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Noncrystalline Solids

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CHAPTER 19: NONCRYSTALLINE SOLIDS

The terms amorphous solid, noncrystalline solid, disordered solid, glass, or liquid have no precise structural meaning beyond the description that the structure is "not crystalline on any significant scale." The principal structural order present is imposed by the approximately constant separation of nearest-neighbor atoms or molecules. We exclude from the present discussion disordered crystalline alloys (Chapter 22) where different atoms randomly occupy the sites of a regular crystal lattice.

DIFFRACTION PATTERN

The x-ray or neutron diffraction pattern of an amorphous material such as a liquid or a glass consists of one or more broad diffuse rings, when viewed on the plane normal to the incident x-ray beam. The pattern is different from the diffraction pattern of powdered crystalline material which shows a large number of fairly sharp rings as in Fig. 2.17 of Chap. 2. The result tells us that a liquid does not have a unit of structure that repeats itself identically at periodic intervals in three dimensions.

In a simple monatomic liquid the positions of the atoms show only a short range structure referred to an origin on any one atom. We never find the center of another atom closer than a distance equal to the atomic diameter, but at roughly this distance we expect to find about the number of nearest-neighbor atoms that we find in a crystalline form of the material.

Although the x-ray pattern of a typical amorphous material is distinctly different from that of a typical crystalline material, there is no sharp division between them. For crystalline powder samples of smaller and smaller particle size, the powder pattern lines broaden continuously, and for small enough crystalline particles the pattern becomes similar to the amorphous pattern of a liquid or a glass.

From a typical liquid or glass diffraction pattern, containing three or four diffuse rings, the only quantity which can be determined directly is the radial distribution function. This is obtained from a Fourier analysis of the experimental x-ray scattering curve, and gives directly the average number of atoms to be found at any distance from a given atom. The method of Fourier analysis is equally applicable to a liquid, a glass, or a powdered crystalline material.

It is convenient to begin the analysis of the diffraction pattern with Eq. (2.43). Instead of writing it for the structure factor of the basis, we write the sum for all the atoms in the specimen. Further, instead of specializing the scattering to the reciprocal lattice vectors $\mathbf{G}$ characteristic of a crystal, we consider arbitrary scattering vectors $\Delta\mathbf{k} = \mathbf{k}' - \mathbf{k}$, as in Fig. 2.6. We do this because

scattering from amorphous materials is not limited to the reciprocal lattice vectors, which in any event cannot here be defined.

Therefore the scattered amplitude from an amorphous material is described by

$$S(\Delta\mathbf{k}) = \sum_m f_m \exp(-i\Delta\mathbf{k} \cdot \mathbf{r}_m) , \quad (1)$$

with f_m the atomic form factor of the atom, as in Eq. (2.50). The sum runs over all atoms in the specimen.

The scattered intensity at scattering vector $\Delta\mathbf{k}$ is given by

$$I(\Delta\mathbf{k}) = S^*S = \sum_m \sum_n f_m f_n \exp[i\Delta\mathbf{k} \cdot (\mathbf{r}_m - \mathbf{r}_n)] , \quad (2)$$

in units referred to the scattering from a single electron. If α denotes the angle between $\Delta\mathbf{k}$ and $\mathbf{r}_m - \mathbf{r}_n$, then

$$I(K, \alpha) = \sum_m \sum_n f_m f_n \exp(iKr_{mn} \cos \alpha) , \quad (3)$$

where K is the magnitude of $\Delta\mathbf{k}$ and r_{mn} is the magnitude of $\mathbf{r}_m - \mathbf{r}_n$.

In an amorphous specimen the vector $\mathbf{r}_m - \mathbf{r}_n$ may take on all orientations, so we average the phase factor over a sphere:

$$\begin{aligned} \langle \exp(iKr \cos \alpha) \rangle &= \frac{1}{4\pi} 2\pi \int_{-1}^1 d(\cos \alpha) \exp(iKr_{mn} \cos \alpha) \\ &= \frac{\sin Kr_{mn}}{Kr_{mn}} . \end{aligned} \quad (4)$$

Thus we have the Debye result for the scattered intensity at $\Delta\mathbf{k}$:

$$I(K) = \sum_m \sum_n (f_m f_n \sin Kr_{mn})/Kr_{mn} . \quad (5)$$

Monatomic Amorphous Materials

For atoms of only one type, we let $f_m = f_n = f$ and separate out from the summation (5) the terms with $n = m$. For a specimen of N atoms,

$$I(K) = Nf^2 \left[1 + \sum'_m (\sin Kr_{mn})/Kr_{mn} \right] . \quad (6)$$

The sum runs over all atoms m except the origin atom $m = n$.

If $\rho(r)$ is the concentration of atoms at distance r from a reference atom, we can write (6) as

$$I(K) = Nf^2 \left[1 + \int_0^R dr 4\pi r^2 \rho(r) (\sin Kr)/Kr \right] , \quad (7)$$

where R is the (very large) radius of the specimen. Let ρ_0 denote the average concentration; then (7) may be written as

$$I(K) = Nf^2 \left\{ 1 + \int_0^R dr \, 4\pi r^2 [\rho(r) - \rho_0] (\sin Kr)/Kr + (\rho_0/K) \int_0^R dr \, 4\pi r \sin Kr \right\} . \quad (8)$$

The second integral in (8) gives the scattering from a uniform concentration and may be neglected except in the forward region of very small angles; it reduces to a delta function at $K = 0$ as $R \rightarrow \infty$.

Radial Distribution Function

It is convenient to introduce the liquid structure factor defined by

$$S(K) = I/Nf^2 . \quad (9)$$

Note that this is not at all the same as $S(\Delta \mathbf{k})$ in (1). From (8) we have, after dropping the delta function contribution,

$$S(K) = 1 + \int_0^\infty dr \, 4\pi r^2 [\rho(r) - \rho_0] (\sin Kr)/Kr . \quad (10)$$

We define the **radial distribution function** $g(r)$ such that

$$\rho(r) = g(r)\rho_0 . \quad (11)$$

Then (10) becomes

$$\begin{aligned} S(K) &= 1 + 4\pi\rho_0 \int_0^\infty dr [g(r) - 1] r^2 (\sin Kr)/Kr \\ &= 1 + \rho_0 \int d\mathbf{r} [g(r) - 1] \exp(i\mathbf{K} \cdot \mathbf{r}) , \end{aligned} \quad (12)$$

because $(\sin Kr)/Kr$ is the spherically symmetric or s term in the expansion of $\exp(i\mathbf{K} \cdot \mathbf{r})$.

By the Fourier integral theorem in three dimensions,

$$\begin{aligned} g(r) - 1 &= \frac{1}{8\pi^3\rho_0} \int d\mathbf{K} [S(K) - 1] \exp(-i\mathbf{K} \cdot \mathbf{r}) \\ &= \frac{1}{2\pi^2\rho_0 r} \int dK [S(K) - 1] K \sin Kr . \end{aligned} \quad (13)$$

This result allows us to calculate the radial distribution function $g(r)$ (also called the two-atom correlation function) from the measured structure factor $S(K)$.

One of the simplest liquids well suited to x-ray diffraction study is liquid sodium. The plot of the radial distribution $4\pi r^2 \rho(r)$ vs. r is given in Fig. 1, together with the distribution of neighbors in crystalline sodium.

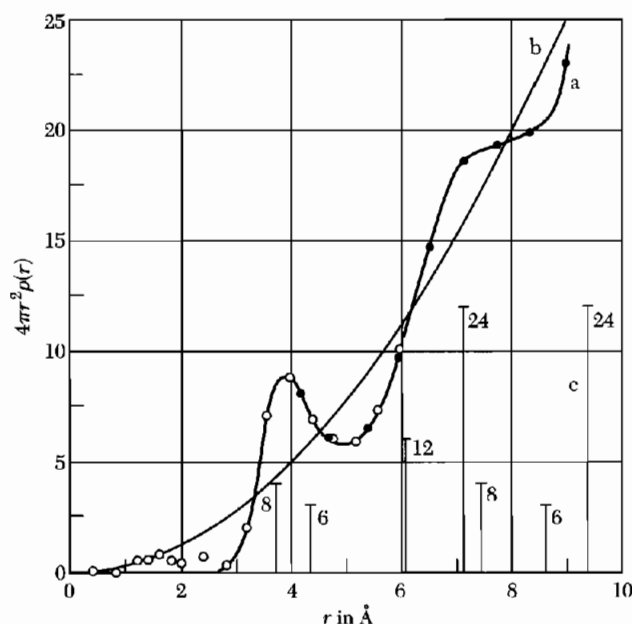


Figure 1 (a) Radial distribution curve $4\pi r^2 \rho(r)$ for liquid sodium. (b) Average density curve $4\pi r^2 \rho_0$. (c) Distribution of neighbors in crystalline sodium. (After Tarasov and Warren.)

Structure of Vitreous Silica, SiO_2

Vitreous silica (fused quartz) is a simple glass. The x-ray scattering curve is given in Fig. 2. The radial distribution curve $4\pi r^2 \rho(r)$ vs. r is given in Fig. 3. Because there are two kinds of atoms, $\rho(r)$ is actually the superposition of two electron concentration curves, one about a silicon atom as origin and one about an oxygen atom as origin.

The first peak is at $1.62 \text{ \AA}$, close to the average Si-O distance found in crystalline silicates. The x-ray workers conclude from the intensity of the first peak that each silicon atom is tetrahedrally surrounded by four oxygen atoms. The relative proportions of Si and O tell us that each O atom is bonded to two Si atoms. From the geometry of a tetrahedron, the O-O distance should be $2.65 \text{ \AA}$, compatible with the distance suggested by the shoulder in Fig. 3.

The x-ray results are consistent with the standard model of an oxide glass, due to Zachariasen. Figure 4 illustrates in two dimensions the irregular structure of a glass and the regularly repeating structure of a crystal of identical chemical composition. The x-ray results are completely explained by picturing glassy silica as a random network in which each silicon is tetrahedrally surrounded by four oxygens, each oxygen bonded to two silicons, the two bonds to an oxygen being roughly diametrically opposite. The orientation of one tetrahedral group with respect to a neighboring group about the connecting

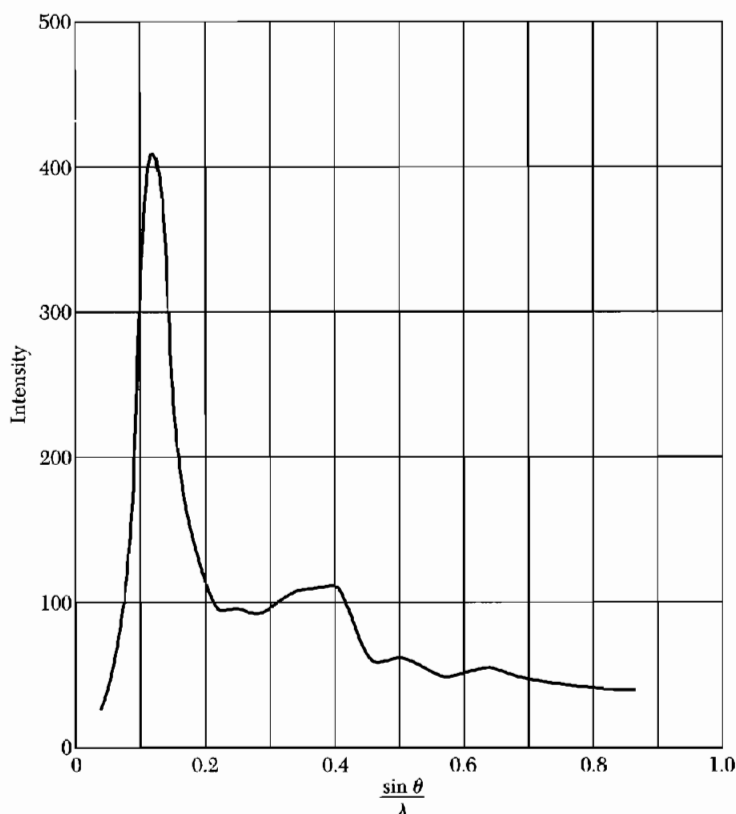


Figure 2 Scattered x-ray intensity vs. scattering angle θ , for vitreous SiO_2 . (After B. E. Warren.)

Si-O-Si bond can be practically random. There is a definite structural scheme involved: each atom has a definite number of nearest neighbors at a definite distance, but no unit of structure repeats itself identically at regular intervals in three dimensions, and hence the material is not crystalline.

It is not possible to explain the x-ray results by assuming that vitreous silica consists of very small crystals of some crystalline form of quartz, such as cristoballite. Small angle x-ray scattering is not observed, but would be expected from discrete particles with breaks and voids between them. The scheme of bonding in glass must be essentially continuous, at least for the major part of the material, although the scheme of coordination about each atom is the same in vitreous silica and in crystalline cristoballite. The low thermal conductivity of glasses at room temperature, as discussed below, also is consistent with the continuous random network model.

A comparison of experimental and calculated x-ray intensity results for amorphous germanium is shown in Fig. 5. The calculations are for a random network model and for a microcrystallite model. The latter model gives a very

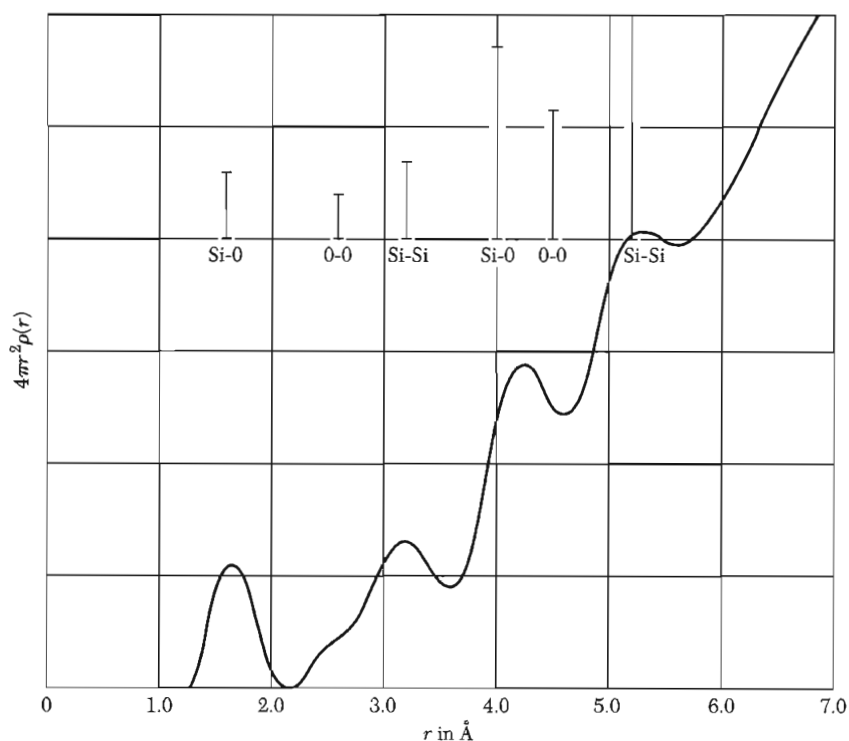


Figure 3 Radial distribution curve for vitreous SiO_2 , as the Fourier transform of Fig. 2. The positions of the peaks give the distances of atoms from a silicon or an oxygen. From the areas under the peaks it is possible to calculate the number of neighbors at that distance. The vertical lines indicate the first few average interatomic distances; the heights of the lines are proportional to the peak areas. (After B. E. Warren.)

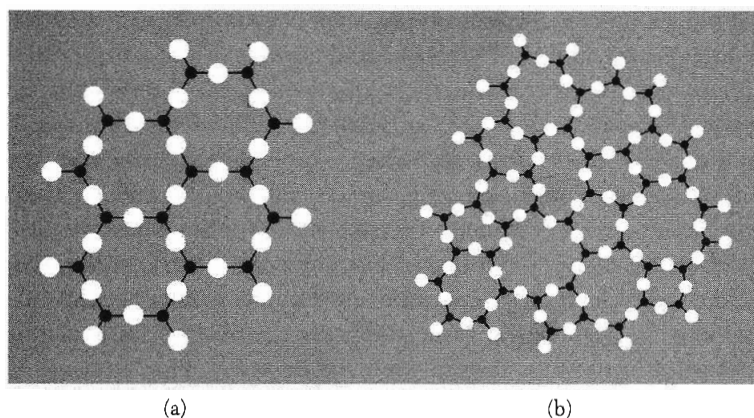


Figure 4 Schematic two-dimensional analogs illustrating the differences between: (a) the regularly repeating structure of a crystal and (b) continuous random network of a glass. (After Zachariasen.)

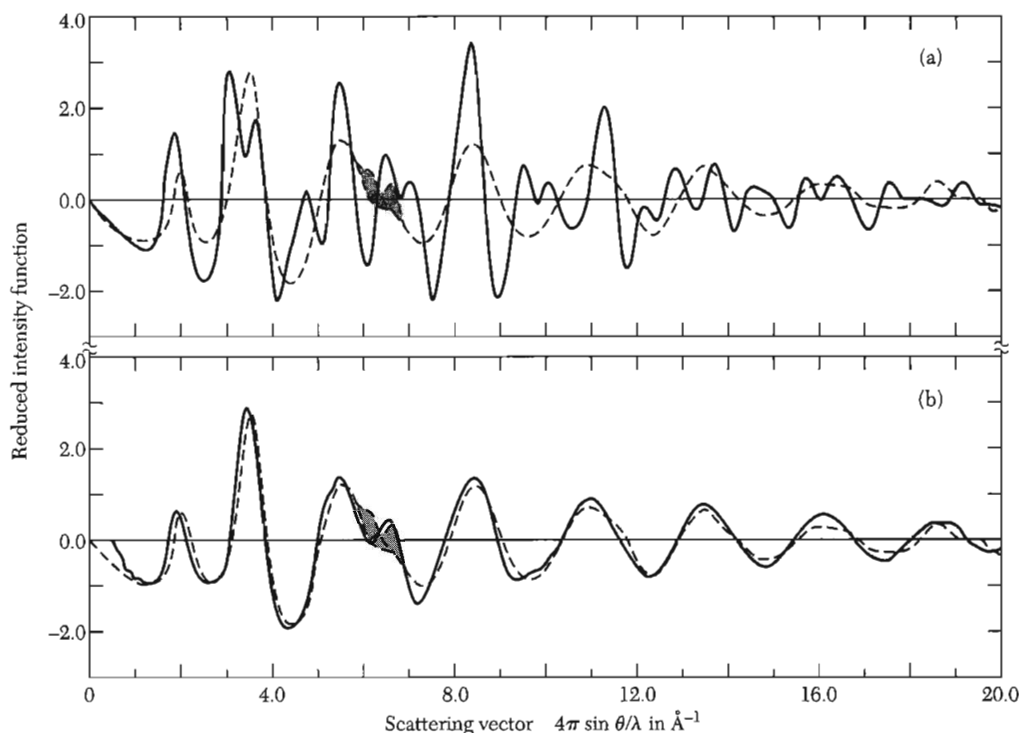


Figure 5 Comparison of experimental (dashed curve) and calculated (solid curve) reduced intensity function for amorphous germanium. (a) Amorphous germanium compared with microcrystallite model. (b) Amorphous germanium compared with random network model. (Results by J. Graczyk and P. Chaudhari.)

poor agreement. The random network model is supported for amorphous silicon by studies of the band gap and spectroscopic work on the $2p$ shell.

GLASSES

A glass has the random structure of the liquid from which it is derived by cooling below the freezing point, without crystallization. Also, a glass has the elastic properties of an isotropic solid.

By general agreement, we say that a liquid on being cooled becomes a glass when the viscosity equals 10^{13} poise, where a poise is the CGS unit of viscosity.¹ This defines the **glass transition temperature** T_g . At temperatures above T_g we have a liquid; below T_g we have a glass. The transition is not a thermodynamic phase transition, only a transition for "practical purposes."

¹The SI unit of viscosity is 1 Nsm^{-2} , so that $1 \text{ poise} = 0.1 \text{ Nsm}^{-2}$. It is quite common to find viscosities given in cp or centipoise, being 10^{-2} poise.

The value 10^{13} poise used to define T_g is arbitrary, but not unreasonable. If we bond a slab of glass 1 cm thick to two plane parallel vertical surfaces, the glass will flow perceptibly in one year under its own weight when the viscosity drops below 10^{13} poise. (For comparison, the viscosity of the mantle of the earth is of the order of 10^{22} poise.)

Relatively few liquids can be cooled fast enough in the bulk to form a glass before crystallization intervenes. Molecules of most substances have high enough mobility in the liquid so that on cooling a liquid-solid melting transition occurs a long time before the viscosity increases to 10^{13} poise or 10^{15} cp. Liquid water has a viscosity 1.8 cp at the freezing point; the viscosity increases enormously on freezing.

We can often make a glass by depositing a jet of atoms of a substrate cooled to a low temperature, a process which will sometimes produce an amorphous layer with glasslike properties. Amorphous ribbons of some metal alloys may be produced in this way in industrial quantities.

Viscosity and the Hopping Rate

The viscosity of a liquid is related to the rate at which molecules undergo thermal rearrangement on a local scale, as by hopping into a vacant neighbor site or by interchange of two neighbor molecules. The physics of the transport process is somewhat different from that of viscosity in the gas phase, but the gas phase result gives a qualitative lower limit to the viscosity of the liquid phase, a limit that applies to nearest-neighbor hopping of atoms.

The gas result (TP 14.34) is

$$\eta = \frac{1}{3} \rho \bar{c} \ell, \quad (14)$$

where η is the viscosity, ρ the density, $\bar{c}$ the mean thermal velocity, and ℓ the mean free path. In the liquid ℓ is of the order of magnitude of the intermolecular separation a . With "typical" values $\rho \approx 2 \text{ g cm}^{-3}$; $\bar{c} \approx 10^5 \text{ cm s}^{-1}$; $a \approx 5 \times 10^{-8} \text{ cm}$, we have

$$\eta(\text{min}) \approx 0.3 \times 10^{-2} \text{ poise} = 0.3 \text{ cp} \quad (15)$$

as an estimate of the lower limit of the viscosity of a liquid. (Tables in chemical handbooks only rarely list values below this.)

We give now a very simple model of the viscosity of a liquid. In order to hop successfully, a molecule must surmount the potential energy barrier presented by its neighbors in the liquid. The preceding estimate of the minimum viscosity applies when this barrier may be neglected. If the barrier is of height E , the molecule will have sufficient thermal energy to pass over the barrier only a fraction

$$f \approx \exp(-E/k_B T) \quad (16)$$

of the time. Here E is an appropriate free energy and is called the activation energy for the process that determines the rate of hopping. It is related to the activation energy for self-diffusion.

The viscosity will be increased as the probability of successful hopping is decreased. Thus

$$\eta \approx \eta(\text{min})/f \approx \eta(\text{min}) \exp(E/k_B T) . \quad (17)$$

If $\eta = 10^{13}$ poise at the glass transition, the order of magnitude of f must be

$$f \approx 0.3 \times 10^{-15} \quad (18)$$

at the transition, using (15). The corresponding activation energy is

$$E/k_B T_g = -\ln f = \ln(3 \times 10^{15}) = 35.6 . \quad (19)$$

If $T_g \approx 2000$ K, then $k_B T_g = 2.7 \times 10^{-13}$ erg and $E = 9.6 \times 10^{-12}$ erg ≈ 6 eV. This is a high potential energy barrier.

Glasses with lower values of T_g will have correspondingly lower values of E . (Activation energies obtained in this way are often labeled as E_{visc} .) Materials that are glass-formers are characterized by activation energies of the order of 1 eV or more; non-glass-formers may have activation energies of the order of 0.01 eV.

When being pressed into molds or drawn into tubes, glass is used in a range of temperatures at which its viscosity is 10^3 to 10^6 poises. The working range for vitreous silica begins over 2000°C , so high that the practical usefulness of the material is severely limited. In common glass, about 25 percent of Na_2O is added as a network modifier to SiO_2 in order to reduce below 1000°C the temperature needed to make the glass fluid enough for the forming operations needed to make electric lamp bulbs, window glass, and bottles.

AMORPHOUS FERROMAGNETS

Amorphous metallic alloys are formed by very rapid quenching (cooling) of a liquid alloy, commonly by directing a molten stream of the alloy onto the surface of a rapidly rotating drum. This process produces a continuous "melt-spun" ribbon of amorphous alloy in industrial quantities.

Ferromagnetic amorphous alloys were developed because amorphous materials have nearly isotropic properties, and isotropic materials should have essentially zero magnetocrystalline anisotropy energy. The absence of directions of hard and easy magnetization should result in low coercivities, low hysteresis losses, and high permeabilities. Because amorphous alloys are also random alloys, their electrical resistivity is high. All these properties have technological value for application as soft magnetic materials. The trade name Metglas is attached to several of these.

The transition metal-metalloid (TM-M) alloys are an important class of magnetic amorphous alloys. The transition metal component is usually about 80 percent of Fe, Co, or Ni, with the metalloid component B, C, Si, P, or Al. The presence of the metalloids lowers the melting point, making it possible to quench the alloy through the glass transition temperature rapidly enough to stabilize the amorphous phase. For example, the composition $\text{Fe}_{80}\text{B}_{20}$ (known as Metglas 2605) has $T_g = 441^\circ\text{C}$, as compared with the melting temperature 1538°C of pure iron.

The Curie temperature of this composition in the amorphous phase is 647 K, and the value of the magnetization M_s at 300 K is 1257, compared with $T_c = 1043$ K and $M_s = 1707$ for pure iron. The coercivity is 0.04 G, and the maximum value of the permeability is 3×10^5 . Coercivities as low as 0.006 G have been reported for another composition.

High coercivity materials can be produced by the same melt-spin process if the spin rate or quench rate is decreased to produce a fine-grained crystalline phase, which may be of metastable composition. If the grain size is arranged to match the optimum size for single domains, the coercivity can be

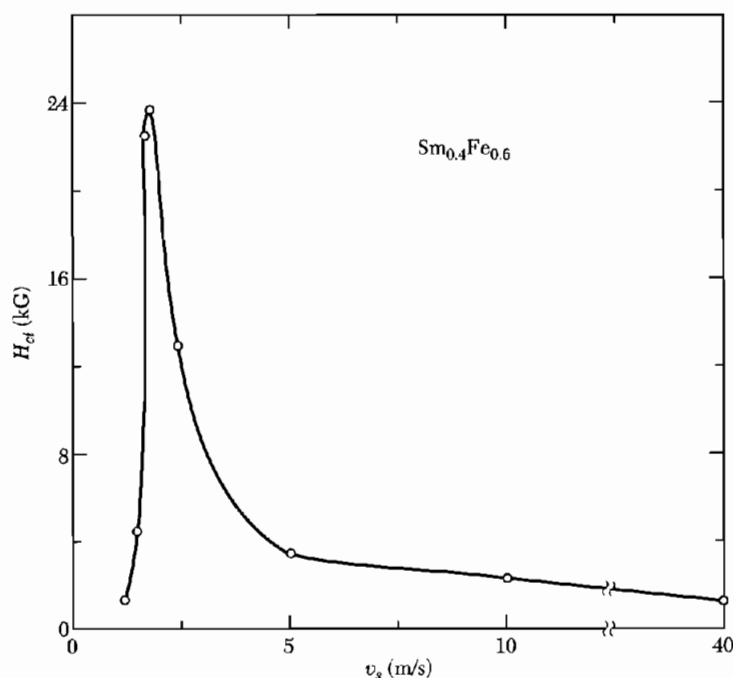


Figure 6 Coercivity at room temperature vs. melt-spin velocity v_s for $\text{Sm}_{0.4}\text{Fe}_{0.6}$. The maximum coercivity is 24 kG and occurs at 1.65 m s^{-1} , which is believed to correspond to single domain behavior in each crystallite. At higher spin rates the coercivity decreases because the deposited material becomes amorphous (more isotropic). At lower spin rates the crystallites anneal to sizes above the single domain regime; domain boundaries give a lower coercivity. (After J. L. Croat.)

quite high (Fig. 6). J. L. Croat has reported $H_{ci} = 7.5$ kG for the metastable alloy $\text{Nd}_{0.4}\text{Fe}_{0.6}$ at the optimum melt-spin velocity 5 m s^{-1} .

AMORPHOUS SEMICONDUCTORS

Amorphous semiconductors can be prepared as thin films by evaporation or sputtering, or in some materials as bulk glasses by supercooling the melt.

What happens to the electron energy band model in a solid without regular crystalline order? The Bloch theorem is not applicable when the structure is not periodic, so that the electron states cannot be described by well-defined $\mathbf{k}$ values. Thus, the momentum selection rule for optical transitions is relaxed; hence all infrared and Raman modes contribute to the absorption spectra. The optical absorption edge is rather featureless. Allowed bands and energy gaps still occur because the form of the density of states vs. energy is determined most strongly by local electron bonding configurations.

Both electrons and holes can carry current in an amorphous semiconductor. The carriers may be scattered strongly by the disordered structure, so that the mean free path may sometimes be of the order of the scale of the disorder. Anderson proposed that the states near band edges may be localized and do not extend through the solid (Fig. 7). Conduction in these states may take place by a thermally-assisted hopping process, for which the Hall effect is anomalous and cannot be used to determine the carrier concentration.

Two distinct classes of amorphous semiconductors are widely studied: tetrahedrally-bonded amorphous solids such as silicon and germanium, and the chalcogenide glasses. The latter are multicomponent solids of which one major constituent is a "chalcogen" element—sulfur, selenium, or tellurium.

The tetrahedrally-bonded materials have properties similar to those of their crystalline forms, provided the dangling-bond defects are compensated with hydrogen. They can be doped with small amounts of chemical impurities, and their conductivity can be sharply modified by injection of free carriers from a metallic contact. By contrast, the chalcogenide glasses are largely insensitive to chemical impurities and to free carrier injection.

Amorphous hydrogenated silicon is a candidate material for solar cells. Amorphous silicon is a much less expensive material than single crystal silicon.

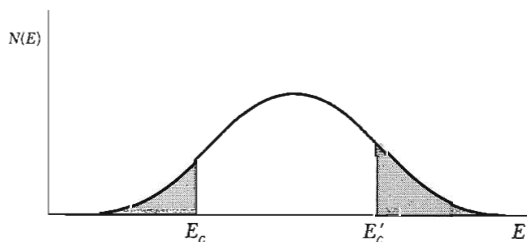


Figure 7 Density of electron states as believed to occur in amorphous solids, when states are non-localized in the center of the band. Localized states are shown shaded. The mobility band edges E_c , E'_c separate the ranges of energy where states are localized and non-localized. (After N. Mott and E. A. Davis.)

Attempts at using pure amorphous silicon, however, failed because of structural defects (dangling bonds) which were impossible to eliminate. Introduction of hydrogen into amorphous silicon appears to remove the undesirable structural defects. Relatively large proportions of hydrogen are incorporated, of the order of 10 percent or more.

LOW ENERGY EXCITATIONS IN AMORPHOUS SOLIDS

The low temperature heat capacity of pure dielectric crystalline solids is known (Chapter 5) to follow the Debye T^3 law, precisely as expected from the excitation of long wavelength phonons. The same behavior was expected in glasses and other amorphous solids. However, many insulating glasses show an unexpected linear term in the heat capacity below 1 K. Indeed, at 25 mK the observed heat capacity of vitreous silica exceeds the Debye phonon contribution by a factor of 1000. Anomalous linear terms of comparable magnitude are found in all, or nearly all, amorphous solids. Their presence is believed to be an intrinsic consequence of the amorphous states of matter, but the details of why this is so remain unclear. There is strong evidence that the anomalous properties arise from two-level systems and not from multi-level oscillator systems; in brief, the evidence is that the systems can be saturated by intense phonon fields, just as a two-level spin system can be saturated by an intense rf magnetic field.

Heat Capacity Calculation

Consider an amorphous solid with a concentration N of two-level systems at low energies; that is, with a level splitting Δ much less than the phonon Debye cutoff $k_B\theta$. The partition function of one system is, with $\tau = k_B T$,

$$Z = \exp(\Delta/2\tau) + \exp(-\Delta/2\tau) = 2 \cosh(\Delta/2\tau) . \quad (20)$$

The thermal average energy is

$$U = -\frac{1}{2}\Delta \tanh(\Delta/2\tau) , \quad (21)$$

and the heat capacity of the single system is

$$C_V = k_B(\partial U/\partial \tau) = k_B(\Delta/2\tau)^2 \operatorname{sech}^2(\Delta/2\tau) . \quad (22)$$

These results are given in detail in *TP*, pp. 62–63.

Now suppose that Δ is distributed with uniform probability in the range $\Delta = 0$ to $\Delta = \Delta_0$. The average value of C_V is

$$\begin{aligned} C_V &= (k_B/4\tau^2) \int_0^{\Delta_0} d\Delta (\Delta^2/\Delta_0) \operatorname{sech}^2(\Delta/2\tau) \\ &= \left(\frac{2k_B\tau}{\Delta_0} \right) \int_0^{\Delta_0/2\tau} dx x^2 \operatorname{sech}^2 x . \end{aligned} \quad (23)$$

The integral cannot be evaluated in closed form.

Two limits are of special interest. For $\tau \ll \Delta_0$, the $\text{sech}^2 x$ term is roughly 1 from $x = 0$ to $x = 1$, and roughly zero for $x > 1$. The value of the integral is roughly $1/3$, whence

$$C_V \approx 2k_B^2 T / 3\Delta_0, \quad (24)$$

for $T < \Delta_0/k_B$.

For $\tau \gg \Delta_0$, the value of the integral is roughly $\frac{1}{3}(\Delta_0/2k_B T)^3$, so that in this limit

$$C_V \approx \Delta_0^2 / 12k_B T^2, \quad (25)$$

which approaches zero as T increases.

Thus the interesting region is at low temperatures, for here by (24) the two-level system contributes to the heat capacity a term linear in the temperature. This term, originally introduced for dilute magnetic impurities in metals, has no connection with the usual conduction electron heat capacity which is also proportional to T .

The empirical result appears to be that all disordered solids have $N \sim 10^{17} \text{ cm}^{-3}$ "new type" low energy excitations uniformly distributed in the energy interval from 0 to 1 K. The anomalous specific heat can now be obtained from (24). For $T = 0.1 \text{ K}$ and $\Delta_0/k_B = 1 \text{ K}$,

$$C_V \approx \frac{2}{3} N k_B (0.1) \approx 1 \text{ erg cm}^{-3} \text{ K}^{-1}. \quad (26)$$

For comparison, the phonon contribution at 0.1 K is, from (5.35),

$$\begin{aligned} C_V &\approx 234 N k_B (T/\theta)^3 \approx (234)(2.3 \times 10^{22})(1.38 \times 10^{-16})(0.1/300)^3 \\ &\approx 2.8 \times 10^{-2} \text{ erg cm}^{-3} \text{ K}^{-1}, \end{aligned} \quad (27)$$

much smaller than (26).

The experimental results (Fig. 8) for vitreous SiO_2 are represented by

$$C_V = c_1 T + c_3 T^3, \quad (28)$$

where $c_1 = 12 \text{ erg g}^{-1} \text{ K}^{-2}$ and $c_3 = 18 \text{ erg g}^{-1} \text{ K}^{-4}$.

Thermal Conductivity

The thermal conductivity of glasses is very low. It is limited at room temperature and above by the scale of the disorder of the structure, for this scale determines the mean free path of the dominant thermal phonons. At low temperatures, below 1 K, the conductivity is carried by long wavelength phonons and is limited by phonon scattering from the mysterious two-level systems or tunneling states discussed earlier for their contribution to the heat capacity of amorphous solids.

As in Chapter 5, the expression for the thermal conductivity K has the form

$$K = \frac{1}{3}cv\ell \quad , \quad (29)$$

where c is the heat capacity per unit volume, v is an average phonon velocity, and ℓ is the phonon mean free path. For vitreous silica at room temperature,

$$\begin{aligned} K &\cong 1.4 \times 10^{-2} \text{ J cm}^{-1} \text{ s}^{-1} \text{ K}^{-1} \text{ ;} \\ c &\cong 1.6 \text{ J cm}^{-3} \text{ K}^{-1} \text{ ;} \\ \langle v \rangle &\cong 4.2 \times 10^5 \text{ cm s}^{-1} \text{ .} \end{aligned}$$

Thus the mean free path $\ell \cong 6 \times 10^{-8} \text{ cm}$; by reference to Fig. 3 we see that this is of the order of magnitude of the disorder of the structure.

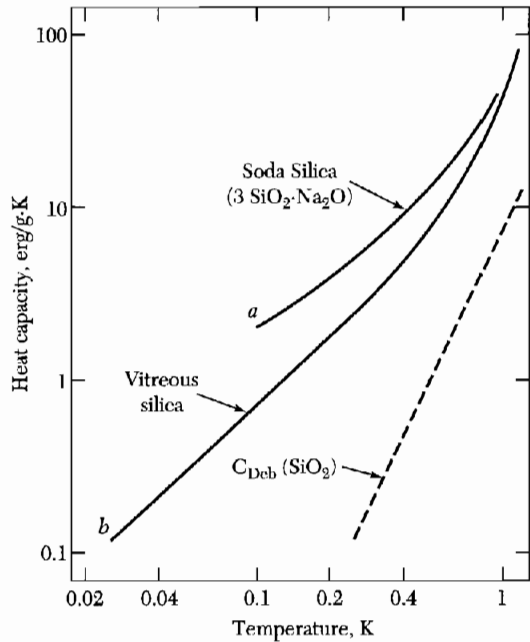


Figure 8 Heat capacity of vitreous silica and soda silica glass as a function of temperature. The heat capacity is roughly linear in T below 1 K. The dashed line represents the calculated Debye heat capacity of vitreous silica.

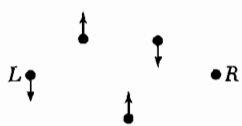


Figure 9 Short phonon mean free path in a disordered structure. A short wavelength phonon that displaces atom L , as shown, will displace atom R by a much smaller distance, because of the phase cancellation of the upper and lower paths from L to R . The displacement of R is $\uparrow + \downarrow \sim 0$, so that the wave incident from L is reflected at R .

This value of the phonon mean free path is remarkably small. At room temperature and above (that is, above the Debye temperature), most of the phonons have half-wavelengths of the order of the interatomic spacing. It is through phase cancellation processes, as in Fig. 9, that the mean free path is limited to several interatomic spacings. No other structure for fused quartz will give a 6 Å mean free path. The normal modes of vibration of the glass structure are utterly unlike plane waves. But the modes, as distorted as they are, still have quantized amplitudes and therefore may be called phonons.

FIBER OPTICS

Fibers of silica-based lightguides carry a high proportion of the data and information transmitted on the surface of the earth and under the seas. The optical fibers consist of a thin core ($\approx 10 \mu\text{m}$) of high-refractive index glass surrounded by a cladding. The digital data are carried by light, with a minimum attenuation near 0.20 dB km^{-1} at wavelengths near $1.55 \mu\text{m}$, which is in the infrared (Fig. 10). A range of 100 km corresponds to a loss of 20 db, power readily supplied by an Eu^{3+} laser amplifier.

The optic window of high-purity glasses near this wavelength is limited on the low frequency side by phonon absorption bands and on the high frequency side by Rayleigh scattering, and, ultimately, by electronic absorption. In the

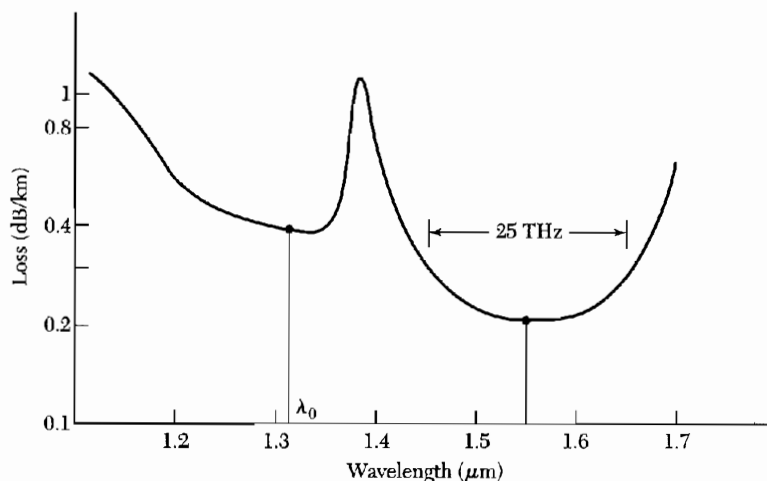


Figure 10 The transmission characteristic of communication-quality optical fibers, showing the attenuation in units of decibels per km as a function of the wavelength of light, in μm . The Rayleigh scattering regime is dominant on the left of the curve, except for a strong impurity absorption line associated with OH ions that accompany SiO_2 ; the line is the second harmonic of a line at $2.7 \mu\text{m}$ known as the "water line." The wavelength marked at $1.31 \mu\text{m}$ is used in 1994 transmission lines; it was replaced by the wavelength $1.55 \mu\text{m}$ available from Eu^{3+} ion amplifiers, which are used every 100 km in typical long distance applications. The power needed to pump the amplifiers is supplied by copper wires. (Courtesy of Tingye Li, AT&T Bell Laboratories.)

optic window the losses are determined by the Rayleigh scattering intrinsic to static fluctuations in the local dielectric constant of an inhomogeneous medium, and the attenuation varies as the fourth power of the frequency.

It is fortunate that an excellent source is available for radiation at $1.55\text{ }\mu\text{m}$. As shown in Fig. 13.24, excited (pumped) erbium Er^{3+} ions can amplify in an erbium-doped section of fiber.

Rayleigh Attenuation

The attenuation of light waves in glass is dominated at wavelengths in the infrared by the same scattering process, called Rayleigh scattering, that is responsible for the blue light of the sky. The extinction coefficient, or attenuation coefficient, h , has the dimension of reciprocal length and for light scattered in a gas is given, after Rayleigh, by

$$h = (2\omega^4/3\pi c^4 N) \langle (n - 1)^2 \rangle, \quad (30)$$

where n is the local refractive index and N is the number of scattering centers per unit volume. The energy flux as a function of distance has the form $\exp(-hx)$.

Derivations of (30) are found in good texts on electrodynamics; the structure of the result may be understood by a general argument: The radiant energy scattered from a dipole element p is proportional to $(dp^2/dt^2)^2$, and this accounts for the factor ω^4 . The local polarizability α enters as α^2 ; if there are N random scattering centers per unit volume, the scattered energy averaged over these random sources will go as $N\langle(\Delta\alpha)^2\rangle$, or $\langle(\Delta n)^2\rangle/N$. Thus we have the essential factors that appear in (30). As applied to a glass, Δn should refer to the variations in polarization around each group of Si—O bonds, and satisfactory numerical estimates of the attenuation may be made in this way.

Problem

1. **Metallic optic fibres?** It has been speculated that metallic wires can act as optic fibres, transmitting light with a long delay appropriate to the high refractive index characteristic of metals. Unfortunately the refractive index of a typical metal is dominated by a free-electron term in $i^{1/2}$, so that the propagation of a light wave is in fact highly damped in a metal. Show that in sodium at room temperature a wave of vacuum wavelength $10\text{ }\mu\text{m}$ will have a damping length of $0.1\text{ }\mu\text{m}$. This may be contrasted with the 100 km damping length found for light in high-quality glass fibres.