Articles

Disordered Materials: A Survey of Amorphous Solids

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A brief historical perspective and a review of the current research on amorphous or glassy materials are presented. Glass formation by natural processes and by laboratory synthesis techniques is described. Recent efforts to characterize and model the atomic scale structure of amorphous phases are surveyed. The relation between amorphous and liquid states is emphasized in a discussion of thermodynamics and kinetics. The topic of crystal-to-glass transformation in the solid state and the related issue of crystal stability and melting are discussed.

ACCORDING TO THE LAWS OF THERMODYNAMICS, A PERfect infinite crystal cannot exist in the real world. Disorder in the form of vacancies, interstitial atoms, impurities, dislocations, grain boundaries, surfaces, and other interfaces disrupts the periodicity of an otherwise "perfect" crystal and in many cases determines the physical properties of the crystal. By contrast, highly disordered solids are those solids that are so irregular that the concept of a reference crystal lattice must be abandoned. Such highly disordered materials are often called amorphous materials or glasses (we use the terms amorphous material and glass interchangeably). The word "amorphous" was derived from the Greek term αμορφος, which means "shapeless." Early researchers categorized solids as amorphous or crystalline materials on the basis of macroscopic properties such as their external shapes, fracture mechanisms, and optical properties long before x-ray diffraction techniques and other methods were available to reveal their atomic structures. Only in this century has an understanding of the microscopic nature of amorphous materials become possible. It is now known that long-range atomic order is totally absent in amorphous materials, but that a short-range order over a distance of a few atoms is still present and may be similar to that found in the crystalline counterpart. However, an amorphous structure is distinctly different from a densely packed assembly of microcrystals and is closely related to the structure of a liquid phase. This article reviews some fundamental aspects of amorphous materials such as synthesis, atomic structure, and thermodynamic and kinetic properties. We attempt to outline the current understanding of some of the universal features of these materials.

Synthesis

Early man's use of glasses probably began with a shiny, sharp, rocklike substance that is now called obsidian. Obsidian is a natural glass that is fused within the earth and heaved to the surface by volcanic action. Primitive people who were fortunate enough to live near supplies of this natural glass valued it highly; it could be cut, filed, and shaped for making arrowheads, knife blades, jewelry, ceremonial masks, and other decorative pieces as well as tools. Some man-shaped obsidian is as old as 70,000 years (*1*).

Thousands of years passed before the discovery of a method of making glass. The discovery of glass-making was recorded by the historian Pliny (*1*) in the first century A.D. Around 5000 B.C. a group of Phoenician sailors beached their ship on the shore of a river in Syria. At mealtime they built a fire under a pot of food that rested on blocks of soda from the ship's cargo. As the fire died down, the blocks of soda sank into the sand. From the center of the bed of coals an elastic rivulet of shiny, greenish-hued material slowly flowed. Soon it hardened; man had just fabricated glass for the first time. The earliest examples of man-made glass have been found among the remains of the ancient Middle Eastern civilizations of about 5000 years ago. It was not until 300 B.C. that a Phoenician artisan (name unknown) invented the blowing iron technique (*1, 2*). This revolutionary glass-making technique has been used ever since. The invention of the blowing iron technique demonstrated an awareness of the special viscosity-temperature behavior of glass. The magnitude of the shear viscosity of a material is a measure of its resistance to a change in macroscopic shape and is proportional to the characteristic time scale for microscopic atomic rearrangements. For a glass-forming liquid, the shear viscosity increases drastically as the temperature decreases to the glass transition temperature. If this liquid is cooled sufficiently fast to a temperature far below the glass transition temperature (see below), a configurationally frozen liquid, or an amorphous state, can be obtained because there is not enough time for atomic rearrangements to lead to a crystalline atomic configuration. The formation of several natural glasses, such as obsidian, involves precisely this sudden cooling of molten materials during volcanic activity.

A variety of amorphous materials including silicates have been synthesized over the last 50 years and are the result of a continuous search for new laboratory techniques that increase the effective cooling rate. Kramer was the first to report on the formation of amorphous metallic alloys in the 1930s (*3, 4*). His method was based on vapor deposition, a technique in which atoms were evaporated from a heated liquid source onto a cold substrate. Some time later Brenner *et al.* (*5*) claimed to have made amorphous metallic alloys by electrodepositing nickel-phosphorus alloys. In the 1950s, Buckel and Hilsch (*6*), using an in situ electron diffraction technique, investigated the structure of a series of amorphous metals that were obtained by vapor deposition of metal vapors onto cryogenically cooled substrates. The first unequivocal demonstration that a metallic alloy could be quenched from a molten state to a glassy one was made in 1960 by Duwez *et al.* at Caltech (*7*). They

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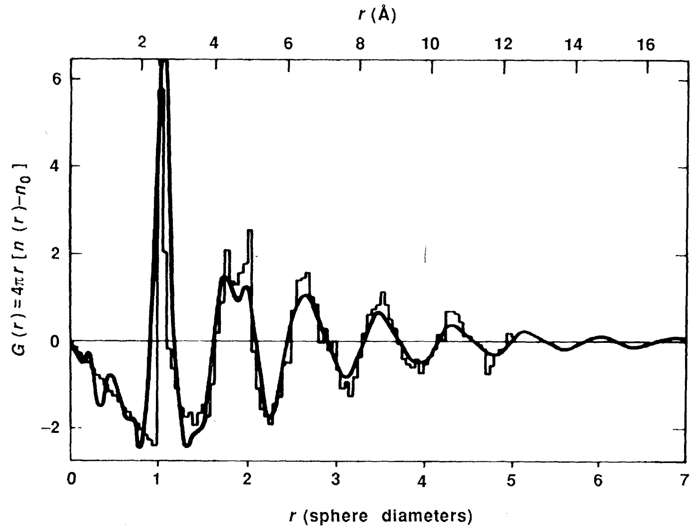

Fig. 1. Comparison of the reduced radial distribution function $G(r)$ for amorphous $Ni_{76}P_{24}$ and the histogram of the reduced radial distribution function for a dense random-close-packing model. [Adapted from (*30*)]

used the method of liquid quenching at cooling rates of 10^6 K/sec or higher. At such high cooling rates, certain metallic alloys can be configurationally frozen to the glassy state, but the technique is still insufficient to produce a pure amorphous metal. In recent experiments, the effective cooling rates induced by pulsed-laser melting of the surface region (~100 Å depth) of materials have been as high as 10^{12} K/sec. It was discovered in the late 1970s that even an amorphous state of elemental silicon could be achieved by such forms of laser-quenching (*8, 9*). It has also been argued that an ultrahigh cooling rate is responsible for amorphous alloy formation during energetic heavy-ion irradiation. In this technique, a dense collisional cascade induced by the incident ion could cause local melting that involves perhaps only a few thousand atoms. An estimated cooling rate of 10^{14} K/sec could be achieved because of the large surface-to-volume ratio of the excited region (*10*).

Quenching from the liquid or vapor state is not the only method by which glass can be made. Electron-beam irradiation, which produces individual atomic displacements in a crystal and does not involve melting, has been observed to induce a crystalline to amorphous transformation (*11, 12*). The point defects created by electron irradiation (vacancies and interstitial atoms) are believed to be responsible for destabilizing the crystalline phase, transforming it directly to a glass. Both heavy- and light-particle irradiation can also cause chemical disorder in a crystalline compound. The chemically disordered crystalline phase that is produced can have a higher free energy than a corresponding amorphous phase; thus amorphization becomes thermodynamically favorable (*10, 13*).

In recent years, irradiation-induced amorphous phase formation has been intensely studied. Its origin, however, dates back to as early as the late 1890s, when Broegger showed that certain originally crystalline minerals had over the course of time assumed the properties of amorphous substances (*14*). Although these minerals retained their original external form, they became lighter in specific gravity, assumed conchoidal fracture, and became optically isotropic. He listed some of these materials, such as gadolinite, euxenite, fergusonite, thorite, zircon, and others, many of which contained thorium or uranium. Broegger called these metamict materials. The term "metamict" was derived from the Greek μεταμιγνυμ, which means "mix otherwise." He further stated that "The reason for the amorphous rearrangement of the molecules might perhaps be sought in the lesser stability which so complicated a crystal molecule as that of these minerals must have in the presence of outside influences" [(*14*); translation in (*15*), p. 138]. The suggestion that the presence of the metamict materials might have been caused by radioactive emanations was first made by Hamberg in 1914 (*16*). X-ray studies on metamict minerals were performed first by Rinne (*17*) for gadolinite in 1915 and by Vegard (*18*) for thorite in 1916. They found that these metamict minerals were either amorphous or at best had very disordered crystalline structures. It is now accepted that the metamict state results from radiation damage to the crystalline structure from bombardment by alpha particles that arise from the decay of the uranium and thorium that are usually contained in these minerals. Reviews of metamict minerals can be found in (*15*) and (*19*).

During the past 2 to 3 years, a number of new methods of forming metallic amorphous alloys from crystalline solids without melting were discovered. In 1983, Yeh *et al.* (*20*) made a rather surprising observation; they found that the dissolution of hydrogen gas in certain crystalline metallic alloys induced amorphization. Schwarz and Johnson (*21*) found that a simple thermal interdiffusion of two elemental polycrystalline metals can result in the formation and growth of an amorphous alloy. The formation and growth of an amorphous metallic alloy by atomic transport in the solid state, or solid-state amorphization, is in fact ubiquitous. Yermakov *et al.* (*22*), Koch *et al.* (*23*), Schwarz *et al.* (*24*), and Politis and Johnson (*25, 26*) reported that amorphous alloys were produced when elemental mixtures of metal powders were mechanically alloyed in a high-energy ball mill. Atzmon *et al.* (*27*) and Schultz and co-workers (*28*) succeeded in producing bulk amorphous alloys by mechanical deformation and alloying of layered binary metal mixtures. Schwarz and Kock (*29*) reported that an initially homogeneous intermetallic compound can transform to the glassy state during ball-milling. These latter experiments involve mechanical driving forces. Again, the material does not actually melt.

Atomic Scale Structure

For crystalline solids, the equilibrium positions of all atoms can be determined from the position of the few atoms in one unit cell. The unit cell is the building block of a crystal. The entire atomic structure follows once the periodic arrangement of unit cells is specified. Since amorphous solids do not have long-range order, a determination of the positions of all the atoms becomes impractical. In fact, the atoms in an amorphous sample of a macroscopic size can in principle assume a huge number of different configurations without any alterations in the physical properties of the bulk sample. As such, the structure of amorphous solids is normally described in terms of statistical distributions. It is not surprising that certain types of short-range atomic order exist in amorphous solids, because physical properties of amorphous materials, such as the density, resemble those of the corresponding crystalline materials. Two types of short-range order exist in amorphous materials. Topological short-range order is characterized by the average number of the nearest neighbors z (or the coordination number) and by the mean separations of these neighbors from the position of a reference atom. For amorphous alloys, the composition of the nearest neighbor shell is not necessarily the same as the average composition; association or dissociation of unlike atoms may occur and give rise to compositional short-range order.

Studies of the short-range order in amorphous materials frequently use x-ray, neutron, or electron diffraction techniques, or a combination of them. Fourier inversion of the diffraction data yields the radial distribution function (RDF) $4\pi r^2 n(r) dr$, where $n(r)$ is the average density of atoms at a distance r from a reference atom. At large r, $n(r)$ approaches the average density n_0 of the solid as a whole. Figure 1 (*30*) shows the reduced radial distribution function $G(r) = 4\pi r[n(r) - n_0]$ for a metallic amorphous nickel-phosphorus alloy; the RDF for amorphous germanium is shown in Fig. 2 (*31*). As will be further discussed below, this type of work was used to establish that the amorphous phase is different from an assembly of microcrystals. The first peak in the RDF is located at the most probable position of nearest neighbor atoms, r_z. The area under this peak determines the value of z. For amorphous metallic solids $z \approx 12$, as compared to $z = 12$ or 8 in the corresponding close-packed or body-centered-cubic crystalline forms of metals. For amorphous semiconducting silicon or germanium $z \approx 4$, as in the crystalline form of these elements. These results demonstrate persistence of metallic or covalent bonding in the amorphous metallic or semiconducting materials, respectively. Amorphous materials can usually be classified as either metallic, covalent, ionic, or polymeric, on the basis of the nature of bonding and short-range order.

The modeling of the structure of amorphous materials has been an active area of research. A typical approach has been to construct atomic-level structural models and to then compare them with available structural information, such as the RDF for real amorphous materials. Models for amorphous materials fall into two general categories: the dense random-close-packing models (DRP) for metallic glasses and the continuous-random-network models (CRN) for covalent or ionic glasses.

Metallic bonding does not usually involve any strongly directional forces. Thus, to a first approximation, the interaction between metallic atoms can be described by pairwise central potentials. A further simplification is to disregard entirely the attractive part of the potential and to consider the short-range repulsive part to be infinitely strong; this is the hard-sphere model. In this model the highest packing density corresponds to the preferred configuration. (Density here is defined as the ratio of the total volume occupied by the spheres to the volume available to them.) The highest packing density that can be achieved empirically occurs with face-centered-cubic packings or hexagonal close-packings, each with a packing density just greater than 0.74. The fact that this packing density has never been rigorously proven to be maximal indicates an incompleteness in our understanding of ordinary, three-dimensional Euclidean space (*32*). On the other hand, this claim is not seriously doubted.

The problem of dense random-packing of spheres has been of concern for several thousand years. Measurement of the amount of grain in a container provides one familiar example. More recently, in studying liquid structure, Bernal and co-workers (*33*) hand-built DRP structures by pouring equal-sized steel balls into football bladders with roughened internal surfaces, and then kneading the bladders. The DRP thus obtained were subsequently analyzed by Finney (*34*). The principal findings included the following: (i) balls in the DRP tend to arrange themselves into regular as well as distorted tetrahedral cluster units, which are further packed into larger units; (ii) the overall DRP density is about 0.64; (iii) atomic clusters with local fivefold symmetry exist. Subsequently, Bennett (*35*) obtained similar results from computer-generated DRP structures. The average coordination number, defined by the average number of nearest neighbors that are either exactly at or only slightly beyond one hard-sphere diameter away, is about 12 to 13, as compared with 12 for close-packed crystalline structures. Cargill analyzed the RDF for many metallic amorphous alloys and compared them with the appropriate DRP model (*30*). The close agreement between the RDFs for amorphous $Ni_{76}P_{24}$ and the one for DRP obtained by Finney is illustrated in Fig. 1. Although an alloy was used instead of a one-component metallic amorphous phase, the metallic radii of nickel and phosphorus are very close, so that a model based on equal spheres is not inappropriate in this case. The splitting of the second peak in Fig. 1 is a ubiquitous feature observed for metallic glasses and it is also a characteristic signature of the DRP structure. Cargill also demonstrated that a microcrystalline model fails to obtain comparable agreement with the experimental RDF (*30*).

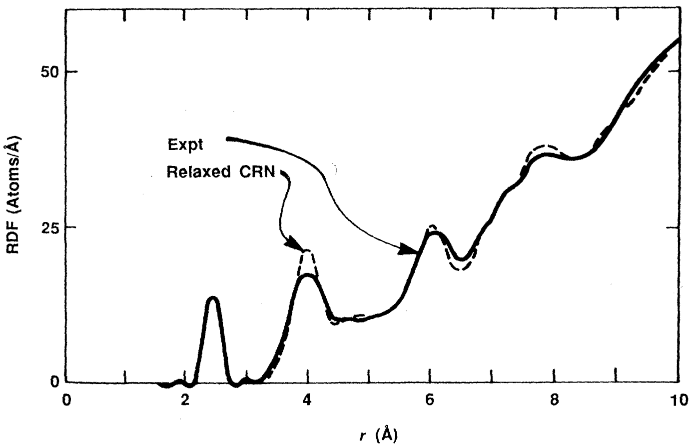

Fig. 2. Comparison of the radial distribution function (RDF) of a refined version of the four-coordinated CRN model with that observed experimentally (Expt) for amorphous germanium. [Adapted from (*31*)]

In covalent solids, both bond angles and bond lengths as well as the number of nearest neighbors are all part of the appropriate bonding scheme. The CRN model for covalent glass originated from Zachariasen (*36*). The term "continuous" means that there are no identifiable boundaries in the structure that separates regions of distinctly different structure or orientation. In such a model the coordination number of each atom is the same as in the corresponding crystalline solid; the bond length is nearly constant. The magnitude of bond angles shows significant spread about some mean value; there are no dangling bonds and no long-range order. Models for amorphous silicon and germanium were first hand-built by Polk (*37*) with ball-and-stick-type representations of atomic-scale structures. The CRN model of amorphous SiO_2 was first built by Bell and Dean (*38*). The RDF for the Polk model agrees to first order with the experimentally determined RDF for germanium. This agreement is further improved for a Polk-type CRN model developed by Steinhardt *et al.* (*31*) (see Fig. 2) that has a relaxed, broadened, and tetrahedrally bonded structure. Such agreement is far better than with any of the microcrystalline-type models for covalent glass. The CRN models are now the basis for the understanding of the structures of most amorphous semiconductors.

A connection between the DRP and CRN structures exists at least in a mathematical sense. Figure 3, taken from a recent review by Venkataraman and Sahoo, demonstrates this point (*39*). Network (A) in Fig. 3 is a two-dimensional statistical network of triangles. Network (B) is obtained by forming the Wigner-Seitz cells and is called the dual of (A). Each Wigner-Seitz cell in (B) is made by passing perpendicularly bisecting planes through each line in (A). A reverse transformation from (B) to (A) can be obtained similarly. The placing of atoms at the vertices of (A) leads to a DRP arrangement as illustrated in (C). Placing atoms at the vertices of (B) leads to a two-dimensional CRN arrangement as illustrated in (D). These ideas have also been extended to three-dimensional space. The study of amorphous structures can therefore benefit from the study of space-filling patterns or tilings of a space.

In two-dimensional Euclidean space, a tiling can be achieved with equilateral and equiangular polygons such as squares and equilateral triangles. These tilings invariably form two-dimensional periodic structures. In three-dimensional Euclidean space, a tiling with equilateral and equiangular polyhedra can, for example, be accomplished by a stacking of cubes. Regular tetrahedra alone, however, cannot fill three-dimensional Euclidean space without introducing "holes" or "defects" (*32*). In three-dimensional Euclidean space at most four spheres can touch one another at a time; their centers form the vertices of a regular tetrahedron. Since the four spheres cannot move closer together, the densest configuration of four spheres is the tetrahedral configuration. This explains why in a DRP structure there are tetrahedral atomic arrangements and also why some of the tetrahedra must be distorted if the structure is to fill space.

Tilings of curved spaces and higher dimensional spaces were originally developed as a branch of pure mathematics (*40*). Recently, these ideas have been introduced to the study of amorphous structures by Kléman and Sadoc (*41*). They postulated that a regular tiling in a curved space provides a good model for amorphous structures if the curved space structure concerned has the same local order as is observed in the actual amorphous structure. They argued that the actual amorphous structure in real space can be obtained by a mapping of the perfect structure in curved space onto Euclidean space. This idea is essentially a prescription for generating and classifying amorphous structures in terms of perfect tiling structures in curved spaces of higher dimensions. A recent review on curved space and amorphous structure can be found in (*39*). Tilings of space can also be related to a variety of natural phenomena, as discussed by Weaire and Rivier (*42*). In particular, a nonperiodic tiling with icosahedral symmetry, similar to one due to Penrose (*43*), has been related to the newly discovered metallic solid phase (14 atomic percent aluminum in manganese) with icosahedral symmetry (*44*). Recently, Nelson has provided an account of this type of quasi-crystalline phases (*45*).

Thermodynamics and Kinetics

From a thermodynamic point of view, amorphous materials are at best metastable. Given sufficient time, they tend to transform to crystalline phases that are thermodynamically more stable. As stated earlier, the amorphous state can be viewed as an extension of the liquid phase to temperatures below the melting point of the competing crystalline solid phase. (For the case of a binary or higher order alloy, one could replace the melting temperature by the liquidus temperature, T_l.) In this temperature regime, called the undercooled regime, the liquid phase will eventually transform by a process of nucleation and growth of crystals. The kinetics that control the rate of crystal nucleation in undercooled liquids have been discussed by Turnbull (*46*) and other investigators (*47, 48*) in terms of classical nucleation theory. The nucleation rate increases precipitously with increasing undercooling down to temperatures well below the melting point. This behavior is ultimately interrupted by a slowing of atomic motion in the liquid and ultimately by a configurational freezing of the atomic arrangement in the liquid as alluded to earlier. The latter freezing phenomenon is referred to as the glass transition. The temperature at which configurational freezing is experimentally observed is found to depend somewhat on the rate at which the liquid is cooled. For ordinary cooling rates achieved, this temperature is nevertheless rather well-defined and is called the glass transition temperature, T_G.

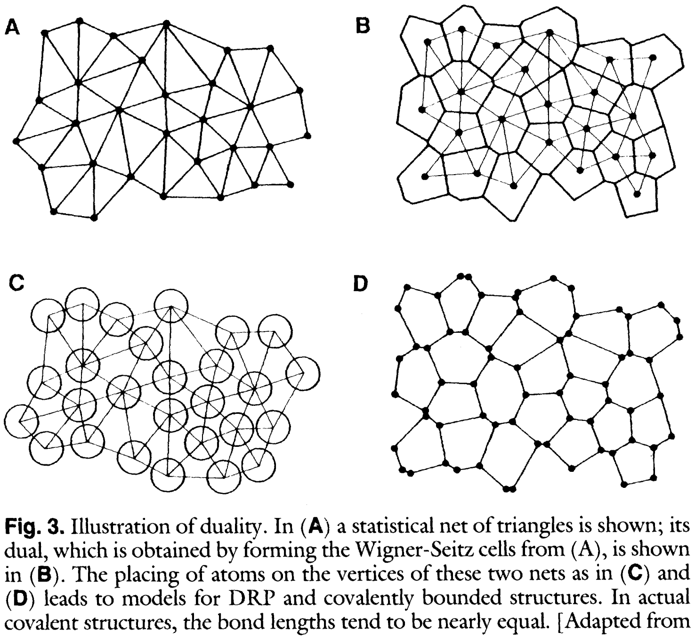

Fig. 3. Illustration of duality. In (**A**) a statistical net of triangles is shown; its dual, which is obtained by forming the Wigner-Seitz cells from (A), is shown in (**B**). The placing of atoms on the vertices of these two nets as in (**C**) and (**D**) leads to models for DRP and covalently bounded structures. In actual covalent structures, the bond lengths tend to be nearly equal. [Adapted from (*39*)]

In the range of temperatures near but above T_G, the atomic mobility of the liquid decreases rapidly with decreasing temperature. Vogel (*49*) and Fulcher (*50*) observed that the viscosity of many liquids in this regime could be described by a phenomenological equation of the form

$$\eta = \exp\left(\frac{b}{T - T_0}\right) \tag{1}$$

where b and T_0 are empirical fitting parameters. T_0 is found to lie near but somewhat below the experimentally observed glass transition temperature.

The earliest attempts to model the glass transition were based on the concept of the free volume in the liquid (*51–54*). It was assumed that a certain fraction of the molar volume of the liquid could be redistributed freely within the liquid structure. This redistribution leads to the transient formation of voids of a size adequate to allow diffusive atomic jumps. With such an approach, it was shown (*53*) that the atomic diffusion constant and viscosity of the liquid should take the forms

$$D = D_0 \exp(-\nu_m/\overline{\nu_f}) \tag{2}$$

and

$$\eta = \eta_0 \exp(\nu_m/\overline{\nu_f}) \tag{3}$$

where $\overline{\nu_f}$ is the average free volume per mole and ν_m is the molar volume. More recently, Grest and Cohen (*55*) proposed a microscopic theory of the glass transition based on the notion of "liquidlike" and "solidlike" atomic cells. They used the results of percolation theory to describe the glass transition as the percolation of "liquidlike" cells as the temperature is increased to T_G. They claimed that the observed glass transition may be a manifestation of an actual thermodynamic phase transition that is empirically obscured by the long time scales that are associated with the sampling of atomic configurations in the vicinity of T_G. Space limitations forbid a detailed discussion of the Grest-Cohen theory. It is fair to say that the glass transition is at best poorly understood and that it remains one of the unsolved problems in the thermodynamics of glasses.

A liquid that can be cooled through the undercooled regime that separates T_l and T_G without the nucleation and growth of detectable amounts of crystalline material is said to be a glass-forming liquid under the given cooling conditions. For a given liquid one defines a critical cooling rate for glass formation, R_c, as the minimum rate necessary to bypass crystallization. Attempts to evaluate the glass-forming ability of liquids have focused on predicting this critical cooling rate. For natural glass-forming systems such as silica, this rate may be so low as to make difficult the practical formation of the crystalline phase. In contrast, a pure liquid metal cannot be quenched to the glassy state even at the cooling rates of 10^{10} to 10^{12} K/sec that are achieved during the transient melting of the metal surface by a picosecond pulsed laser (*56*). Certain metallic alloys form glasses at the more conventional cooling rate of 10^4 to 10^6 K/sec that are achieved by the rapid-quenching techniques first developed by Duwez and co-workers (*57*), which are now used for the commercial production of metallic glasses. Much experimental and theoretical effort has been devoted to determining the factors that control glass formation in liquid metallic alloys (*46, 58, 59*). A few general conclusions can be drawn. First, in binary or ternary alloys that are characterized by relatively low-lying liquidus curves (for example, a deep eutectic point in a binary system), easy glass formation is frequently observed near the compositions corresponding to these features. In such cases, the temperature interval $\Delta T = T_l - T_G$ is small and the temperature range over which nucleation of crystals must be bypassed is reduced (*46*). Second, the ease of nucleation of a crystalline phase often depends on the degree of complexity of the unit cell of the crystal. Glass formation is favored at compositions such that the competing crystal structures contain many atoms at a large number of nonequivalent positions in the unit cell.

Unusual Methods of Synthesis

So far we have discussed the thermodynamic and kinetic aspects that favor glass formation from the liquid state. As mentioned previously, there are a variety of other methods for the synthesis of amorphous materials. These methods include various forms of vapor-quenching, such as thermal evaporation, plasma sputtering, and chemical vapor deposition. We shall not discuss them in detail. Rather, we focus on some recently developed and unusual methods of entering the amorphous phase. In particular, it has been found that crystalline solids can be transformed to the amorphous phase under certain nonequilibrium conditions. Johnson has surveyed the thermodynamic and kinetic aspects of such crystal-to-glass transformations (*60*). Here we cite a few interesting experimental examples and briefly outline some of the principles used to explain how a crystal becomes unstable with respect to an amorphous phase.

To illustrate one set of circumstances, we consider the thermodynamic stability of a crystalline solid solution that consists of atoms of two different sizes, as shown in Fig. 4. When such atoms are forced to lie on a single coherent lattice, local strains develop and the overall packing efficiency may be rather poor. Hume-Rothery noted over 30 years ago that equilibrium solid solutions of two metals tend to be compositionally restricted whenever the atomic radii of the metals differ by more than 15 percent (*61*). More recently, Egami and Waseda (*62*) and Johnson (*60*) noted that crystalline solutions of atoms of two different sizes should actually become mechanically or topologically unstable. This problem is similar to a mechanical stability problem addressed by Thorpe (*63*) in which a lattice of balls and springs is randomly vandalized by the removal of springs. Thorpe showed (*63*) that such a lattice also became mechanically unstable when a critical fraction of springs was removed.

A mixture of two sizes of atoms might be more efficiently and stably packed if the crystal lattice is abandoned in favor of an amorphous arrangement, as illustrated in Fig. 4B. An arrangement such as that in Fig. 4C might be more stable still, but it requires an equiatomic mixture of the two atoms in order to form. This latter arrangement could be characterized as a stoichiometric intermetallic compound. Under certain circumstances, such as the forced mixing of two crystalline metals at low temperature (for example, in the mechanical alloying of two metals at low temperature or the mixing of the two metal layers by ion-induced collisional cascades), one can imagine that unstable solutions (Fig. 4A) are produced that transform to a glass (Fig. 4B). Further transformation to a thermodynamically more stable compound (Fig. 4C) is suppressed at low temperatures either by the inability of the intermetallic compound to nucleate or by the absence of long-range atomic diffusion that in turn prevents regions of suitable composition from forming. The system is trapped in the metastable glassy state by the solid-state process. Further examples and details can be found in (*60*).

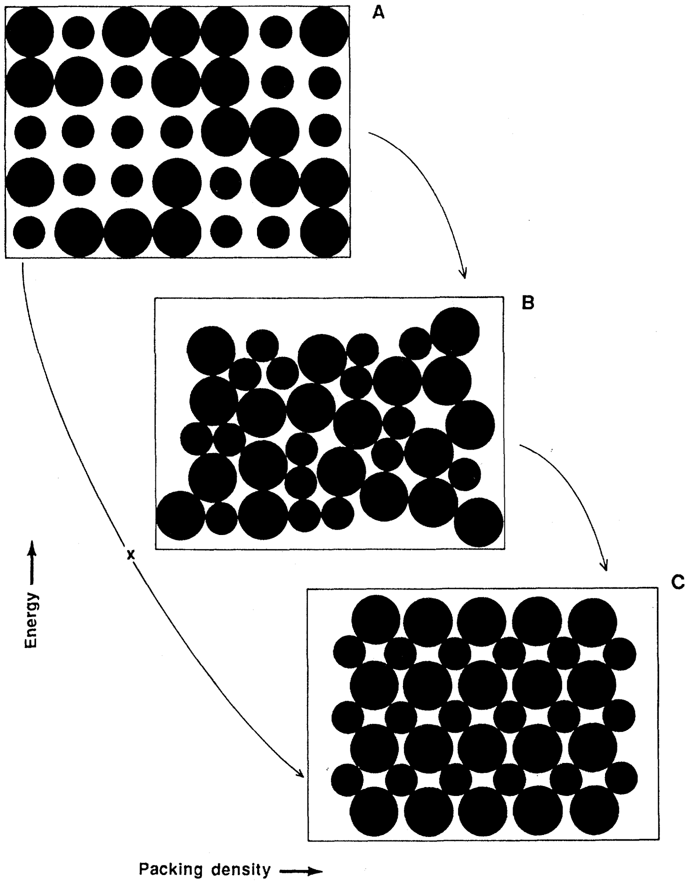

Fig. 4. Illustration of an unstable solid solution (**A**), a metastable amorphous alloy (**B**), and an equilibrium crystalline compound (**C**).

When an unstable crystalline solid transforms to an amorphous phase, this transformation frequently exhibits features that are associated with ordinary melting. For example, the amorphization frequently begins at grain boundaries, surfaces, or other defect sites, as does ordinary melting (*64*). Further, as the transformation proceeds, a sharp interface that separates the amorphous materials from the untransformed crystalline material is always observed. This again is characteristic of melting and other first-order phase transformations. Solid-state amorphization thus provides an interesting case in which to study "melting" and crystal stability under controlled kinetic conditions. It provides new insight into the atomic structure and thermodynamic properties of the glassy phase.

Summary

We have outlined some of the features of glassy materials that have occupied and continue to occupy researchers. This field has contributions from such diverse disciplines as materials science, chemistry, physics, and mathematics. The problem posed by attempts to characterize the structure, thermodynamics, and kinetic aspects of amorphous solids is of a broad nature. Amorphous materials also play a dominant role in a variety of new technologies that ranges from magnetic bubble and optical memory devices to solar cells and corrosion- or wear-resistant coatings. With the combined driving forces of fundamental science and technological advance, amorphous materials will remain as an active research area during the upcoming decades. This will further our understanding of a subject that dates from ancient times.

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