Conduction in Non-Crystalline Materials

SIR NEVILL MOTT

OXFORD SCIENCE PUBLICATIONS

Conduction in Non-Crystalline Materials

SIR NEVILL MOTT

Emeritus Professor of Physics,
Cavendish Laboratory, University of Cambridge

CLARENDON PRESS · OXFORD
1987

Oxford University Press, Walton Street, Oxford OX2 6DP
Oxford New York Toronto
Delhi Bombay Calcutta Madras Karachi
Petaling Jaya Singapore Hong Kong Tokyo
Nairobi Dar es Salaam Cape Town
Melbourne Auckland
and associated companies in
Beirut Berlin Ibadan Nicosia

Oxford is a trade mark of Oxford University Press

Published in the United States
by Oxford University Press, New York

© Sir Nevill Mott, 1987

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior permission of Oxford University Press

British Library Cataloguing in Publication Data

Mott, N. F.
Conduction in non-crystalline materials.
1. Amorphous semiconductors
I. Title
537.6'22 QC611.8.A5
ISBN 0-19-851981-8

Library of Congress Cataloging-in-Publication Data
Mott, N. F. (Nevill Francis), Sir, 1905—
Conduction in non-crystalline materials.
Bibliography: p.
Includes index.
1. Energy-band theory of solids. 2. Free electron theory of metals. 3. Amorphous substances—Electric properties. I. Title.
QC176.8.E4M66 1986 530.4'1 86-12813
ISBN-0-19-851981-8

Typeset and Printed in Northern Ireland by
The Universities Press (Belfast) Ltd.

Preface

There are now available several books about non-crystalline solids. E. A. Davis and I published *Electronic processes in non-crystalline materials* in 1971, with a second edition in 1979. S. R. Elliott's *Physics of amorphous materials* appeared in 1984 and Richard Zallen's *Physics of amorphous solids* in 1983. There are also books in the Springer series in which several authors share, for instance *Fundamental physics of amorphous semiconductors* (ed. F. Yonezawa, 1980), and *The physics of amorphous silicon* (ed. J. O. Joanopoulos and G. Lucovsky, 1984). On the related problem of highly doped semiconductors there is the excellent book of Shklovskii and Efros (1984).

My aims in adding yet another book mainly on the theory are the following. The first is to provide a reasonably small book which I hope can serve as an introduction both for students of experiment and of theory. The next is to bring my earlier book with Davis up to date; so much has happened since 1979 that much of the theory presented there is in need of revision. And finally, I hope to show more fully that in my earlier books that non-crystalline semiconductors are by no means the only materials to which the concepts described here can be applied; vitreous silicon dioxide, amorphous metals, and impurity bands in doped semiconductors will play an equal role.

I have called this book *Conduction in non-crystalline materials* because it is here that the theory differs most from that for crystals. But conduction includes photoconduction, effects of a magnetic field, and so on, and so optical and magnetic effects can by no means be excluded.

Finally I would like to thank several colleagues who have looked through all or parts of the manuscript, particularly E. A. Davis, M. Kaveh, and M. Pepper.

Cambridge N.M.
April 1986

Contents

此为试读，需要完整PDF请访问：www.ertongbook.com

1 Introduction

1.1. Conduction in crystalline systems

Before the appearance of quantum mechanics we had little understanding of why some solids, such as the metals, were good conductors of electricity and others were not. The Hall effect gave a measure of the number of free electrons in a metal, the Hall constant R_H being, according to theories then available, equal to $1/nec$, n being the number of electrons per unit volume, e the electronic charge, and c the speed of light. From the experimental values of this quantity it appeared that the number of free electrons in a metal was of the same order as the number of atoms. In insulators, on the other hand, all electrons seemed to be stuck; none were free to move. This could not be explained, nor could many other properties of solids. A major success of electron theory was, however, the explanation of the Wiedermann–Franz ratio of the electrical (σ) to the thermal (K) conductivity of metals (Lorentz 1905); theory gave

$$K/\sigma = 2(k_B/e)^2T$$

where k_B is the Boltzmann constant and T the absolute temperature. This is in fair agreement with experiment. But outstanding problems were, why the mean free path, particularly at low temperatures, is so large in comparison with the interatomic distance, and why the free electrons do not contribute a large term ($\frac{3}{2}nk_B$) to the specific heat, in addition to that ($3Nk_B$) from the thermal vibrations. Here n is the number of electrons per unit volume and N the number of atoms.

Pauli in 1926 first applied the Fermi–Dirac statistics to account for the analogous problem of the paramagnetism (why the free electrons do not contribute a large paramagnetism equal to $n\mu^2/k_BT$, μ being the magnetic moment of the electron). Arnold Sommerfeld, who for decades had presided over the outstanding school at Munich, saw Pauli's paper in proof (Hoddeson and Baym 1980) and extended it to the problem of the specific heat. If Fermi–Dirac rather than classical Boltzmann statistics describe the energies of the electrons, these will be spread over a range of energies equal to E_F, the Fermi

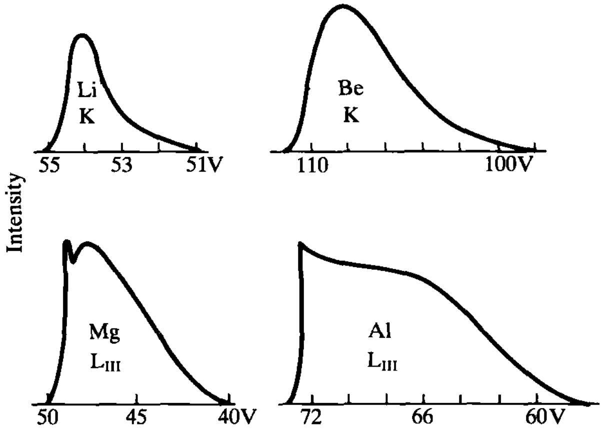

Fig. 1.1. X-ray emission bands of light metals (O'Bryan and Skinner 1934).

energy, of the order of several electron volts (eV) and therefore large compared with k_BT; only a fraction $\sim k_BT/E_F$ of them would have any thermal energy. Thus the internal energy would be $\sim n(k_BT)^2/E_F$ and the specific heat $\sim nk_B^2T/E_F$. That the electron energies were indeed spread over a range of several eV was first shown experimentally through the X-ray emission band of light metals by O'Bryan and Skinner (1934); some of their results are shown in Fig. 1.1. A small specific heat linear in T at low temperatures was first observed in silver in 1934 by Keesom and Kok in the Netherlands; their results agreed well with the theory for a free-electron gas (Fig. 1.2).

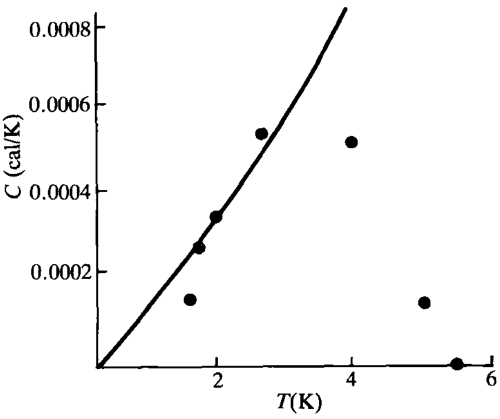

Fig. 1.2. Linear term in the specific heat of silver (Keesom and Kok 1934). The full line shows the theoretical value.

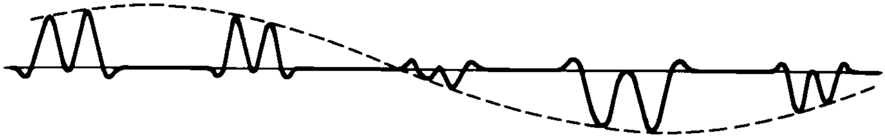

Fig. 1.3. Showing a typical wave function of type (1.2) using a tight binding model; the diagram shows the real or imaginary part. (From Ashcroft and Mermin 1976, p. 185, Fig. 10.7.)

Sommerfeld, however, did not address the problem of an electron moving in the periodic field of a crystal. This was first done in a seminal paper by Bloch (1928), who considered the Schrödinger equation

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \tag{1.1}$$

where $V(= V(x, y, z))$ is a periodic function of position. Here ψ is the wave function and $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. The solutions of such an equation are

$$\psi = \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})u(x, y, z) \tag{1.2}$$

where $u(x, y, z)$ has the same periodicity as V. A typical solution is shown in Fig. 1.3. This solution represents a plane wave modulated by the crystal field. It does not show any scattering; the wavevector $\mathbf{k}$, and thus the momentum of an electron, has a constant value. Thus Bloch could argue that the long mean free paths observed at low temperatures were to be expected. Resistivity is a result of deviations from the perfect crystal lattice resulting either from thermal vibrations or from the presence of impurities. As regards thermal vibrations, scattering should be proportional to the square of the displacement of an atom from its mean position, so that above the Debye temperature the resistivity will be proportional to $k_B T/f$, where fX is the restoring force on an atom for a displacement X. Bloch also showed how the possible energies $E(k_x, k_y, k_z)$ of an electron were divided into zones (the Brillouin zones) with gaps between them.

A. H. Wilson (1931) first pointed out that the model gives a clear distinction between metals and insulators. In metals one or more zones are partly occupied, so that a surface in k-space (the 'Fermi surface') separates occupied from empty states; the Fermi surface is a sphere only if $E(\boldsymbol{k})$ is a function only of the magnitude of $\boldsymbol{k}$, for instance equal to const $|\boldsymbol{k}|^2$. In insulators all zones are full or empty, and there is a gap between the highest occupied band (the valence band) and the lowest empty band (the conduction band). Thus electrons are not 'stuck'; on the contrary they are mobile, but unless an electron is removed from the valence band thermally or by the absorption of radiation, exactly as many electrons move in one direction as in the other. Moreover, an (extrinsic) semiconductor is a material in which impurities (dopants) provide occupied states with energies just below the conduction band, so that at room temperature many or most of the electrons are free to move.

As is well known, this model of Bloch and Wilson has survived for the treatment of semiconductors throughout the enormously important developments of germanium and silicon technology, which have taken place since the end of the Second World War. We shall show, however, particularly in Chapter 7, that, since the existence of zones depends on the assumption that the material is crystalline, it is not adequate to account for the (obvious) property of oxide glasses that they are transparent, and therefore that a gap exists. A gap, then, cannot depend essentially on the properties of the solution of eqn (1.1) with a crystalline form of $V(x, y, z)$. Gaps must exist for some forms of $V(x, y, z)$ appropriate to non-crystalline materials. This will be apparent when we consider Anderson's random potential introduced in Chapter 3.

We will now emphasize a difference between the theories of semiconductors and of metals. In the former, we have to do with a low concentration of electrons in the conduction band; interaction between them is rarely important, except in the formation of 'excitons' when an electron and positive hole form a bound pair. On the other hand, in metals the interaction term e^2/r_{12} is large, r_{12} being the distance between pairs of electrons. Early work neglected this, but it was essential to show that, in spite of this large term, a sharp Fermi energy and a sharp Fermi surface existed. Jones *et al.* (1934) were the first to show the former, in an attempt to explain the sharp upper limit to the X-ray emission bands shown in Fig. 1.1, while the discussion of the Fermi surface is due to Landau (1957). The sharp upper limit is thought to exist in amorphous as well as crystalline metals, though the Fermi surface does not. Interaction between electrons leads to surprisingly small effects in the electrical properties of crystalline metals, perhaps the most important being a small term in the resistivity proportional to T^2 resulting from electron–electron collisions (Landau and Pomeranchuk 1936; Baber 1937). In non-crystalline metals this interaction is more important as we shall see in Chapter 5.

We finish this section by setting down a few formulae which will be used later in this book.

In metals, the conductivity depends only on the properties of electrons at the Fermi surface (or in a non-crystalline material at the Fermi energy). For a spherical Fermi surface, one can write for the conductivity σ

$$\sigma = ne^2\tau/m,$$

where n is the number of electrons per unit volume, e the electronic charge, τ the time of relaxation, and m the effective mass. The time of relaxation is related to the mean free path l by the equation

$$l = v\tau$$

where v is the velocity of an electron at the Fermi surface. In terms of l, we can write

$$\begin{aligned}\sigma &= ne^2l/mv\\ &= ne^2l/k_F\hbar\end{aligned}$$

where k_F is the wave vector at the Fermi surface. Since each state in k-space is associated with a volume $8\pi^3$, for n we have

$$\tfrac{1}{2}n = (4\pi/3)k_F^3/8\pi^3,$$

where the factor $\frac{1}{2}$ comes from the two spin directions; then

$$\sigma = 4\pi k_F^2e^2l/12\pi^3\hbar.$$

$4\pi k_F^2$ is the Fermi surface area S_F, so

$$\sigma = e^2S_Fl/12\pi^3\hbar, \tag{1.4}$$

an equation which will be used in this book.

Naturally these equations depend on the assumption that, if we write $a = n^{-\frac{1}{3}}$ so that a is the mean distance between the electrons, l is large compared with a. This is called the weak-scattering limit. One of the main themes of this book is the problem of what happens when $l \sim a$. A principle due to Ioffe and Regel (1960) suggests that it cannot be smaller; we shall show why in § 3.2.

1.2. Non-crystalline systems

In this book we treat conduction in the following systems.

1. *Impurity conduction in doped and compensated semiconductors.* In silicon or germanium lightly doped with, say, phosphorus, the

此为试读，需要完整PDF请访问：www.ertongbook.com

energy, denoted by ε_1, needed to remove an electron from the phosphorus into the conduction band is of order

$$\varepsilon_1 = me^4/2\hbar^2\kappa^2.$$

Here, m is the effective mass and κ the dielectric constant. The wave function of an electron attached to the phosphorus P^+ ion is like that of a hydrogen atom with radius a_H given by

$$a_H = \hbar^2\kappa/me^2.$$

For concentrations n of dopant greater than n_c where

$$n_c^{\frac{1}{3}}a_H \simeq 0.25,$$

the material behaves like a metal, in the sense that the conductivity tends to a finite value as the temperature tends to zero. This kind of metal–non-metal transition cannot be treated without considering interaction (Chapter 4). But for smaller concentrations, conduction can take place by direct transfer of electrons from one centre to another if the material is *compensated.* This means that it contains a lower concentration of an acceptor (for instance boron). Then all the acceptors will be negatively charged; some of the donors will be neutral and contain an electron and others positively charged and thus empty. The form of conduction which results is called 'impurity conduction'.

It has been extensively studied (cf. Shklovskii and Efros 1984). Since the radius a_H is in general large compared with the lattice parameter, distortion of the lattice by a trapped electron and such phenomena as polaron formation and Stokes shift have in general a negligible influence. These systems, investigated at the very lowest available temperatures, are therefore ideal for seeking to understand in its simplest form the motion of electrons in a non-periodic field. But this is a problem where electron–electron interactions play a major role. We devote Chapter 4 to this phenomenon.

2. *Non-crystalline metals.* These often show interesting electrical properties, including a negative temperature coefficient of resistance. They can be described through concepts of the same kind as those developed for heavily doped semiconductors, and are treated in § 2.4 and Chapter 5.

3. *Polaron motion.* This is a phenomenon of importance in both crystals and some non-crystalline materials, and is discussed in Chapter 6.

4. *Non-crystalline semiconductors.* The earliest investigations were on the properties of amorphous selenium, used by the Xerox

company in the electrostatic copying process known as xerography, and those of Kolomiets and co-workers in Leningrad on the chalcogenide glasses (see Kolomiets 1964). These are glasses with, for example, a composition such as As_2Te_3 and also alloy glasses containing arsenic, tellurium, silicon, and germanium. More recently amorphous silicon containing upwards of 5 per cent of hydrogen has been extensively studied. These materials have—in the main—the same co-ordination number as in the crystal, if this exists; in this they are unlike liquid and amorphous metals, for which there is no integral co-ordination number. Thus As will normally be bounded to three neighbours, Si or Ge to four, and Te and Se to two. The explanation of their properties is based on the assumption that conduction and valence bands exist, as in a crystalline material, but that the lowest states in these bands can act as traps; they are said to be localized. Also a fully co-ordinated material would have a gap in the energy spectrum between the bands, but 'defects'—that is points where the co-ordination is abnormal—do give rise to (localized) states in the gap. A major achievement of Kolomiets's school was to show that the chalcogenide glasses cannot be doped; the conductivity depends little on purity. On the other hand doping is possible in deposited films of silicon, and this has led to the development of p–n junctions in amorphous silicon and their use as photocells. These amorphous semiconductors are treated in Chapter 7.

5. *Liquid metals.* These have properties which differ somewhat from those of amorphous metals. The classical Ziman theory is described in Chapter 2, and effects resulting from short mean free paths in Chapter 8.

6. *Vitreous SiO_2 and its formation by oxidation of silicon.* Vitreous silicon dioxide has one of the largest band gaps known ($\sim$10 eV). It is not, therefore, a semiconductor, but electrons and holes can be injected, and their mobilities measured.

7. *Two-dimensional conductors,* particularly those in the inversion layer between a semiconductor and its oxide.

2 Transport in liquid and amorphous metals; weak-scattering systems

---

2.1. Introduction

In metals, if the mean free path l is sufficiently large, eqn (1.4) can be used for the conductivity whether the metal is crystalline or not. In this chapter we consider the use of this equation for non-crystalline systems, particularly for liquid and amorphous metals.

Probably the earliest paper dealing with electrons in a field that is not periodic is that of Nordheim (1931) on the resistivity of alloys. For a substitutional impurity in a metal, the potential which scatters the electrons is

$$V_B - V_A$$

where V_A is the potential (or pseudopotential) of the atom of the lattice and V_B of the impurity. This was dramatically shown by the fact that the values of the increase in the resistivity of Cu resulting from 1 per cent of Zn, Ga, and Sn in solid solutions are in the ratio 1, 4, 9 (Linde 1931, 1932*a*, *b*; Mott and Jones 1936, p. 293) and thus vary as $(z-1)^2$, where z is the charge on the atomic core, which is one for copper. Nordheim considered alloys (such as silver–gold) in which the two elements are miscible over the whole range of compositions. If we consider two elements, for which the atomic potentials are V_A, V_B, present in the ratio $1-x$, x, the average potential is

$$V_{av} = (1-x)V_A + xV_B.$$

Thus, in each A atom the divergence from this potential is $x(V_B - V_A)$ and in each B atom $(1-x)(V_B - V_A)$. The total scattering, and hence the resistivity at low temperatures, is thus proportional to

$$\{(1-x)x^2 + x(1-x)^2\}\langle U^2\rangle = x(1-x)\langle U^2\rangle$$

where

$$U = \int \psi_{k'}^{*}(V_B - V_A)\psi_k \, d^3x$$

and $\langle\ \rangle$ denotes an appropriate average over all angles of scattering. In alloy systems such as Ag–Au and Pd–Pt, a variation of the low-temperature resistivity ρ as $x(1-x)$ is observed.

2.2. Liquid metals

The theory of Nordheim is a weak-scattering theory; it does not consider interference between multiply-scattered waves, and is therefore valid only if $l \gg a$, where a is the distance between atoms and l the mean free path. The same is true of the theory of the resistivity of liquid metals, first presented by Ziman in 1961 and valid also in the limit $l \gg a$. This work, which made use of the recently developed theory of pseudopotentials, proposed that the scattering potential of each atom in a solid or liquid could be replaced by a *small* pseudopotential. Scattered waves from neighbouring atoms could interfere destructively, but only interference between waves scattered by pairs is considered. Chapter 3 discusses how to go beyond this approximation.

The elements of Ziman's theory are as follows (cf. Faber 1972). First of all, since the scattering is treated as a perturbation and since there is no axis of symmetry, the Fermi surface is taken to be spherical and one starts therefore with the concept of a degenerate electron gas of *free* electrons. Thus the amplitude scattered by two atoms at a distance R from each other is

$$\{1-\exp(\mathrm{i}\mathbf{q}\cdot\mathbf{R})\}f(\theta)$$

where $\mathbf{q}=\mathbf{k}-\mathbf{k}'$, the change in the wave vector on scattering, and $f(\theta)$ is the amplitude scattered by a single atom through an angle θ. Neglecting multiple scattering, the conductivity then is given by (1.4) with

$$\frac{1}{l}=N\int S(q)(1-\cos\theta)\,|f(\theta)|^2\,2\pi\sin\theta\,\mathrm{d}\theta. \qquad (2.1)$$

Here N is the number of atoms per cm^3 and $S(q)$ is the structure factor, given by

$$S(q)=N^{-1}\int\{1+\exp(\mathrm{i}\mathbf{q}\cdot\mathbf{R})\}^2P(R)\,\mathrm{d}^3x. \qquad (2.2)$$

$P(R)$ is here the pair distribution function, $P(R)\,\mathrm{d}^3x$ being the probability that another atom is in the volume d^3x at a distance R from a given atom. Using first-order perturbation theory for $f(\theta)$, we find, following Faber and Ziman (1965), for the resistivity

$$\rho = \frac{3\pi}{\hbar e^2 v_F^2 \Omega} \int_0^{2k_F} \frac{|v(\mathbf{q})|^2 S(q) q^3 \, dq}{4k_F^4} \tag{2.3}$$

where

$$v(q) = \int V(r) \exp\{i(\mathbf{q} \cdot \mathbf{r})\} \, d^3x/\Omega,$$

and where v_F and k_F are the values of the velocity and wave vector at the Fermi surface, respectively; the integral is over the volume Ω. Figure 2.1 shows schematically the behaviour of $S(q)$ and $v(q)$. The possibility of applying perturbation theory depends on the fact that $v(q)$ is small for values of q such that $S(q)$ is large.

One of the most successful applications of the theory is to the temperature-dependence of the resistivity of liquid metals. This is large and positive for monovalent metals, small and sometimes

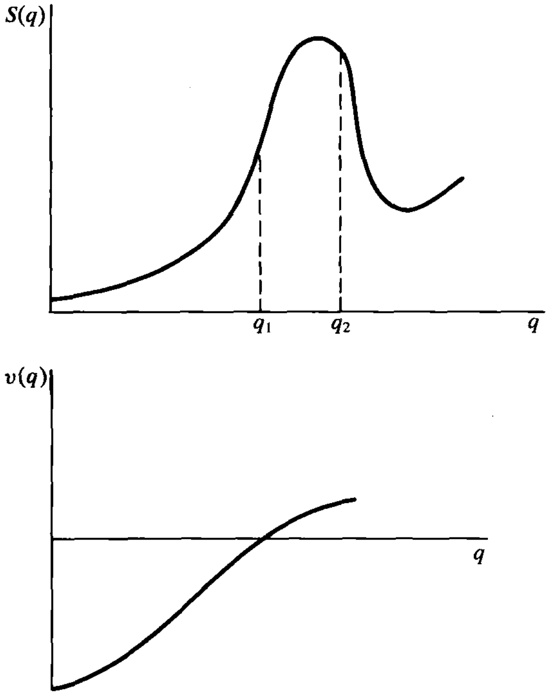

Fig. 2.1. The structure factor $S(q)$ and pseudopotential $v(q)$ for a liquid metal; q_1 and q_2 show the values of $2k_F$ for monovalent and divalent metals.

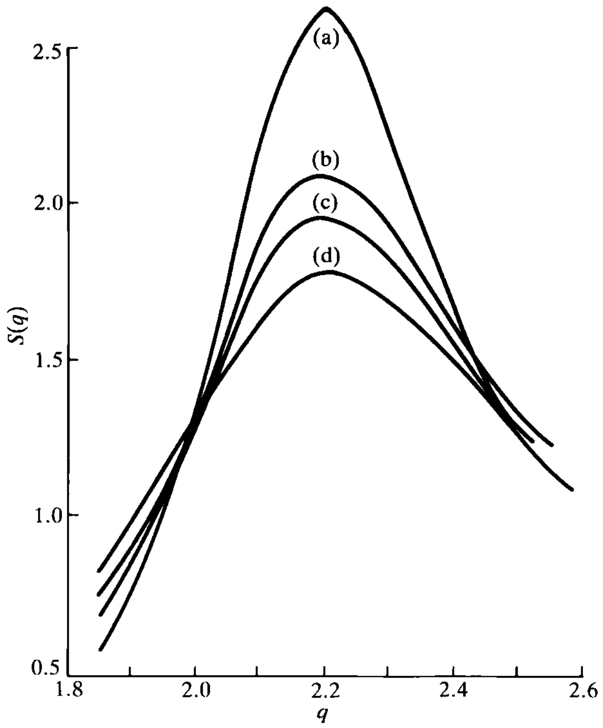

Fig. 2.2. The function $S(q)$ for liquid lead determined from neutron scattering at different temperatures. (a) 340 °C; (b) 600 °C; (c) 780 °C; (d) 1100 °C. (From North *et al.* 1968.)

negative for divalent metals. This is explained as caused by the variation with temperature of the structure factor $S(q)$, which can be determined from neutron diffraction. Figure 2.2 shows the results of North *et al.* (1968) for liquid lead at various temperatures. This behaviour is typical. For monovalent metals the resistivity is determined by the left-hand side of the peak. It is observed that the resistivity of monovalent liquid metals at constant volume is proportional to the absolute temperature; this suggests that $S(q)$ is also proportional to T over the range for which $|v(q)|^2$ is significant. For very low q, the structure factor will be given by the Ornstein–Zernike formula

$$S(q) = k_B T/\beta\Omega$$

where β is the bulk modulus and Ω the atomic volume. This equation describes the contribution from macroscopic fluctuations of density

此为试读，需要完整PDF请访问：www.ertongbook.com