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The electrical
resistivity of metals
and alloys

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Preface

The electrical resistance or resistivity of a conducting solid can be experimentally determined without much difficulty and for many years it has been used as a research tool to investigate various microstructural and physical phenomena. However, unlike conventional diffraction methods which are capable of mapping out scattered intensities in two- or three-dimensional space, an electrical resistivity measurement gives only a single value (at any fixed temperature and structural state) representing an average over all directions of conduction electron scattering. As there is no means of performing the back-transform from this single point, the analysis of resistivity data in terms of microstructure must incorporate calculations of conduction electron scattering based on some model of the structure or microstructure concerned. With the refinement and greater availability of more direct methods, particularly X-ray, neutron or electron diffraction, transmission and analytical electron microscopy (especially atom-probe field ion microscopy which allows an atom-by-atom picture of a material to be established) there has been a declining utilisation of such an indirect method in microstructural investigations. Nevertheless, while a resistivity study may require support from some other technique to allow an unambiguous interpretation of the results, there are many cases where such studies still have particular value, either by virtue of their simplicity or lack of alternative techniques. These include studies of defects, pre-precipitation processes, short and long range ordering or phase separation (particularly with respect to transformation kinetics) and determination of critical transformation compositions and/or temperatures. These studies make use of the sensitivity of the conduction electron scattering process to microstructural details right down to the atomic scale, and the fact that it provides a convenient average over the volume of a specimen.

The electrical properties of metals and alloys are also of great practical importance, especially in applications involving heating, temperature measurement, signal and power transmission, precision resistances, switching devices, semiconducting and thin film devices or simply specification of purity. Development of new methods and materials for such applications will be assisted by a knowledge of the physical processes which determine those properties. On a more fundamental

level there is the basic need to understand the process of scattering of conduction electrons in solids, particularly in inhomogeneous (i.e. real) solids. In this regard, determination of the resistivity also provides a useful test of some of the elegant electronic band structure determinations that have been carried out over the last few years.

There have been many good texts devoted to the basic aspects of electrons in solids and reviews of specific topics such as electrical properties of pure metals, galvanomagnetic properties of pure metals and deviation from Matthiessen's rule. However, to the author's knowledge there has been no other text devoted to the problem of understanding the electrical properties of concentrated and often inhomogeneous solids. It is hoped that this text will help fill the gap.

This book is thus unashamedly devoted to understanding the electrical properties of real metals and alloys. Because of the complexity of the structures concerned, this often means that some aspects of the work lack the elegance of the more profound theoretical works on ideal materials. Nevertheless, it is hoped that the text will be of use to those interested in such properties and indicate where more research effort is required. Rather than devote space to a formal derivation of basic equations concerning electron states in solids (which is available in many other texts), we will assume that these are known and concentrate more on the aspects of electrical conduction, particularly its dependence upon composition and atomic or magnetic structure.

The general problem is introduced in Chapter 1 in terms of simple diffraction concepts, modified slightly to take band structure effects into account. This has the advantage that those readers who have expertise in the allied fields of X-ray, neutron or electron diffraction but who are less confident in matters concerning electron states will nevertheless be readily able to gain a feeling for the problem. However, it would be wrong to pretend that the electrical properties of alloys which may have complicated electronic, atomic and magnetic structures could be understood quantitively on the basis of a simple theory. In such cases a full understanding of the problem requires facility with complicated and often highly specialised techniques. While it is beyond the scope of this book to give a full tutorial in such techniques, the general models and formalisms will be introduced and related to the problems at hand. Thus, while a reader may not be familiar with ensemble averages or Green's functions, it is hoped that he or she will be able to gain an understanding of the direction taken by modern theoretical approaches, of the problems that have been addressed and to what extent a satisfactory solution has been found. It may then be possible to judge whether efforts should be made to become more familiar with the particular techniques

concerned. However, it is necessary to have a good grounding in
quantum mechanics in order to achieve mastery of many of the
advanced techniques and readers are so warned. The first chapter also
introduces the problems associated with anisotropy of scattering over
the Fermi surface and finite conduction electron mean free path, and a
working definition of 'short' and 'long' range effects is given. The
similarity between replacive disorder (i.e. that to do with atom type) and
displacive disorder (i.e. that to do with atomic position) is also briefly
discussed and Matthiessen's rule is introduced. The foundation of the
Boltzmann equation is also considered as are some of the methods of
solution and alternative approaches.

The second chapter is entirely concerned with a discussion of
microstructure and definition of parameters which are required for the
description of atomic positions and correlations in crystalline or
amorphous solids. These concepts are extended to magnetic structures
in Chapter 3 and some of the dynamic aspects of isolated spins and spin
systems are also discussed. Nearly free electron theory and the
pseudopotential approximations are discussed in Chapter 4.

The concepts developed in Chapters 1, 2 and 4 are brought to bear on
the determination of the electrical resistivity in Chapter 5, allowing
formulation of equations relating this to a variety of structures
containing short and long range atomic correlations. The effects of static
and dynamic atomic displacements are also considered. Some of the
methods appropriate to non-simple metals and alloys are introduced in
Chapter 6. The resistivity of the magnetic and nearly magnetic structures
discussed in Chapter 3 is considered in Chapter 7. However, the situation
here is much less satisfactory as it appears that the assumption of
independent electrons made explicit in the earlier chapters is not
adequate to determine the magnetic spin–spin correlations. There is still
much work to be done in deriving a realistic first principles calculation of
the resistivity of such materials. The particular problems associated with
the critical point, high resistivity materials and amorphous metals are
considered in the final chapter.

In order to allow for an uninterrupted development of the theory,
particularly in Chapters 5 and 6, examples and applications of the
concepts and equations derived are generally given in separate sections
following those devoted to the presentation and development of that
theory. Thus, if a reader is interested in a specific problem, he or she
should be able to follow almost from first principles and without too
much interruption the development of the theory relating to that
problem, but will need to turn to the appropriate later section to find the
examples and applications.

The symbols used throughout this book are generally the same as widely employed in the literature. However, as the range of topics covered is quite broad, this often means that the same symbol is used in a different context in relation to different problems. For example, the symbol α is initially used as an atomic correlation parameter but is also used to indicate the ratio of sub-band resistivities in a two-band model of conduction as well as a critical exponent. This problem could be avoided by the invention of a new set of symbols but only at the risk of greater confusion. Where practical a distinction is made with the aid of sub- and superscripts and in all cases the parameters are redefined when they take on a new meaning. Similarly, this work draws on the results of many different fields and, despite efforts to promote the acceptance of SI units, many of these fields have evolved their own 'preferred' units such as Rydbergs or electron-volts for energies associated with electron states and still the micro-ohm cm as the unit of resistivity. Thus, while the formulas derived in this text are correct within the SI system of units, again in order to avoid confusion at the interface between this work and the majority of other published results, the input data and results will generally be given in terms of these preferred units. The conversion factors necessary to obtain SI units are given in Appendix A.

Finally, it is with much pleasure that I acknowledge the valuable discussions that I have had with many colleagues throughout the world and which have been invaluable in moulding the contents of this book. Rather than offend anybody by my forgetfulness which could lead to unintentional omissions from a list of names, I would simply like to thank them all for their interest and helpfulness. With regard to the actual production of this text the situation is much more straightforward as most of the work has fallen on comparatively few shoulders. In this regard I would especially like to thank my wife Kathy for word-processing my scratchy handwriting and for putting up with a rather obsessed author for the past twelve months, Mrs L. Lyons for producing the bulk of the artwork and Mrs J. Thompson for photographic assistance. Much of the work was completed while I was on study leave from the Department of Materials Engineering and I would like to thank that Department and Monash University for the opportunity of taking the leave and the members of the Physics Department at Monash for their hospitality during this period.

<div align="right">P. L. Rossiter
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Contents

1 Basic concepts

1.1 Introduction

Understanding the physical processes that determine the electrical resistivity of a concentrated metallic alloy is a daunting task because of the large number of possible contributions that could be involved. In addition to conduction electron scattering from thermally induced atomic displacements (which may depend upon concentration and degree of atomic and magnetic order) there will be other direct contributions from atomic and magnetic disorder, strain and band structure effects. The magnitude of such effects will be influenced by the homogeneity of the microstructure and will depend specifically upon whether the spatial extent or 'scale' of the inhomogeneity is greater or less than the conduction electron mean free path length.

The purpose of this first chapter is to introduce in a general way the relationship between the electrical resistivity and conduction electron scattering and band structure effects. It will be assumed that the reader is familiar with the fundamental concepts of electron waves in solids which have been very adequately considered in a variety of other texts (Ashcroft & Mermin 1976; Coles & Caplin 1976; Harrison 1970; Kittel 1976; Mott & Jones 1936; Blatt 1968; Ziman 1960, 1969, 1972). Other topics which are not specifically considered in detail in this text but which have been considered elsewhere include the electrical properties of pure metals (Meaden 1966; Wiser 1982; Pawlek & Rogalla 1966; Bass 1984; van Vucht *et al.* 1985), galvanomagnetic effects (Hurd 1974; Jan 1957), deviations from Matthiessen's rule (Bass 1972) and the electrical properties of intermetallic compounds (Gratz & Zuckermann 1982; Gratz 1983; Schreiner *et al.* 1982; Dugdale 1977, p. 279). A compilation of experimental data relating to the electrical resistivity of binary metallic alloys and rare-earth intermetallic compounds has recently been published by Schröder (1983).

1.2 Conduction electron scattering in solids

The electrical resistivity of a solid can be determined by passing a current i through the specimen of cross-section area a and measuring the resultant voltage drop v over a distance l. The electrical resistivity ρ is

then given by

$$\rho = \frac{va}{il}$$

$$= \frac{ra}{l}, \tag{1.1}$$

where r is the resistance of the specimen between the potential contacts. Despite the general acceptance of SI units, the resistivities of metals and alloys are usually given in units of $\mu\Omega$ cm (units are discussed in more detail in Appendix A). Under the influence of an applied field the conduction electrons drift through an ionic array, the resistivity being determined by the rate at which they are scattered from some initial state Φ_k into a final state $\Psi_{k'}$. This may be represented in k-space as shown in Figure 1.1. As evident from the Fermi–Dirac distribution of electron energies (discussed later in relation to equation (1.23)), only electrons within an energy range $\sim k_BT$ about the Fermi surface can increase their energy by some small amount under the influence of the external field. However, since the Fermi energy $E_F \gg k_BT$ over the normal range of temperatures of interest, the vectors $\mathbf{k}$ and $\mathbf{k}'$ must terminate on the sharply defined Fermi surface. Note also that in the case of a spherical Fermi surface the maximum amplitude of the scattering wave vector is equal to $2k_F$. This scattering rate will be determined by the strength of the scattering potential $V(\mathbf{r})$ and, in non-simple metals, the availability of states into which the electrons can be scattered. In terms of Fermi's

Fig. 1.1. Schematic representation of the scattering of a conduction electron from an initial state $\mathbf{k}$ to a final state $\mathbf{k}'$.
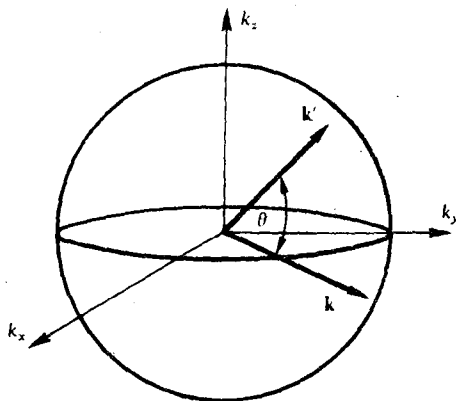
'golden rule' the scattering probability can be written as

$$P_{kk'} = \frac{2\pi}{\hbar} |\langle \Psi_{k'} | V(\mathbf{r}) | \Phi_k \rangle|^2 N(E_F), \tag{1.2}$$

where $\langle \Psi_{k'} | V(\mathbf{r}) | \Phi_k \rangle$ is the scattering amplitude for transitions between an initial state Φ_k and a final state $\Psi_{k'}$ (i.e. the matrix element of the scattering potential $V(\mathbf{r})$ between the states Φ_k and $\Psi_{k'}$) and $N(E_F)$ is the density of states at the Fermi energy E_F into which the electrons can be scattered. This latter term arises because of the necessity to have vacant states ready to accept the scattered electrons. Readers who may be unfamiliar with the notation in equation (1.2) should not despair. Examples will be given in the following chapters which show that many of the quantities required are available in the literature and that, in certain simplified cases, calculations can be performed on a programmable calculator or personal computer.

This scattering rate may be approximately described in terms of a relaxation time τ averaged over the Fermi surface. In the simple case of a spherical Fermi surface (i.e. free conduction electrons) $|\mathbf{k}'| = |\mathbf{k}| = k_F$ and the scattering probability $P_{kk'}$ will depend only upon the angle θ between $\mathbf{k}$ and $\mathbf{k}'$. The relaxation time averaged over the Fermi surface can then be written as (see Chapter 5)

$$\frac{1}{\tau} \propto \int P(\theta)(1 - \cos \theta) \, dS$$

or $\tag{1.3}$

$$\frac{1}{\tau} \propto \int P(\theta)(1 - \cos \theta) \sin \theta \, d\theta,$$

where $P(\theta)$ is now simply the probability of scattering through an angle θ into the element of area dS on the Fermi surface and the integration variables are discussed in Appendix B. The term $(1 - \cos \theta)$ essentially arises because we are only interested in the total change in momentum resolved in the direction of the electric field. For example, it we take the x direction to be in the direction of the applied field, the change in the contribution to the current from an electron will depend only upon the change in the x component of its velocity. Since the wavevector $\mathbf{k}$ of a free electron will be in the same direction as its velocity, the change in the contribution to the current will be proportional to $(k_x - k'_x)/k_x$. (A more rigorous derivation will be given in Section 5.1.) The geometry of the problem in three dimensions is shown in Figure 1.2 and leads to the following relationships:

$$\left. \begin{array}{l} k_x = k_F \cos \alpha \\ k'_x = k_F (\cos \alpha \cos \theta + \sin \alpha \sin \theta \cos \phi) \end{array} \right\}. \tag{1.4}$$

Averaging over ϕ then gives the required result $(k_x - k_x')/k_x = 1 - \cos\theta$. This term also has an important physical implication: it indicates that scattering through large angles is more important in determining the resistivity than small angle scattering. The significance of this fact will be emphasised in later chapters.

The final step in determining the resistivity is given by the Drude formula

$$\rho = \frac{m}{ne^2\tau}, \tag{1.5}$$

where n is the number per unit volume of electrons of mass m and charge e. It should be emphasised that this simple derivation has been given mainly to illustrate the link between the scattering process and the electrical resistivity. The assumptions of free electrons and a uniform scattering rate over a spherical Fermi surface are clearly severe restrictions on its applicability. One might expect them to be reasonable in the case of monovalent metals where the Fermi surface lies entirely within the first Brillouin zone, but generally the distortion of the Fermi surface and its intersection with the Brillouin zone boundaries might be expected to produce deviations from such simple behaviour in most metals or alloys. Nevertheless, in many concentrated alloys of interest (particularly those that do not contain transition metals) it appears that the Fermi surface is still roughly spherical, at least as far as the majority charge carriers are concerned, so that a 'nearly' free electron calculation can proceed. In other cases one clearly must take into account the effects of stronger scattering on the band structure of the alloy. These problems are discussed in more detail in relation to specific alloy systems in the chapters that follow. At this stage let us continue to use this simple model to illustrate some more features of the scattering process.

Fig. 1.2. Scattering geometry in three dimensions: ϕ is the angle between the planes defined by $\mathbf{k}$, $\mathbf{k}'$ and $\mathbf{k}$, x axis and α is the angle between $\mathbf{k}$ and the x axis.
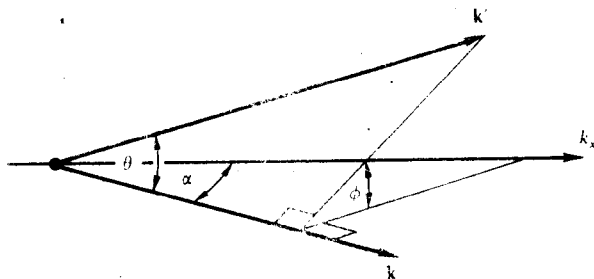
The degree of periodicity of the ionic array determines the amount of electron scattering and hence the electrical resistivity. For example, in a perfectly periodic array (implying an infinite array of identical ions each at rest on a periodic lattice site) the electrons will suffer only Bragg scattering. (We treat here the general case where the electron wavelength is small enough to allow diffraction by the lattice, i.e. the Fermi surface intersects one or more Brillouin zone boundaries. If this is not the case there will be no Bragg scattering to worry about.) While the probability of scattering is then very large at the Bragg wavevectors, the scattering probability averaged over the Fermi surface is zero. This is because the Bragg scattering is very sharp and localised to a vanishingly small fraction of the Fermi surface, the width of the Bragg peaks being inversely proportional to the number of ions in the array, N. This behaviour is illustrated in Figure 1.3 which shows schematically the

Fig. 1.3. Bragg scattering: (*a*) in an ideal diffraction experiment and (*b*) superimposed on the Fermi surface. The Brillouin zone boundary is shown as a dashed line.