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Microscopic Calculations of the Stability of Metallic Glasses

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We show that metallic glasses are stabilized by the close matching between the minima in the interionic potentials and the maxima of the partial pair-distribution functions. We use an *ab initio* pseudopotential method to calculate the interionic potentials for transition-metal-free glasses (Mg-Zn, Ca-Mg, and Ca-Al). The amorphous structure is determined using cluster relaxation and thermodynamic variational techniques. Our theory demonstrates that there is a close relation between glass formation and the formation of topologically close-packed intermetallic compounds.

Metallic glasses obtained by rapid quenching from the liquid state are of particular scientific and technological interest because of their many unusual physical properties.¹ Models based (i) on the destabilization of the crystalline mixture² and (ii) on the stabilization of the liquid phase³ by packing effects⁴ or electronic effects⁵ have been proposed for the stability of amorphous metallic alloys. Very recently the study of metallic glasses formed by simple metals only has attracted much attention. The discovery⁶ of the first transition-metal-free amorphous alloy Mg_{0.7}Zn_{0.3} has been followed by the production of

metallic glasses in the systems Mg-Ga and Ca and Sr with Mg, Al, Ga, and Zn.⁷

We present here the first microscopic calculations of the stability of metallic glasses, based on the pseudopotential approach to the interionic forces and model calculations of the amorphous and liquid structures. We show that the glassy and the liquid states are stabilized by the close matching of the minima in the interionic potentials and the maxima in the pair distribution functions (PDF's). At a majority concentration of the smaller atoms, the interionic distances of a topologically close-packed intermetallic com-

pound (a Laves phase in the present case) coincide with the minima in the potential. Possible crystalline compounds with a majority concentration of the larger atoms are usually not of the close-packed type and a cursory inspection of possible structures shows that their interatomic distances are incompatible with the pair potentials. We show that the structures of the amorphous and liquid alloys are determined by the short-range interionic forces. Thus the size ratio is one of the dominant factors in the formation of metallic glasses, quite in the same manner as for the formation of a Laves phase. Deviations of the effective-size ratio from the atomic-radius ratio indicate strong chemical-bonding effects which also contribute to the formation of close-packed compounds, both in ordered and disordered structures.

At large distances, the pair potentials oscillate as $\cos(2k_F r)$ and the PDF's as $\sin(Q_p r)$. Here k_F is the Fermi wave number and Q the wave number of the first maximum in the corresponding partial structure factor. If $Q_p \sim 2k_F$, the wavelengths of the oscillations in the potentials and in the PDF's are approximately the same. This allows one to place not only the nearest, but also the more distant neighbors into the minima of the potential energy (similar arguments have also been used by Beck and Oberle in a qualitative discussion of the stability of Au-Si Glasses⁸). The Nagel-Tauc criterion⁵ $Q_p \approx 2k_F$ is best fulfilled for a valence-electron concentration (VEC) of ~ 1.7 electrons per atom. Our calculations show that, depending on the size ratio, the VEC may vary between 1.7 and 2.5 electrons per atom.

These general arguments are illustrated by detailed calculations on some binary simple-metal systems forming metallic glasses (Mg-Zn, Ca-Mg, Ca-Al). The interionic forces are calculated using an optimized first-principles pseudopotential based on orthogonalized plane waves.^{9,10} We have shown that this method yields a very successful description of the stability and the thermodynamic properties of crystalline¹⁰ and liquid alloys¹¹ and we refer to those papers for a detailed representation of the theory. The interionic forces in an alloy depend on the chemical nature of the components and on their concentration: For the pseudoatom charge densities and the interionic potentials of Ca-Al alloys, this is demonstrated in Fig. 1. We see that, upon alloying, the effective diameter of the Ca-ion shrinks, whereas the Al-ion is slightly expanded. This is a microscopic explanation for an effect which is

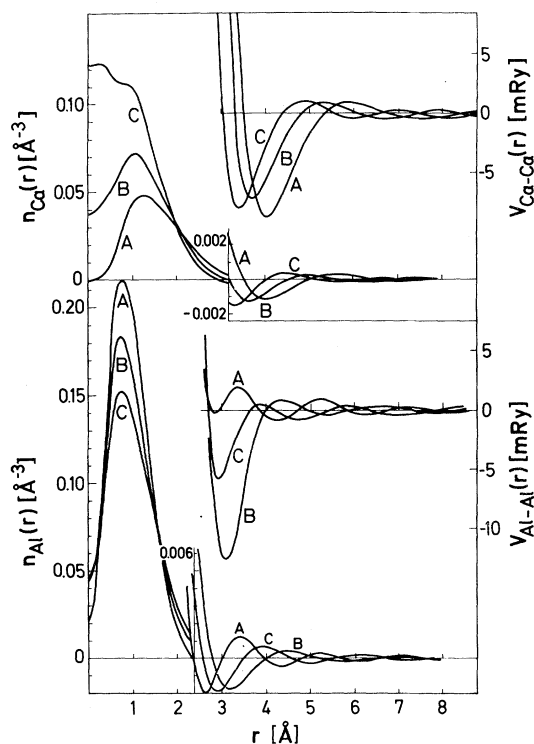


FIG. 1. Pseudoatom charge density $n(r)$ and effective interionic pair potential $V(r)$ for Ca and Al ions in the pure metals (curve A) and in alloys of the composition $\text{Ca}_{0.67}\text{Al}_{0.33}$ (Curve B) and $\text{Ca}_{0.33}\text{Al}_{0.67}$ (curve C), demonstrating the "chemical compression" of the Ca ion in the alloy.

well known in the metallurgical literature as the "chemical compression."¹² The effective-size ratio deduced from the repulsive parts of the interionic potentials of the pure metals is approximately equal to the atomic-radius ratio, $r_{\text{Ca}}/r_{\text{Al}} = 1.38$. In the alloy CaAl_2 it is reduced to $r_{\text{Ca}}/r_{\text{Al}} = 1.22$, the ideal radius ratio for the occurrence of a Laves phase. In fact the interatomic distances of the cubic C15-phase CaAl_2 exactly coincide with the first minima of our pair potentials. Similar alloying effects can be seen in all simple metal systems, though they are certainly much weaker in homovalent alloys such as Mg-Zn and Ca-Mg. In both cases, the occurrence of a hexagonal C14 Laves phase is correctly predicted by our theory.¹³

The structure of the glassy alloys is described by a relaxed model structure of 800 atoms with periodic boundary conditions. An inner section of 800 atoms inside a regular rhombic dodecahedron taken from Finney's dense random packing of hard spheres (DRPHS) model¹⁴ was relaxed using our microscopic interionic potential. De-

tails of the relaxation procedure (which is similar to the one described earlier by one of the authors¹⁵) will be published elsewhere.¹⁶

In Fig. 2 the total and the two partial PDF's are shown for the $Mg_{0.7}Zn_{0.3}$ glass. The PDF's show the splitting of the second peak and the relative heights of the subpeaks as usually observed in metallic glasses. The partial structure factor and the x-ray and neutron-scattering intensities have been calculated and are in reasonable agreement with preliminary results of Rudin and Oberle.¹⁷ More important in the present context is that the peaks of the PDF's correspond to the minima in the interatomic potentials—this means that the structure of the glass corresponds to an energetically very favorable spatial arrangement, just in the same manner as the Laves-phase $MgZn_2$ in the same system is stabilized by the close matching between the interatomic distances and the minima in the pair potentials.

The structure and thermodynamics of liquid metals and alloys are well described by a com-

bination of the pseudopotential theory with a thermodynamic variational method based on the Gibbs-Bogoljubov inequality and a hard-sphere description of binary liquid mixtures.^{11,18} We apply this method to metallic glasses at room temperature ($T = 25^\circ C$). This is equivalent to treating the glass as an undercooled liquid. In Fig. 2 the variationally determined hard-sphere PDF's for the Mg-Zn glass (average packing density¹⁹ $\eta = 0.620$) are compared with the PDF's of the relaxed-model cluster. The position, height, and shape of the oscillations are very well reproduced, and we can investigate the interrelation between the PDF's and the pair potentials in much less than one-hundredth of the computer time necessary for a cluster calculation. We show in Fig. 3 the pair potentials and PDF's of $Ca_{0.67}Mg_{0.33}$, both in the liquid ($T = 900^\circ C$, $\eta = 0.465$) and in the glassy ($T = 25^\circ C$, $\eta = 0.626$) states. Again the potentials and the PDF's are very well "in phase" over the whole range of nonnegligible interionic forces. For the Ca-Mg system this is true for

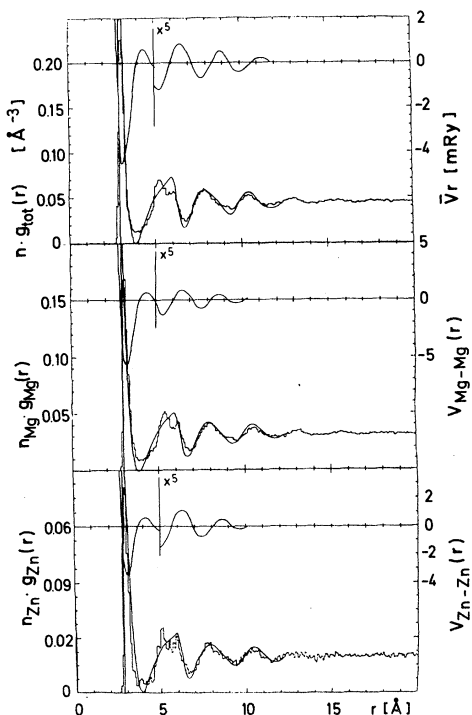


FIG. 2. Total and partial pair-distribution functions $g(r)$ for the $Mg_{0.7}Zn_{0.3}$ glass. The histogram shows the result of the cluster-relaxation calculation, the continuous line the result of the thermodynamic variational technique ($T = 25^\circ C$). The average and the partial interionic pair potentials are also shown (right-hand scale).

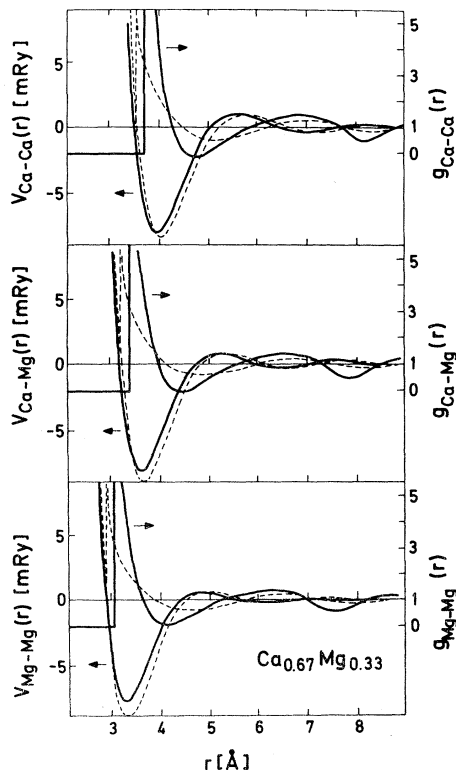


FIG. 3. Interionic pair potentials $V(r)$ and pair distribution functions $g(r)$ for a $Ca_{0.67}Mg_{0.33}$ alloy in the glassy (bold lines, $T = 25^\circ C$) and in the liquid (broken lines, $T = 900^\circ C$) states.

TABLE I. Gibbs free enthalpy ΔG (in kcal/g at.%) of formation for solid ($T=0^\circ\text{K}$) and liquid ($T=900^\circ\text{C}$) Ca-Mg alloys.

	at.% Ca			33
	84	67	50	
Solid solution				
ΔG (theory)	1.1	2.2	2.1	1.5
Laves phase (C14)				
ΔG (theory)				-3.6
(expt. ^a)				-3.2
Liquid solution				
ΔG (theory)	-1.3	-1.6	-2.1	-2.3
(expt. ^a)	-1.4	-2.1	-2.5	-2.5
(expt. ^b)	-1.3	-1.8	-2.2	-2.0

^aHultgren *et al.*, Ref. 20.

^b $T=1010\text{ K}$, Sommer *et al.*, Ref. 21.

all concentrations. For the Ca-Al system, potentials and PDF's are very well "in phase" on the Ca-rich side, but as the Al content is increased, the maxima of the PDF's move out of the minima of the potentials for second and higher neighbors.

We have supplemented this still somewhat qualitative consideration by a full thermodynamic calculation of the Gibbs free enthalpy ΔG of formation (for details of the method, see Ref 11) of solid and liquid solutions and of the Laves phase in the Ca-Mg system (Table I). There is an excellent agreement between theory and experiment. The solid solution is unstable ($\Delta G > 0$), the ΔG of the liquid solution is large and negative, with a minimum at ~ 60 at.% Ca, the ΔG of the Laves phase being still more negative.

We have shown that the destabilization of possible crystalline phases and a stabilization of disordered (liquid or amorphous) phases both cooperate in the formation of metallic glasses. The stabilization is due to a very favorable close packing dominated by the size ratio and the VEC. The theory underlines the similarity of the chemical bonding in metallic glasses and close-packed intermetallic compounds. Preliminary results demonstrate that our theory gives a very good description of the electrical and optical properties of metallic glasses.

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