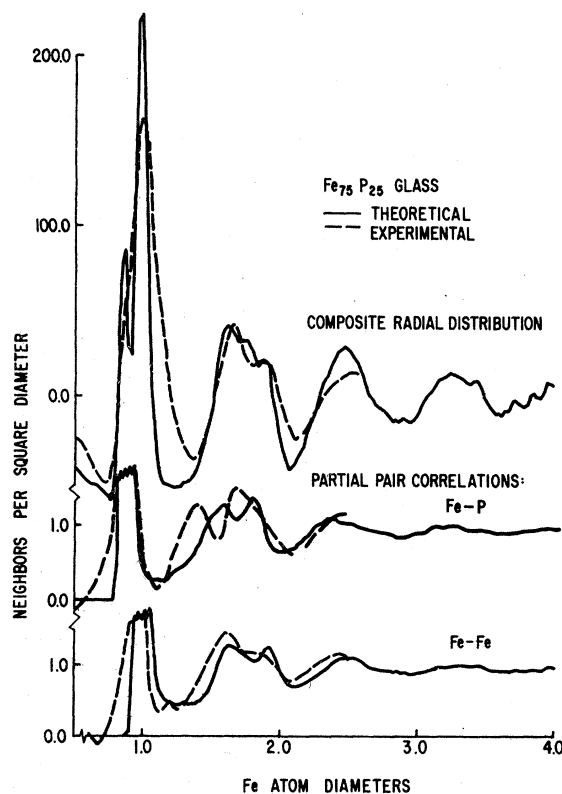


FIG. 4. Comparison of calculated and measured reduced radial distribution functions for $\text{Fe}_{75}\text{P}_{25}$ (top); the experimental data is from Waseda *et al.* (Ref. 8). The partial pair-correlation functions for two types of pairs are compared below.

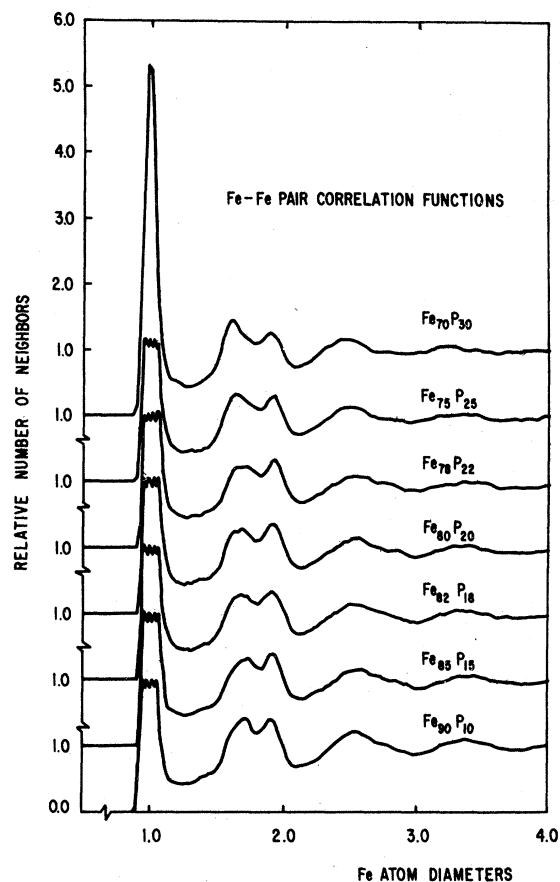


FIG. 5. Partial pair-correlation functions for Fe-Fe pairs in models of Fe-P glass as a function of composition. Note particularly the behavior of the inner half of the second peak.

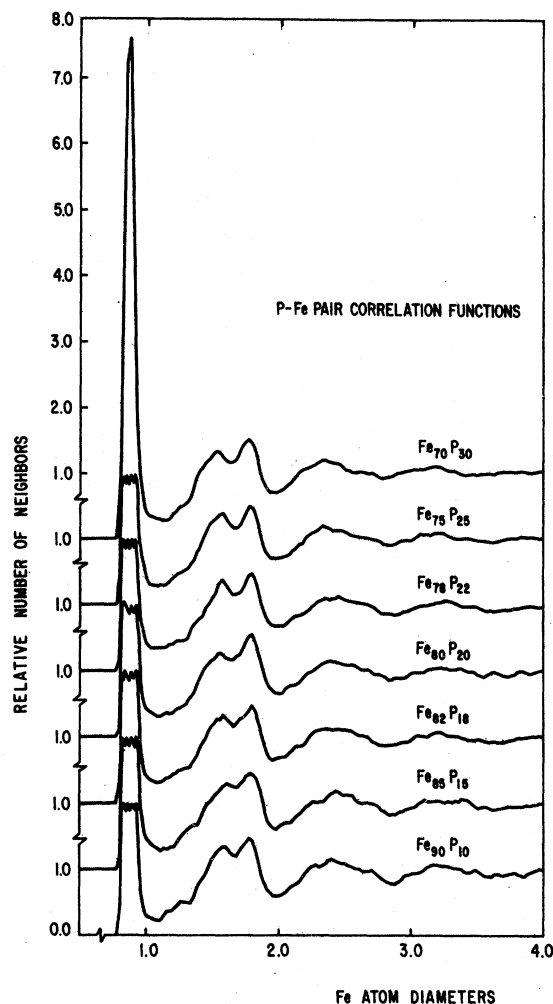


FIG. 6. Same as Figure 4, except for Fe-P pairs.

shell to smaller distances has important consequences to be discussed later.

Even more dramatic changes occur with composition in Fe-B simulated glass structures. The reduced radial distribution functions of three such structures are shown in Fig. 7. The first-neighbor shell is resolved into the Fe-B and Fe-Fe distances. The first subpeak height in the second-neighbor shell is smaller than the second, which is in agreement with measurements.¹⁸⁻²² A new feature not observed for Fe-P or Pd-Si models appears between the first- and second-neighbor shells and is more pronounced as the B content is increased; it occurs at 1.5 Fe atom diameters. As the size of the metalloid is increased, the feature disappears. The PCF data shown in Figs. 8(a)-8(c) confirm that this feature is due to Fe-Fe neighbors and imply physically that a new kind of Fe neighbor shell becomes increasingly occupied as the B content is increased. The effect is not due to the nature of the interatomic

potentials because it remains even when the strength of the Fe-B interaction is weakened so as to equal that of the Fe-Fe interaction; however, the calculated width of the shell may be too narrow due to the stiffness of the 6-12 potentials. We suggest that the short-range order in the system may be divided into two classes above and below the composition $x_0 \approx 15$. The "boundary" value of x_0 may vary with sphere size ratio; it is thus possible that more accurate measures of Fe-Fe and Fe-B separations in the glass could cause a shift of 1 or 2 at. % in the predicted value of x_0 .

Direct experimental support for two classes of short-range order is not yet available; however, indirect evidence abounds. Hasegawa and Ray and co-workers⁴ observe a distinct break in the plot of density versus composition for FeB glasses at $B \approx 20$ at. %. This is consistent with two regimes of short-range order in the alloys. Suzuki²² reports

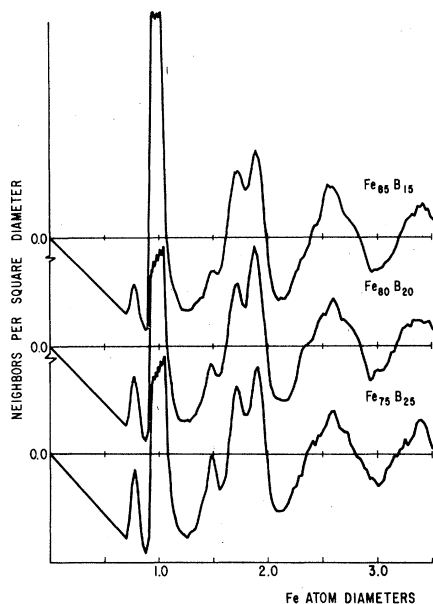


FIG. 7. X-ray reduced radial distribution function for three compositions of Fe-B. Note the rising feature between the first and second-neighbor shells.

some sharp changes in RDF peak shapes at $x = 17\%$ B. There are two crystallization¹ peaks in calorimetric measurements below 17% B and only one above. Finally the Curie temperature shows⁴ a noticeable kink at this same composition. Less closely connected are the observations by Shull *et al.*²³ on La-Ga glassy alloys, which have atomic "sizes" roughly comparable to those of Fe and B. They see a break in the Debye temperature and a "bump" in the specific heat at 22 at. % Ga. The important point in all this is to recognize that for the first time it has been demonstrated that structural models can exhibit strong compositional variations of their short-range order, which may correlate with corresponding variations of the physical properties of the alloys.

For completeness, the RRDF of Pd₃₀Ge₂₀ is shown in Fig. 3. The difference between the radii of Pd and Ge radii is now sufficiently small that the two near-neighbor distances are not resolved. Hayes *et al.*⁹ claim to have measured the width of the Pd-Ge near-neighbor distribution to be of the order of 0.1 Å. The full width at half-maximum of the first peak of the Pd-Ge PCF in the simulated structure is 0.21 Å. The theoretical width is based on atoms interacting via very stiff potentials (chosen as such to illustrate details which might otherwise have been hidden); it is highly unlikely that interactions in the real glass are as rigid. It is, therefore, surprising that Hayes *et al.* have come to the conclusion stated above. Perhaps

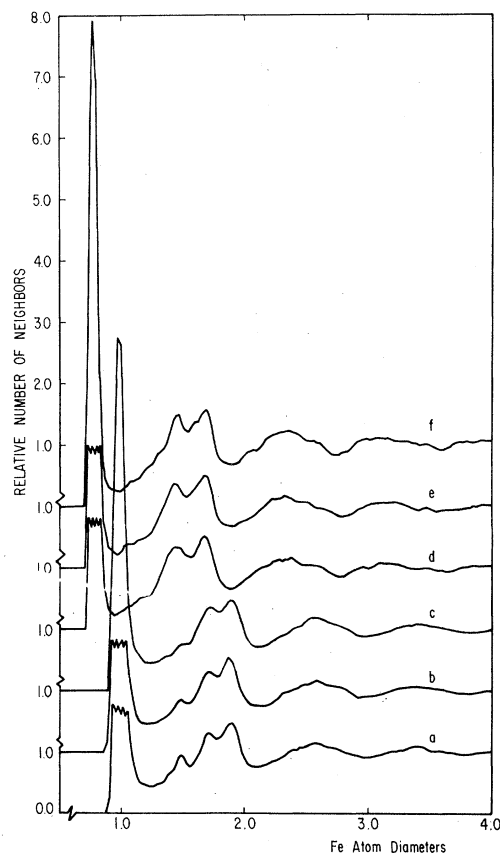


FIG. 8. Partial pair-correlation functions for Fe-Fe pairs in models of (a) Fe₇₅B₂₅, (b) Fe₈₀B₂₀, and (c) Fe₈₅B₁₅; (d)-(f) exhibit the Fe-B pair correlations for the same models. The new feature in Fig. 2 is due to Fe-Fe neighbors at 1.5 Fe atom diameters.

the "peak" function used in their data reduction and measured from crystalline PdGe is slightly different from the "peak" function that would be obtained from a crystal of composition closer to the glass, e.g., Pd₃Ge. It would be most informative to have the same information deduced from EXAFS on the Pd edge.

IV. SITE COORDINATIONS

An informative guide to the short-range order characteristic of a given type atom site is found in the number and type of near neighbors coordinating that site. Table I displays the variation in these numbers with both alloy type and alloy composition. Pd-Si (or Fe-P) glasses are represented in the first rows, Fe-B in the second, and Pd-Ge in the third. The first number listed for each composition is the number of TM neighbors around a TM site; the second number is the number of *M* neighbors of a TM site. The total TM site coordination is shown on the

TABLE I. Number of atoms in near-neighbor shell for various metallic glass alloys as deduced from the structural models discussed in the text.

Composition	Coordination numbers						
	70/30	76/24	78/22	80/20	82/18	85/15	90/10
Pd-Si							
(Fe-P)							
TM-TM	10.34	10.43	10.72	10.22	10.49	10.59	10.65
TM-M	3.29	2.52	2.19	2.05	1.78	1.44	0.85
Total	13.63	12.95	12.91	12.27	12.27	12.03	11.50
M-TM	8.40	8.21	8.26	8.44	8.36	8.46	8.21
Fe-B							
TM-TM		10.97		10.79		11.25	
TM-M		1.94		1.51		1.06	
Total		12.91		12.30		12.31	
M-TM		6.89		6.41		6.56	
Pd-Ge							
TM-TM				10.23			
TM-M				2.18			
Total				12.41			
M-TM				9.29			
$N_{\text{Pd-Pd}}$ (in PdGe) = 10.23, $N_{\text{Ge-Pd}} = 9.29$				Experimental			
$\langle N_{\text{Fe-Fe}} \rangle$ (in FeP) = 10.49, $\langle N_{\text{P-Fe}} \rangle = 8.33$				$N_{\text{Pd-Pd}}$ [in Pd ₆₀ Si ₂₀ (Suzuki)] = 10.4			
$\langle N_{\text{Fe-Fe}} \rangle$ (in FeB) = 10.99, $\langle N_{\text{B-Fe}} \rangle = 6.62$				$N_{\text{Pd-Si}}$ [in Pd ₆₀ Si ₂₀ (Suzuki)] = $\frac{1.8}{12.2}$			
				Total			
				$N_{\text{Fe-Fe}}$ [in Fe ₇₅ P ₂₅ (Waseda)] = 10.4			
				$N_{\text{Fe-P}}$ [in Fe ₇₅ P ₂₅ (Waseda)] = $\frac{2.6}{13.0}$			
				Total			
				$N_{\text{P-Fe}}$ [in Fe ₇₅ P ₂₅ (Waseda)] = 8.1			
				$N_{\text{Ge-Pd}}$ [in Pd ₇₈ Ge ₂₂ (Hayes)] = 8.6 ± 0.5			

third line. The final number is the total *M* site coordination; recall that *M-M* near neighbors are prohibited. The lower right of the table summarizes measured values. Suzuki *et al.*⁶ were able to deduce separate contributions from the resolved first peak of the RDF they measured; the data from the model structures are well within expected bounds. Likewise the agreement with the results of Waseda *et al.*⁸ is excellent; note that these experiments also count the average number of Fe neighbors for each P as 8.1. The only other experimental determination of metalloid coordination was made by Hayes *et al.*⁹ for Pd₈₀Ge₂₀; while the model number is satisfactorily close, it is possible that the experimental number is small for the same reasons that the distribution is so narrow (see Sec. III).

The most striking observation to be made from Table I is that the metalloid coordination is essentially constant with alloy composition variation. The average numbers are given in the lower left of Table I. This suggests an important feature

of the structure of metallic glasses: *the metalloid is the center of a molecular unit with a fixed structure* which depends on the nature of the TM-M interaction. The units pack together to form the glass and the extra TM atoms fill the space between units. This is in agreement with the ideas of Gilman²⁴ who argues that such molecular units exist in the liquid state near eutectic compositions. He suggests that these units retain their identity as the liquid is rapidly quenched to the glass state; it is interesting to note that the same state has been reached in this work starting from a one-at-a-time addition algorithm. Further evidence of the correctness of the calculated numbers comes from a comparison with metalloid site coordinations in Pd₃Si, Fe₃P, and Fe₃B. Pd₃Si and Fe₃P have nine nearest neighbors distributed^{6,25} over 0.085 TM diameters while Fe₃B has a structure with B atoms at the center of a very tight and nearly regular trigonal prism.²⁵ A speculation worthy of further investigation is that the "efficiency" of the packings of the mole-

cular units is connected with the depth of the eutectic in the liquidus curve. This, however, is a conceptually difficult geometrical problem which has, to date, eluded precise specification; further probes of the present structures are in progress to quantify this point.

V. ENERGETIC CONSIDERATIONS

As the structures are relaxed under the influence of the Lennard-Jones potentials, the computer program keeps track of the sums of interaction energies for each type pair separately. The quantity minimized is the total of these sums,

$$E_{\text{tot}} = E_{11} + E_{12} + E_{21} + E_{22},$$

where the subscript 1 implies a TM species and 2 implies an M species. For example, E_{12} is the sum of all the interactions of a type-1 (TM) atom as center with all type-2 (M) neighbors. If there are N atoms in the relaxation, the various energies above can be expressed on a per atom basis

$$E'_{\text{tot}} \equiv E_{\text{tot}}/N, \quad E'_{ij} \equiv E_{ij}/N, \quad (i, j = 1, 2).$$

Defining new quantities ϵ_{ij} by $E'_{ij} \equiv c_i c_j \epsilon_{ij}$, permits writing the total energy per atom as

$$E'_{\text{tot}} = \sum_{ij} c_i c_j \epsilon_{ij}, \quad (1)$$

where c_i is the fraction of type i atoms in the model. Equation (1) may be interpreted in the same way as the expression given by Cargill⁵ for the composite RDF of a multicomponent system: ϵ_{ij} is the average energy of interaction of a pair of $i+j$ atoms. Some of these quantities are plotted in Fig. 9 as a function of metalloid content. The vertical scale is expressed in units of the strength of the interaction, but are numerically arbitrary. The important feature to note is the increase in average interaction energy as metalloid content is increased. The rate of increase for TM- M interactions is greater than for TM-TM because of the greater strength of the potential. The origin of the increase is found in the behavior of the inner half of the second peak of the partial PCF's (see Sec. III). More second neighbors are packing closer to the central atom and, hence, are sampling space with lower potential energy. In effect, the structure relaxes to pack the atoms in such a way as to increase the energy required to separate each pair of atoms as more metalloid atoms are added to the alloy. Expressed in different terms, more energy is required, *on average*, to disrupt bonds.

There are important experimental observations which have heretofore escaped explanation, but which correlate with the above energetic feature

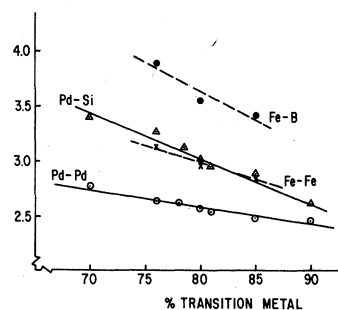


FIG. 9. Average energy required to disrupt a pair of atoms as labeled; \cdot and \times are calculated from models of Fe-B glass alloys, while Δ and \circ are for Fe-P glasses.

of the model structures. Micro-hardness and the temperature of the melt \leftrightarrow glass transition, T_g , are both measures of the difficulty of disrupting bonds. Both quantities have long been known to increase with metalloid content. Hasegawa and co-workers⁴ have measured increases in both quantities for Fe-B glass alloys as B is added. Further experimental work is summarized by Naka *et al.*,²⁶ but there is a great deal more such information which is largely unpublished, perhaps for lack of explanation.

VI. DENSITY

From the beginning of attempts to simulate models of glass structure with computers,¹⁵ the mass density has been an elusive quantity: the calculated numbers are always too low. Density is, in fact, a difficult quantity to calculate for nonperiodic media. A proper calculation requires the determination of the average volume of the Voronoi polyhedra²⁷ surrounding the atomic sites, i.e., determining the volume inside which resides exactly one atom. One such calculation²⁸ has been done on the structure $\text{Fe}_{76}\text{P}_{24}$ reported here; the result is 7.02 g/cm^3 . This compares with the actual density of 7.03 g/cm^3 . The approximate calculations for $\text{Fe}_{78}\text{P}_{22}$, described in Sec. II, yield $6.7 \pm 0.3 \text{ g/cm}^3$ for all of the Fe-P structures. A more worrisome point is the fact that the approximately calculated density for the three Fe-B structures is only 6.4 g/cm^3 ; this system has measured densities⁴ from 7.1 to 7.4 g/cm^3 . More accurate calculations are in progress to resolve this point.

VII. SUMMARY AND CONCLUSIONS

Computationally simulated and relaxed DRPS structures containing two "size" spheres have been studied over a range of compositions and for

systematically differing binary alloys of the TM-M type. Statistical summaries of information from models have been shown to agree with those deduced from experiments on real glasses. Some new ideas have emerged from this work which should be useful guides in understanding measurements of properties of metallic glass alloys. There are two points which should be verified directly: the first is the presence of a new Fe-Fe distance shell in the Fe-B glass system and the

second is the structural origin of the increase in the energy associated with a pair of interacting atoms as metalloid content is increased. Confirmation would support the most important suggestion from this work, namely, that the glass structure consists of some relatively well defined molecular units. Future work will be immediately concerned with identifying these units and discovering the way their packing affects the properties of the glass state.

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