
Physics of amorphous materials

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Preface and acknowledgements

This book has been written to be an introduction to the science of amorphous materials, a subject which receives scant mention in conventional solid-state texts. It is aimed at final year undergraduates, beginning graduate students and researchers in solid-state physics or chemistry, materials science or engineering. Some background of (crystalline) solid-state physics is assumed, say between the levels of Kittel's *Introduction to Solid-State Physics* and Ziman's *Principles of the Theory of Solids*, because it was felt that in a book of this length such background materials could not easily be incorporated; however, no knowledge of amorphous materials is assumed.

When I first considered the idea of writing such a book as this, it seemed to me that a general understanding of amorphous materials had been established, and that much of what remained to be done in the field lay in the realms of 'engineering' new materials and filling in the details of the theories proposed to account for their properties. It seemed to me then to be an appropriate time to take stock and write a general introduction to the field of amorphous solids, covering a wide range of their properties, and bridging the gap for the newcomer to the field to such specialized monographs on the subject as the classic work by Mott and Davis, *Electronic Processes in Non-Crystalline Materials*. However, as is usual in these matters, I have found myself overtaken by events. Recent work has thrown into the melting pot many of the 'established' ideas – the example of scaling theories of electron localization and their relation to mobility edges and the so-called minimum metallic conductivity, springs immediately to mind. I felt that such important developments could not be left out, but this immediately led to problems since it is difficult in an introductory textbook to deal with recent controversial ideas. I have tried to resolve this dilemma by mentioning the new concepts, certainly, but putting them into historical perspective, as it were, and pointing out their relation and relevance to previous ideas. In this way, I hope I will have given the reader a flavour of the vitality of this rapidly expanding branch of solid-state science.

I have also tried to make this book into something of a reference work by the inclusion of several tables of useful parameters, such as glass-transition, melting, superconducting and Curie temperatures, electrical and optical gaps for amorphous semiconductors, etc. These are all quantities which practising researchers use on a day-to-day basis, and in this small way, I hope that this book might be of some value to them, since I believe that such collections of data are not readily available together elsewhere. I have also given perhaps more references to the original literature than is usual in a textbook, but have kept the number down by referring, where possible, to reviews although references to original works have been given

where these have been seminal to the development of their aspect of the field. I hope that in this way, the beginning researcher will find his way into the literature. A collection of problems and exercises are given at the end of each chapter which illustrate or extend points raised in the text.

The layout of this book differs somewhat from that conventionally adopted in texts dealing with the crystalline solid state. The first chapter begins with a series of definitions of the terms 'amorphous', 'glassy' etc., followed by a review of various preparative techniques which can be used to produce non-crystalline materials. Such a discussion is necessary because there is no unique structure of an amorphous solid (unlike a single crystal); non-crystalline materials produced in different ways can have very different structures and hence physical properties, even though the composition might be the same. One of the most common and important methods of producing amorphous materials is to freeze a liquid sufficiently rapidly that crystallization is precluded; in this way a 'glass' is formed. Chapter 2 is devoted to a study of the glassy state, considering the kinetic, thermodynamic and other factors which control the glass transition, and discussing those material parameters which can facilitate glass formation.

The structure of amorphous materials is one of the recurrent themes of this book. The determination of the structure of a solid is a difficult task when there is no periodicity; special experimental techniques need to be employed and these form the subject of the first part of Chapter 3. Even when such techniques are used, only a limited amount of local structural information is generally obtainable, and the construction of structural models can be a most useful route to a further understanding of the structure, particularly medium-range order; modelling is also discussed in Chapter 3. Amorphous materials are seldom structurally homogeneous, and different preparative techniques can result in various growth morphologies, e.g. phase separation in melt-quenched glasses or the inclusion of voids in vapour-deposited films; this 'macroscopic' structure, and the experimental techniques which probe it, form the last part of the chapter.

The absence of a periodic lattice in amorphous materials has several effects; an immediate consequence is that there is no reciprocal lattice and so k is no longer a good quantum number for excitations in the solid, such as phonons or electrons. Thus the Bloch formalism cannot be used to simplify the mathematical description of the excitations, and the phonon (or electron) states cannot be described in terms of dispersion curves, $\omega(\mathbf{q})$ (or band structures, $E(\mathbf{k})$); instead the only quantity which is a valid description of excitations in a non-crystalline solid is the 'density of states', and the various methods which have been used to compute it are described in Chapter 4 for the case of phonons, and again in Chapter 5 for electrons.

One seemingly universal feature of amorphous solids is the existence of very low-energy excitations, describable as 'two-level systems', which affect thermal properties in a variety of ways: they can act as internal degrees of freedom, thereby giving rise to an anomalous specific heat, and they can act as scattering centres for phonons, thereby controlling the thermal conductivity and ultrasonic absorption. Two-level systems form the subject of the last part of Chapter 4.

Electronic excitations, manifested as transport or optical properties, are the other dominant theme of this book. It is convenient to divide the discussion, on structural grounds, into two: Chapter 5 deals with the electronic behaviour of 'ideal'

(i.e. defect-free) amorphous semiconductors, and Chapter 6 considers the electronic (and other) properties associated with a variety of structural defects. A consequence of the presence of structural disorder is the possibility that excitations, whether vibrational or electronic, may become spatially localized. Different models for electron localization, such as scaling theories or that giving rise to a minimum metallic conductivity and a mobility edge, are introduced in Chapter 5. Electrical transport in amorphous semiconductors, discussed in terms of these models, and in terms of a rival theory involving localized, self-trapped charge carriers (small polarons), also form part of Chapter 5.

The structural, electronic, magnetic and mechanical properties of amorphous metals form the subject of Chapter 7. It was felt that amorphous metals merited a separate chapter in view of the fact that, while they exhibit certain features in common with other amorphous solids (electron localization effects for example), many of their properties are very different to those shown by amorphous semiconductors and insulators discussed earlier in the book.

Finally, I owe an enormous debt of gratitude to those in the Cavendish Laboratory in Dr A. D. Yoffe's group, principally Professors Davis and Mott, who guided my first forays in this field and whose influence has been incalculable, and more recently to those in Professor J. M. Thomas's group in the Department of Physical Chemistry, from whom I have gained many new insights. I am also extremely grateful to Professor E. A. Davis, Drs P. H. Gaskell, M. R. J. Gibbs, J. Klinowski, E. Marseglia, W. A. Phillips and A. C. Wright and Messrs T. G. Fowler and A. J. Lowe for reading parts of this book, for their valuable comments and for pointing out many errors. I am also especially grateful to Dr P. Extnance for reading the galley proofs. Any mistakes that remain, however, are my sole responsibility. I am also grateful to Mrs M. Pomery, Mrs M. Crosbie and Miss J. Rowe for typing various parts of the manuscript, to Mr E. Smith and his colleagues for preparing the photographs, to Mrs K. I. Johnson for preparing the index and Mrs W. Roberts for running the literature search to generate Fig. 1.1. Last, but not least, I am grateful to Penelope for putting up with a rather unsociable author during the time that it has taken to write this book.

It is well known that in the writing of any text, the person who benefits most from the process is the author himself. I think this to be true in this case, but I hope a little rubs off on others.

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Glossary of symbols

α	optical absorption coefficient
α^{-1}	localization length
α_d	disorder parameter of CTRW theory
α_T	coefficient of thermal expansion
α_ρ	temperature coefficient of resistivity
b	neutron scattering length
C_p	heat capacity (constant pressure)
C_v	heat capacity (constant volume)
γ	temperature coefficient of the electrical gap
$\gamma(r)$	shape factor (SAXS)
γ_g	gyromagnetic ratio
Γ	Urbach edge parameter
D	diffusion constant
\mathbf{D}	force constant matrix
Δ	energy level splitting
ΔE_σ	activation energy of electrical conductivity
E_A	valence band edge
E_B	conduction band edge
E_c	conduction band mobility edge
E_F	Fermi energy (level)
E_g	band gap
E_o	optical band gap (mobility gap)
E_v	valence band mobility edge
ϵ_1	real part of dielectric constant
ϵ_2	imaginary part of dielectric constant
$f(E)$	Fermi-Dirac distribution function
$f(\mathbf{k})$	atomic scattering (form) factor
F	Helmholtz free energy
$F(\mathbf{k})$	reduced scattering intensity
g	Lande g-factor
g_s	Lande g-factor (free spin)

$g(E)$	density of states ($\text{eV}^{-1} \text{ cm}^{-3}$)
G	Green function
$G(r)$	reduced radial distribution function
η	viscosity
η_p	atomic packing fraction
η_q	quantum efficiency
H	magnetic field
H_c	superconducting critical magnetic field
H_{∞}	coercive magnetic field
θ	bond angle
θ_C	Curie temperature
θ_D	Debye temperature
I	nuclear spin
\mathbf{I}	identity tensor
$I(\mathbf{k})$	scattering intensity
$J(r)$	radial distribution function
\mathbf{k}	scattering (or momentum) vector
k_B	Boltzmann constant
K_u	uniaxial magnetic anisotropy constant
κ	thermal conductivity
κ_d	Ginzberg-Landau parameter (dirty limit)
κ_T	isothermal compressibility
ℓ	mean free path
λ	electron-phonon coupling constant
λ_s	magnetostrictive constant
Λ	spin-orbit interaction tensor
m_e	electron mass
\mathbf{M}	dipole moment vector
M_s	saturation magnetization
$M(\mathbf{k})$	modification function
μ	magnetic moment
μ_B	Bohr magneton
μ_d	drift mobility
μ_c	average band conduction mobility
μ_H	Hall mobility
$\mu(E)$	mobility at energy E
$\mu_X(E)$	X-ray absorption coefficient
$n(\omega)$	Bose occupation number
$N(E)$	integrated density of states ($\text{eV}^{-1} \text{ cm}^{-3}$)

Glossary of symbols

ν_{el}	characteristic electronic frequency
ν_0	characteristic phonon frequency
$p(\omega)$	Raman depolarization ratio
$P(\phi)$	dihedral-angle distribution
$P(\omega)$	participation ratio
Π	Peltier coefficient
q	configuration coordinate
\mathbf{Q}	scattering vector
Q_∞	quadrupole coupling constant
R_{H}	coefficient
ρ^0	average density
$\rho(E)$	density of states (eV^{-1})
$\rho(r)$	atomic density function
$\rho(T)$	electrical resistivity
S	thermopower
$S(\mathbf{Q}, \omega)$	dynamic structure factor
σ_E	electrical conductivity at energy E
σ_f	fracture strength
σ_{min}	minimum metallic conductivity
$\sigma(\omega)$	a.c. conductivity
T_c	superconducting transition temperature
T_f	fictive temperature
T_g	glass-transition temperature
T_m	melting temperature
U	Hubbard (correlation) energy
U_{eff}	effective Hubbard energy
W_D	disorder energy
W_H	polaron hopping energy
W_p	polaron energy
$W(T)$	Debye-Waller factor
ϕ	dihedral angle
$\chi(k)$	EXAFS intensity
$\chi'(\omega)$	real part of dielectric susceptibility
$\chi''(\omega)$	imaginary part of dielectric susceptibility
Z	atomic number
ω	radial frequency

Glossary of abbreviations

AC	actinide metal
AE	alkaline earth metal
BCS	Bardeen, Cooper and Schrieffer (theory)
CBH	correlated barrier hopping
CFO	Cohen, Fritzsche and Ovshinsky (model)
CON	chemically ordered network
CRN	continuous random network
CTRW	continuous time random walk
CVD	chemical vapour deposition
DRP	dense random packing
DRPSS	dense random packing of soft spheres
DSC	differential scanning calorimetry
DTA	differential thermal analysis
EDC	energy distribution curve
ESCA	electron spectroscopy for chemical analysis
ESR	electron spin resonance
EXAFS	extended X-ray absorption fine structure
GD	glow discharge (decomposition)
HREM	high-resolution electron microscopy
IR	infra-red
IVAP	intimate valence alternation pair
LA	longitudinal acoustic
LCAO	linear combination of atomic orbitals
LEED	low-energy electron diffraction
LO	longitudinal optic
M	metalloid
MD	molecular dynamics
NMR	nuclear magnetic resonance
NQR	nuclear quadrupole resonance
ODMR	optically detected magnetic resonance
OHC	oxygen hole centre
PL	photoluminescence
PLE	photoluminescence excitation (spectrum)
QMT	quantum-mechanical tunnelling
RCN	random covalent network
RDF	radial distribution function
RE	rare earth metal

Glossary of abbreviations

RPA	random-phase approximation
S	simple metal
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
T	transition metal
TA	transverse acoustic
TCR	temperature coefficient of resistivity
TE	early transition metal
TL	late transition metal
TLS	two-level system
TO	transverse optic
UPS	ultra-violet photoemission spectroscopy
VAP	valence alternation pair
XANES	X-ray absorption near-edge structure
XPS	X-ray photoemission spectroscopy

Contents

<i>Preface and acknowledgements</i>	<i>vii</i>
<i>Glossary of symbols</i>	<i>x</i>
<i>Glossary of abbreviations</i>	<i>xiii</i>
1 Preparation	1
1.1 Introduction	1
1.2 Definitions	3
1.3 Preparation of amorphous materials	6
1.4 Summary	22
2 Glasses	23
2.1 Introduction	23
2.2 The glass transition	24
2.3 Theories for the glass transition	26
2.4 Factors that determine the glass-transition temperature	37
2.5 Glass-forming systems and ease of glass formation	38
Problems	50
Bibliography	51
3 Structure	53
3.1 Introduction	54
I MICROSCOPIC STRUCTURE	55
3.2 Experimental techniques and short-range order	55
3.3 Structural modelling	94
3.4 Medium-range structure	110
II MACROSCOPIC STRUCTURE	118
3.5 Experimental techniques	118
3.6 Examples of macroscopic structure	122
Problems	131
Bibliography	133

64187

4	Vibrations	135
4.1	Introduction	135
4.2	Vibrational excitations	136
4.3	Computational methods	142
4.4	Experimental probes	150
4.5	Low-temperature properties	158
	Problems	169
	Bibliography	172
5	Electrons	173
5.1	Introduction	174
5.2	Electronic density of states	178
5.3	Localization	192
5.4	Transport properties	208
5.5	Small polarons	228
5.6	Optical properties	234
	Problems	245
	Bibliography	245
6	Defects	247
6.1	Introduction	247
6.2	Types of defect	246
6.3	Defect-controlled properties	274
	Problems	310
	Bibliography	310
7	Amorphous metals	311
7.1	Introduction	311
7.2	Structure	316
7.3	Electronic properties	331
7.4	Magnetic properties	350
7.5	Mechanical properties	357
	Problems	359
	Bibliography	360
	<i>Appendix: Suppliers of amorphous materials</i>	<i>361</i>
	<i>References</i>	<i>362</i>
	<i>Index</i>	<i>375</i>

I Preparation

- I.1 Introduction**
 - I.2 Definitions**
 - I.3 Preparation of amorphous materials**
 - I.3.1 Thermal evaporation
 - I.3.2 Sputtering
 - I.3.3 Glow-discharge decomposition
 - I.3.4 Chemical vapour deposition
 - I.3.5 Melt quenching
 - I.3.6 Gel desiccation
 - I.3.7 Electrolytic deposition
 - I.3.8 Chemical reaction
 - I.3.9 Reaction amorphization
 - I.3.10 Irradiation
 - I.3.11 Shock-wave transformation
 - I.3.12 Shear amorphization
 - I.4 Summary**
-

I.1 Introduction

Amorphous materials *per se*, are not new; the iron-rich siliceous glassy materials recovered from the moon by the Apollo missions are some billions of years old, and man has been manufacturing glassy materials (principally from silica) for thousands of years. What is new, however, is the *scientific study* of amorphous materials, and there has been an explosion of interest recently as more new materials are produced in an amorphous form, some of which have considerable technological promise. This can be seen perhaps most strikingly in the number of scientific papers published on the subject each year, and this is shown in Fig. 1.1 for the period 1967 to 1981. This is obviously a fast-moving field, and any textbook on the subject runs the risk of becoming out-dated rather rapidly. Nevertheless, it is felt that sufficient is now known about the amorphous state to warrant a general, introductory text on the subject, particularly in view of the fact that amorphous materials rarely receive more than a passing mention in the conventional solid-state texts which deal almost wholly with *crystalline* materials.

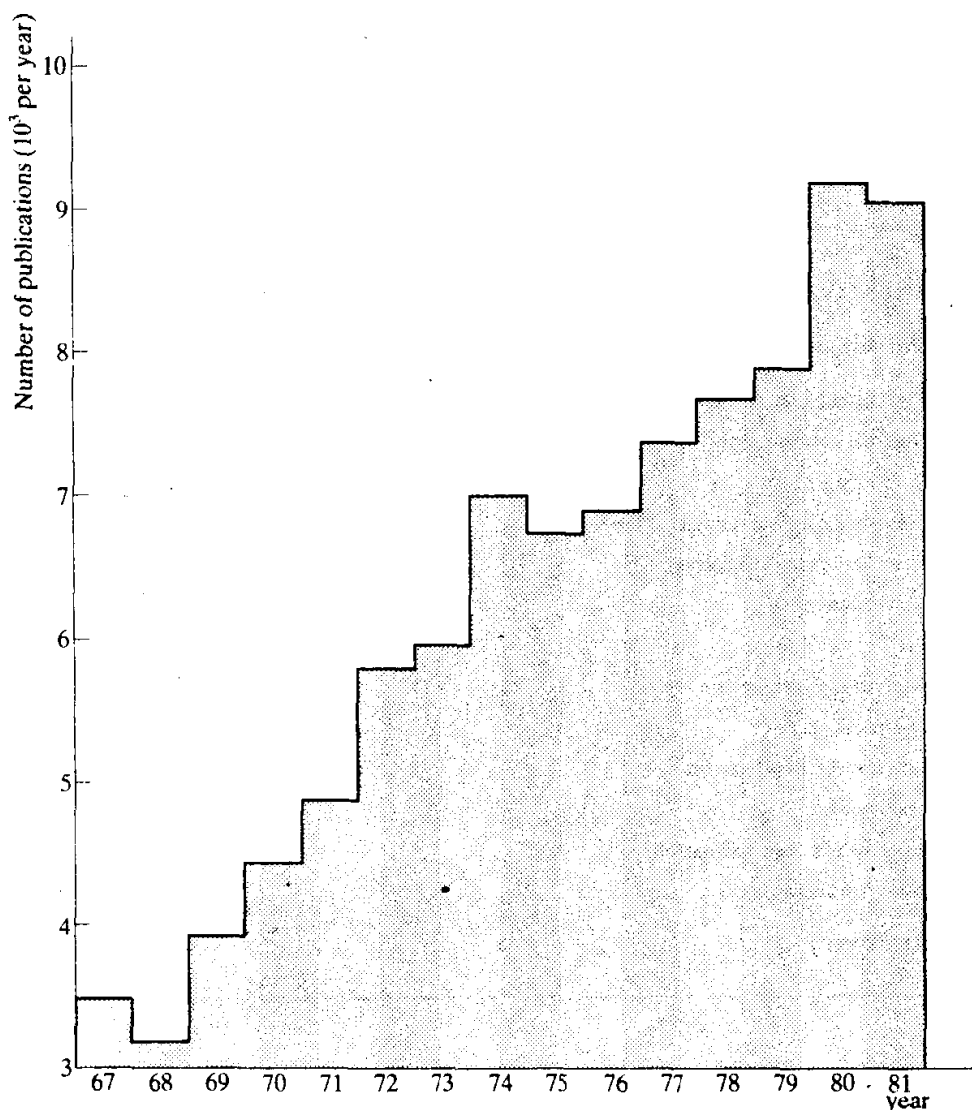


Fig. 1.1 Number of publications on amorphous materials published each year for the period 1967–1981. (Source: *Chemical Abstracts*).

The interest in amorphous materials is perhaps twofold. Firstly, there is the materials science aspect; a wide diversity of materials can be rendered amorphous – indeed almost all materials can. This is in sharp contrast to the knowledge of the average layman, for whom the word ‘glass’ signifies only that transparent material (made from silica with the addition of a few alkali oxides) which is placed in windows.

The second interest in amorphous materials is in the fundamental physics of such systems: Why is window ‘glass’ transparent when the conventional solid-state explanation of band gaps depends crucially on the assumption of periodicity in the underlying lattice and hence on the presence of Bloch electron wavefunctions? Furthermore, amorphous materials exhibit many properties which are unique to them and are not shared by crystalline solids at all.

It is the purpose of this book, then, to guide the reader through the murky

waters of the subject, beginning with a description of various ways of producing amorphous materials, giving a discussion of their structure and properties, and incorporating some technological applications. In this way, it is hoped that interest in, and appreciation of, the fascinating field of the amorphous state will be quickened.

1.2 Definitions

This book is concerned with non-crystalline (or amorphous) materials which possess randomness to some degree. But what kind of randomness, and how much? We will try to answer the first question here and leave the second for discussion in Chapter 3.

Randomness can occur in several forms, of which topological, spin, substitutional, or vibrational disorder are the most important. These types of disorder are illustrated schematically in Fig. 1.2. Disorder is not a unique property, it must be compared to some standard, and that standard is the perfect crystal. This can be defined in the following way:

A perfect crystal is that in which the atoms (or groups of atoms or 'motifs') are arranged in a pattern that repeats periodically in three dimensions to an infinite extent.

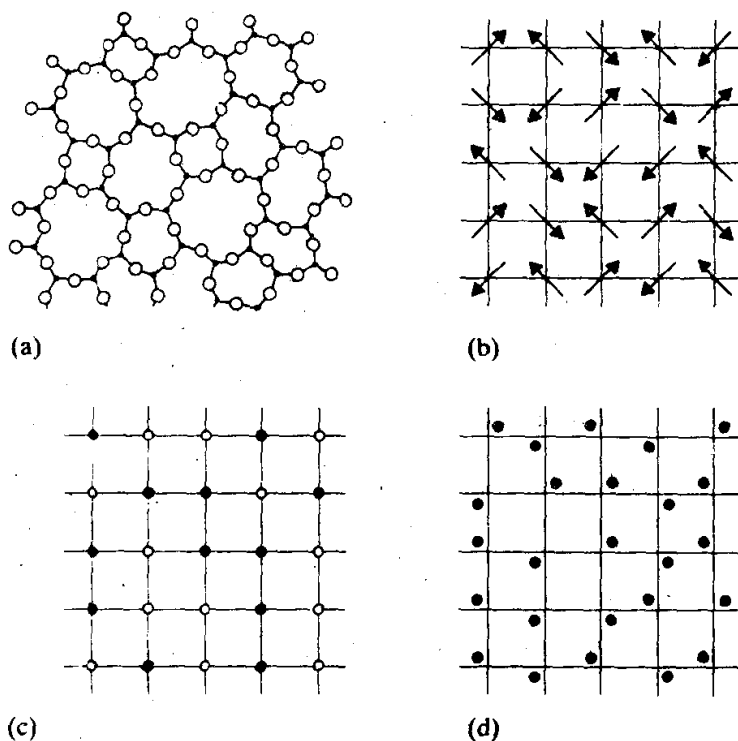


Fig. 1.2 Types of disorder:

- (a) topological disorder (no long-range order);
- (b) spin disorder (on regular lattice);
- (c) substitutional disorder (on regular lattice);
- (d) vibrational disorder (about equilibrium positions of a regular lattice).

With this definition, an imperfect crystal can simply be one which is finite and ends at surfaces (non-infinite extent), or one which possesses a defect, e.g. a vacancy or interstitial foreign atom or a dislocation (non-periodic). However, the forms of disorder with which we are concerned are more drastic than these small perturbations to perfect crystallinity.

Topological (or geometric) disorder is that form of randomness in which there is no translational periodicity whatsoever (Fig. 1.2(a)), and this type of positional disorder forms the theme of this book. Nevertheless, there are 'degrees' of topological disorder: certain amorphous materials have considerable short-range (or local) order while others have little; both have no long-range order however. All amorphous or glassy solids are therefore distinguished by their lack of periodicity.

Another variety of randomness is spin (or magnetic) disorder, in which the underlying perfect crystalline lattice is preserved, but each atomic site possesses a spin or magnetic moment, and this is oriented randomly (Fig. 1.2(b)). This situation occurs in some dilute magnetic alloys such as Cu-Mn or Au-Fe, with from 0.1 to 10 at. % magnetic component. The local moments are frozen into particular, but random, orientations because the 'exchange' interaction between moments in a metal has an oscillatory spatial dependence, and so randomly distributed moments in a *metallic* host suffer a corresponding distribution of exchange interactions, and hence become randomly oriented. These, and those materials which are topologically disordered *and* possess a randomly oriented spin, are termed 'spin glasses', and must not be confused with true glasses which are defined below.

A further kind of randomness is substitutional disorder (Fig. 1.2(c)) in which, although the underlying crystalline lattice is preserved, the material is in fact an alloy (say Cu-Au) with one type of atom randomly substituting for the other in the lattice. These systems are of great importance in metallurgy and other branches of materials science, and for the case of binary alloys are described by the Bragg-Williams theory.

The final category of randomness considered here is vibrational disorder of a crystalline lattice (Fig. 1.2(d)). Of course the concept of a perfect crystal is only valid at the absolute zero of temperature (if zero-point motion is ignored), and at any finite temperature the random motion of atoms about their equilibrium positions destroys the perfect periodicity. It is important to note, however, that vibrational disorder is *not* another form of topological disorder, since although the atoms are vibrating, they do so about their equilibrium *crystalline* positions which of course are not topologically disordered.

There is a considerable amount of confusion in the literature concerning the terms 'amorphous', 'non-crystalline' and 'glassy' and there are as yet no universally accepted definitions. At the outset, therefore, we will define what in this book we mean by these terms. We begin with the word 'amorphous':

Amorphous materials do not possess the long-range order (periodicity) characteristic of a crystal.

The terms amorphous and non-crystalline are synonymous under this definition, and can be used interchangeably. The precise degree of randomness which an amorphous solid possesses is the subject of Chapter 3. The term 'glass' is