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Context and content

Introduction

1.1 Ordered crystalline metals

Our understanding of the electrical conductivity of metals began almost a century ago with the work of Drude and Lorentz, soon after the discovery of the electron. They considered that the free electrons in the metal carried the electric current and treated them as a classical gas, using methods developed in the kinetic theory of gases.

A major difficulty of this treatment was that the heat capacity of these electrons did not appear in the experimental measurements. This difficulty was not cleared up until, in 1926, Pauli applied Fermi–Dirac statistics to the electron gas; this idea, developed by Sommerfeld and his associates, helped to resolve many problems of the classical treatment. The work of Bloch in 1928 showed how a fully quantal treatment of electron propagation in an ordered structure could explain convincingly many features of the temperature dependence of electrical resistance in metals. In particular it showed that a pure, crystalline metal at absolute zero should show negligible resistance.

From these beginnings followed the ideas of the Fermi surface, band gaps, Brillouin zones, umklapp processes and the development of scattering theories: the scattering of electrons by phonons, impurities, defects and so on. By the time of the Second World War, calculations of the resistivity of the alkali metals showed that the theory was moving from qualitative to quantitative success.

In 1950, the recognition that the de Haas–van Alphen effect provided a measure of the extremal cross-section of the Fermi surface normal to the

applied magnetic field made possible a big advance in the experimental study of Fermi surfaces. This was matched by a corresponding development of their theoretical calculation.

The isotope effect in superconductivity was discovered about this time and provided the clue that the electron–phonon interaction was implicated in the phenomenon. In 1957 the BCS theory of superconductivity, giving an explanation of many of its aspects, was published by Bardeen, Cooper and Schrieffer. This was a problem that had for a long time resisted a satisfying theoretical understanding[1].

Experimental improvements made possible the measurement of electron velocities over the Fermi surface and also the electron lifetimes under different scattering mechanisms. By putting together all this information within the theoretical framework that had been developed it was possible, by the 1970s, to explain the electrical conductivity of simple metals in considerable detail. But this was not universally accepted; there was a protracted argument as to whether the ground state of, for example, potassium, involved charge density waves. Most people involved finally concluded that the answer was no.

Transition metals, having the added complication of an incompletely filled d-band, had not received such detailed study either by experiment or theory. Nonetheless, it was felt that the same experimental methods and theory that had been so successful for the simple metals could lead to a comparable understanding of the pure transition metals if the effort were forthcoming. In short, pure crystalline metals were thought to be understood[2].

1.2 Disordered metals

The simplest examples of disordered metals are the liquid alkali metals and though their electrical properties had been measured, the understanding of their conductivity had not made much progress until the Ziman theory of 1961. The problem in a liquid metal is twofold: How do you describe the structure of the ions in the liquid and how do you calculate the scattering of conduction electrons from them? Ziman exploited the use of the structure factor to answer both questions. The diffraction of neutrons and X-rays yields the structure factor of liquid metals; this gives directly the probability of scattering of the incident waves as a function of scattering angle. These diffraction experiments

[1,2] See *Notes*, commencing on p.223.

are so designed that as far as possible only one scattering event takes place within the target material and so these results can also be used to describe the scattering of plane-wave electrons. Moreover, although the structure of liquids cannot be described theoretically in a fully satisfactory way, there are approximate methods that allow one to calculate it so that experimental or theoretical structure factors of the metals provide a fairly direct way of calculating the electrical resistivity.

The Hall coefficient of most simple metals is free-electron-like. Therefore the dynamics of the electrons in the liquid are straightforward and all that is required in addition to the structure factor is the form factor or scattering cross-section of the appropriate ions. This is usually deduced from the pseudopotential of the ion, which in turn can be calculated or found semi-empirically from suitable measurements on the corresponding crystal.

The Ziman theory and its development have been able to account for the magnitude and temperature coefficient of the resistivity of a number of simple metals as well as the thermoelectric power (thermopower, for short) and pressure coefficient of resistivity. It can also explain the systematic differences between the temperature coefficients of resistance of monovalent and polyvalent simple metals. It has, however, been less successful with liquid transition metals.

A different class of disordered metals is provided by alloys. Let us consider for simplicity an alloy of two components, which we can call A and B. A crystalline alloy can be formed either in an ordered structure with appropriate numbers of A and B ions corresponding to its molecular composition (e.g. A_2B_3) or in a disordered but still crystalline structure, in which the two (or more) components are distributed randomly on the lattice sites of the crystal. The latter are sometimes referred to as random solid solutions and it is these that concern us here; the ordered alloys can be treated in much the same way as single component crystals. Calculations on, for example, the silver–palladium series, which form continuous random solid solutions right across the composition range, have indicated that notions such as the Fermi surface and **k**-vector derived from ordered structures can still be useful in such materials, and experiments with angle-resolved photo-emission have tended to support this view. Calculations of electron transport properties by means of theories derived originally for ordered metals have been reasonably successful, at least in broad outline.

1.3 Beyond Boltzmann theory

All these successes of our theoretical understanding, with the exception of the BCS theory of superconductivity, have been achieved within the compass of what is usually referred to as Boltzmann theory. Essentially this means that the mean free path of the conduction electrons is assumed to be long compared to the wavelength of the electrons at the Fermi level. This in turn implies that one scattering event is independent of another and any interference between the scattered wave and the wave before scattering can be ignored. If, however, the mean free path is very short as it is in highly disordered metals or alloys, this interference can become important. This book is largely concerned with the consequences of this new situation.

1.4 Metallic glasses

The discovery of how to make solid amorphous alloys by rapid quenching from the melt led to an explosion of measurements of the electronic properties of these new materials. These alloys are generally referred to as metallic glasses because like window glass they have a structure that resembles that of a liquid when the constituent atoms are frozen in their instantaneous positions. As a consequence of the high disorder the conduction electrons have a very short mean free path and thus their behaviour does not correspond with Boltzmann theory. The measurements on metallic glasses coincided with the extension of the theory to take account of these interference effects and so, at least for bulk materials, metallic glasses became the testing ground for the new theories. In what follows, therefore, I shall try to explain what the theories have to say and consider how far they account for the experimental measurements on metallic glasses.

As we have seen, liquid metals have been much studied as examples of highly disordered metals but because they are liquids they suffer from a number of severe disadvantages as experimental subjects. They do not exist at low temperatures; indeed their range of stability (between freezing point T_F and boiling point T_B) is very limited when expressed as a ratio T_B/T_F. They are subject to convection currents when heated and can be corrosive and difficult to handle and contain.

Metallic glasses, although unstable at higher temperatures because they revert to the crystalline phase, can be studied at low temperatures where many of the most interesting phenomena reveal themselves. As it turns

out many alloys, albeit in restricted ranges of composition, are fairly easy to make in ribbon form, which is very suitable for measurement of their electrical properties such as conductivity, Hall coefficient and thermo-power.

In order to understand the methods of making metallic glasses and the limitations that their stability in terms of composition and temperature range imposes, I outline some of the main features of the production and structure of these glasses in the next chapter. Thereafter the important ideas of the Boltzmann theory of electrical conduction are explained, culminating in Chapter 5 in their application in the Ziman theory to the electrical properties of simple liquid metals.

In Chapter 6 the specifically low-temperature behaviour of metals including the electron–phonon interaction is examined since these features are not involved in the Ziman theory; in Chapter 7 the notion of quasi-particles and interactions between electrons are discussed and in Chapter 8 the properties of transition metals are outlined. Then as a final consideration of Boltzmann theory the Hall effect and magnetoresistance are considered because these properties are very important to our understanding of high-resistivity materials.

Chapters 11 to 14 then concentrate on how recent theories have gone beyond Boltzmann theory in their attempts to explain a wide range of unusual low-temperature behaviour. The theories are here applied specifically to the resistivity and magnetoresistance of metallic glasses. Before finally attempting a quantitative comparison of experiment and theory, Chapter 15 is concerned with the thermopower of metallic glasses, a property that gives valuable information about the behaviour of electrons but is not so directly responsive to the new interference and interaction effects. Chapter 16 provides a comparison between theory and experiment in a selection of metallic glasses; it attempts to show how far the new theories can account naturally and convincingly for electron conduction in highly disordered metallic conductors.

I have made no attempt to deal with strongly magnetic metals, whose electrical properties, even in the crystalline state, are still not fully understood; nor have I discussed the two-level systems found in glasses, since they appear to make no significant contribution to the properties of metallic glasses in the temperature range discussed here.

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Production and structure of metallic glasses

2.1 What are metallic glasses?

The word 'glass' as we normally use it refers to window glass. As we all
know, this is a brittle, transparent material with vanishingly small elec-
trical conductivity. It is in fact a material in which the constituent mole-
cules are arranged in a disordered fashion as in a liquid but not moving
around; that is to say, each molecule keeps its same neighbours and the
glass behaves like a solid. Most of the solids that physicists have hitherto
dealt with are crystalline i.e. their atoms or molecules are arranged in
strictly ordered arrays. This is the essential difference between a so-called
'glass' and a crystal: *a glass has no long-range order*. Although the word
'glass' was originally used to designate only window glass it has now
taken on this generalised meaning of what we may call an amorphous
solid.

   Electrically insulating glasses have been studied for a long time and it
was generally thought that in order to form a glass by cooling a liquid
it was necessary to have a material composed of fairly complicated
molecules so that, on cooling through the temperature range at which
crystallisation would be expected to occur, the molecules would have
difficulty in getting into their proper places and could be, as it were,
frozen in a disordered pattern at lower temperatures without the ther-
mal energy necessary to get into their ordered positions. This general
picture is correct and helpful although the expectations based on it have
proved in some respects wrong. It was thought that because metals and
alloys are usually of simple atoms, it would be impossible to form a
glass from such constituents. It therefore came as a considerable sur-
prise when, in 1959, Pol Duwez and his co-workers at the California
Institute of Technology showed that an alloy of gold and silicon could
be made to form a glass. The secret in part was to increase the rate of

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cooling from the melt to such an extent that even with such simple constituents, their atoms did not have time to take up their ordered positions before diffusive motion became impossible through lack of thermal energy.

Since then many alloys have been made to form glasses although, as we shall see, there are limits to the combinations of metals and to the ranges of concentrations for which glass formation is readily possible. These glassy alloys are typically characterised by metallic properties: they conduct electricity comparatively well, they have a shiny appearance and they are ductile i.e. not brittle. In fact they are, as we shall see, truly metallic and this explains why they are called 'metallic glasses'.

2.2 Properties of glasses in general

Before we discuss the question of how to produce metallic glasses, let us first look at some of the properties of glasses in general. Figure 2.1 shows how the volume (per unit mass, say) of a glass-forming material changes with temperature. Consider first what happen when the material is cooled very slowly and crystallises; we assume for simplicity that we are dealing with a system of a single component since this does not alter the essential points. The volume changes abruptly at the freezing point T_F (in almost all systems it contracts as shown in the figure). Thereafter, as it cools further, the volume slowly diminishes as indicated by the dashed line marked A in Figure 2.1. If however we cool the material in such a way that it forms a glass there is no discontinuity at the freezing point and the volume diminishes smoothly through this region as shown by the line marked B in the figure. In this case, however, the path followed and the ultimate volume reached depend on the cooling rate as indicated by the two lines B and C which correspond to different cooling rates, C being the faster.

At sufficiently low temperatures, it is possible to make changes to the state of the glassy material in a perfectly reversible manner by, for example, changes in pressure or temperature. If however the temperature is too high, spontaneous irreversible changes may occur. This is because there is always a tendency for the glass to move towards the truly stable thermodynamic state which is that of the crystal. For this reason the glassy state is an unstable state although it is often referred to as metastable. The term 'metastable' is however better reserved for the supercooled liquid which is a liquid cooled carefully below its freez-
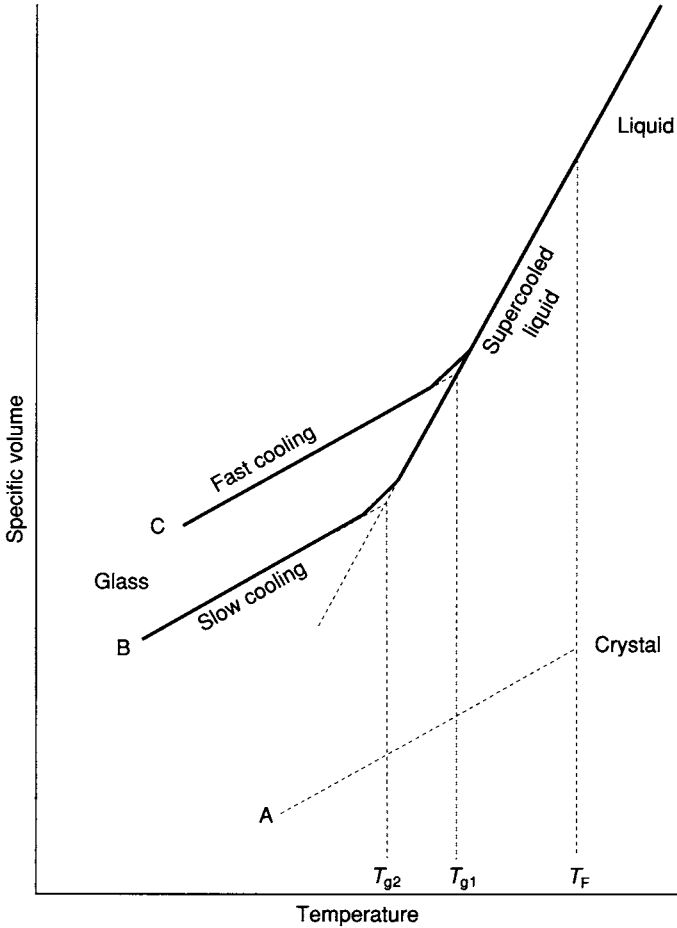
Fig. 2.1 Specific volume of a glass as a function of temperature, showing also the crystal and supercooled liquid. The final volume of the glass depends on the cooling rate.

ing point so as to retain its full liquid properties. Such a liquid can undergo perfectly reversible changes provided that there are no nucleation sites which would trigger crystallisation. When this does occur it is sudden and complete. One may think of the supercooled liquid as separated by a large free energy barrier from the crystalline state. The glassy state, on the other hand, is separated from the crystalline state by a succession of quite small potential barriers each leading to

further unstable states which lead ultimately to that of the crystal. The supercooled liquid is as it were at the bottom of a substantial valley whereas the glass is perched rather precariously on the side of a hill at whose base is the crystalline state.

In Figure 2.1 the supercooled liquid is shown as existing below the freezing point and the line that shows the volume of this liquid is continued to low temperatures even though it might in practice be very difficult or even impossible to achieve this metastable state at such temperatures. This line is, however, a useful extrapolation. The temperature at which the line referring to the glass departs from the equilibrium line of the supercooled liquid is called the glass transition temperature T_g. As we see, different cooling rates yield different transition temperatures and in metallic glasses these can differ by as much as 100 K with the corresponding densities differing by up to 0.5%.

   If the glass is allowed to warm up from low temperatures, it begins to recrystallise at some temperature which depends on how it was cooled and on how quickly is it warmed. It is therefore clear that the properties of glassy materials depend on their past history. Fortunately the electrical properties in which we are interested are reasonably reproducible if the specimens are made with standard techniques and are not allowed to become too warm. In practice this means confining experiments to systems that are stable at temperatures up to at least room temperature. Even so it is sometimes necessary to store the specimens at low temperatures in, for example, liquid nitrogen when they are not being used for experiments. In general, however, if suitable fairly straightforward precautions are taken, the reproducibility of the measurements on these metallic glasses is quite adequate to produce a clear picture of their electrical properties.

2.3 How are metallic glasses produced?

As we know from experience most liquids tend to crystallise on cooling and as we have already seen, a glass will be formed from the liquid only if we can cool it through the region of the freezing point sufficiently fast. The key to producing metallic glasses is thus to be able to cool them rapidly from the melt. As we shall see, there are other techniques that can be used but we shall first consider those based on rapid cooling because they have been most commonly used and with great success.

2.3.1 Melt spinning

In the melt spinning process a jet of molten alloy is squirted onto a rapidly rotating roller which absorbs the heat and so continuously cools the liquid as it strikes the moving surface. A typical apparatus is illustrated in Figure 2.2. This shows the quartz crucible which has a jet at its bottom end. The alloy is melted by a radiofrequency heating coil around the crucible. The roller is usually made of copper because of its good thermal conductivity and when it is spinning at high speed the alloy is driven onto it through the jet by increasing the pressure of gas (helium or argon, say) above the liquid. In this way a ribbon of metallic glass about $50\,\mu m$ thick flies off the roller. For a typical charge of order $10\,g$ some 20 or so metres of ribbon are produced in a tenth of a second. It can be quite spectacular. Even more so if it goes wrong! Cooling rates achieved in this way can be as high as a million degrees a second. The ribbons are necessarily thin; the thickness cannot be increased beyond about $100\,\mu m$ for most alloys as it would be impossible to achieve high
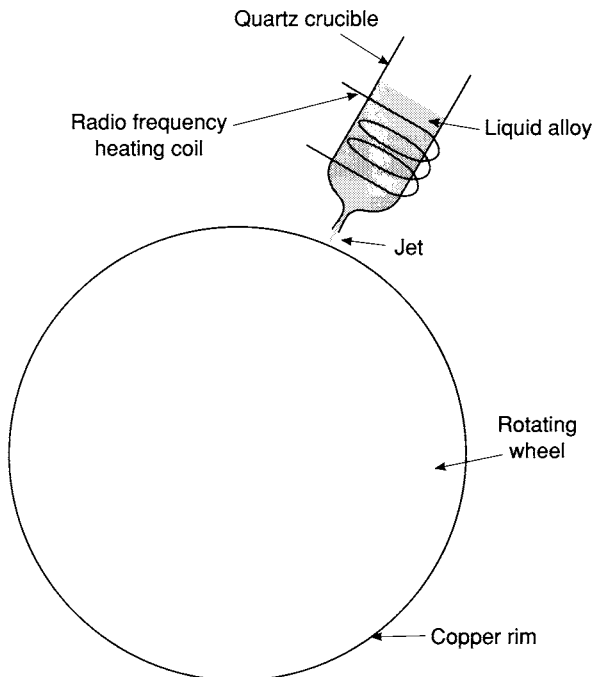

Fig. 2.2 Melt spinning apparatus, showing the copper-rimmed wheel, the molten alloy in the crucible and RF heating coil.