TABLE III. Percentages of $3d$ electrons having t_{2g} or e_g symmetry.

	$f(330)/f(411) = 1.013 \pm 0.007$	
$J_4\, 3d^{4++}$	$t_{2g} = 76\%$	$e_g = 24\%$
$J_4\, 3d^6$	$t_{2g} = 72\%$	$e_g = 28\%$
	$f(442)/f(600 = 1.014 \pm 0.007$	
$J_4\, 3d^{4++}$	$t_{2g} = 72\%$	$e_g = 28\%$
$J_4\, 3d^6$	$t_{2g} = 69\%$	$e_g = 31\%$

are approximately 72% in the t_{2g} sublevels and 28% in the e_g sublevels. This is in agreement with the measured population in the bcc metals iron[16] and vanadium,[17] and in contrast with nickel where, as one would expect, no marked asphericity effects are present.

ACKNOWLEDGMENTS

We are greatly indebted to J. J. De Marco for supplying the chromium crystal and for his help at all stages of the present research. We also want to thank Dr. C. B. Walker for kindly computing some TDS corrections, Dr. C. R. Natoli for many helpful discussions, and G. Menichelli for helping to collect the data.

---

*Present address: Programma Plutonio, C. S. N. Casaccia, 00100, Roma, Italia.

[1] M. Diana *et al.*, Phys. Rev. 187, 973 (1969).

[2] J. J. De Marco, Phil. Mag. 15, 483 (1967).

[3] M. J. Cooper, Phil. Mag. 7, 2059 (1962).

[4] M. J. Cooper, Phil. Mag. 10, 177 (1964).

[5] J. J. De Marco *et al.*, Phil. Mag. 16, 1013 (1967).

[6] N. Nilsson, Arkiv Fysik 12, 247 (1957).

[7] C. B. Walker and D. R. Chipman, Acta Cryst. A25, 395 (1969).

[8] C. B. Walker and D. R. Chipman, Acta Cryst. A26, 447 (1970).

[9] R. H. Wilson *et al.*, Acta Cryst. 21, 635 (1966).

[10] J. L. Feldman, Phys. Rev. B 1, 448 (1970).

[11] L. D. Jennings, Acta Cryst. A24, 472 (1968).

[12] D. T. Cromer, Acta Cryst. 18, 17 (1965).

[13] A. J. Freeman and R. E. Watson, Acta Cryst. 14, 231 (1961).

[14] R. J. Weiss, *X-Ray Determination of Electron Distributions* (North-Holland, Amsterdam, 1966), p. 61.

[15] R. E. Watson and A. J. Freeman, Acta Cryst. 14, 27 (1961).

[16] R. J. Weiss and J. J. De Marco, Phys. Letters 18, 92 (1965).

[17] J. J. De Marco and R. J. Weiss, Phys. Rev. 140, A1223 (1965).

PHYSICAL REVIEW B VOLUME 5, NUMBER 10 15 MAY 1972

Theorem on the Magnetoconductivity of Metals

Gregory H. Wannier
University of Oregon, Eugene, Oregon 97403

(Received 3 December 1971)

Under rather general assumptions it can be proved that the conductivity of a metal is monotonically nonincreasing with magnetic field. In the proof given it is assumed that the electron motion can be described by a fermion Boltzmann equation with arbitrary multiple band structure and an arbitrary law of scattering. However, the magnetic field is to enter only through the Lorentz force term. Exceptions to the theorem are known; they arise probably because the magnetic field influences the scattering process.

A remark by Pippard[1] that the magnetoresistance can be proved positive under very general assumptions has led the author to investigate this question. The result of this investigation is the following much stronger theorem:

If the magnetic field acts on electrons in a band or band system only through its contribution to the Lorentz force, and if the behavior of the electrons is adequately described by a Boltzmann equation, then the electrical conductivity of a metal is a monotonically nonincreasing function of the magnitude of H. Conductivity is here defined as the number with which E^2 is to be multiplied to get the power dissipation per unit volume. The statement is restricted to the Ohmic range.

We shall outline the proof for a single band and indicate at the end its generalization to band systems. We take the behavior of the electrons to be controlled by an equation of the following form:

$$\frac{\partial f(\vec{k})}{\partial t} + \frac{e}{\hbar}\left(\vec{E} + \frac{1}{\hbar c}\,\frac{\partial W(\vec{k})}{\partial \vec{k}} \times \vec{H}\right)\cdot \frac{\partial f(\vec{k})}{\partial \vec{k}}$$

$$+\int R(\vec{k},\vec{k}')\{f(\vec{k})[1-f(\vec{k}')]e^{\beta W(\vec{k})}-f(\vec{k}')[1-f(\vec{k})]e^{\beta W(\vec{k}')}\}\,d\vec{k}'=0\,. \tag{1}$$

Here $R(\vec{k},\vec{k}')$ is the rate of scattering into unit volume of $\vec{k}'$ space; it is positive and symmetric in its two arguments. The representation of the relaxation processes used here is reasonably general. By including with every process its inverse, the Fermi distribution is automatically the stationary solution in the absence of an $\vec{E}$ field, and, in addition, normalization is automatically preserved in time. Admittedly, the equation is somewhat schematic about the relaxation mechanism; it is hoped that the form is sufficiently general to represent adequately a variety of such mechanisms.

The first step consists in calculating the entropy production resulting from (1). This means, incidentally, proving an H theorem for it. First we get the energy balance by multiplying with the energy-band function $W(\vec{k})$ and integrating:

$$\frac{d}{dt}\int W(\vec{k})fd(\vec{k})-\frac{e\vec{E}}{\hbar}\cdot\int\frac{\partial W}{\partial\vec{k}}fd\vec{k}+\iint R(\vec{k},\vec{k}')$$
$$\times W(\vec{k}')\{f(1-f')e^{\beta W}-f'(1-f)e^{\beta W'}\}d\vec{k}d\vec{k}'=0\,. \tag{2}$$

The equation shows the power output going partly into an increase of the energy of the electrons, partly into the relaxation mechanism where it becomes all "heat," by assumption. The second line is thus one term in the total entropy production. There is a second contribution from the electron system itself which reads

$$\frac{Se}{k_B}=\frac{V}{4\pi^3}\int[-f\ln f-(1-f)\ln(1-f)]\,d\vec{k}\,,$$

$$\frac{1}{k_B}\frac{dS_e}{dt}=-\frac{V}{4\pi^3}\int\frac{\partial f}{\partial f}\ln\frac{f}{1-f}\,d\vec{k}\,.$$

Inserting $\partial f/\partial t$ from (1), we get for this contribution

$$\frac{1}{k_B}\frac{dS_e}{dt}=\frac{V}{4\pi^3}\iint R(\vec{k},\vec{k}')\ln\frac{f}{1-f}$$
$$\times[f(1-f')e^{\beta W}-f'(1-f)e^{\beta W'}]\,d\vec{k}\,d\vec{k}\,. \tag{3}$$

To get the total entropy production we add the second line of (1), multiplied by $\beta V/4\pi^3$, to this expression. We find

$$\frac{1}{k_B}\frac{dS}{dt}=\frac{V}{8\pi^3}\iint R(\vec{k},\vec{k}')$$
$$\times\{\ln[f(1-f')e^{\beta W}]-\ln[f'(1-f)e^{\beta W'}]\}$$
$$\times\{f(1-f')e^{\beta W}-f'(1-f)e^{\beta W'}\}d\vec{k}\,d\vec{k}'\,. \tag{4}$$

An H theorem is thus proved because the two curly brackets have the same sign.

We now come to the specific transformation necessary to prove the theorem stated above. Since it appears to be valid only in the Ohmic range, we treat $\vec{E}$ as a perturbation, but not $\vec{H}$. Such a treatment is not contradictory, because the equilibrium distribution is a solution of (1) for all $\vec{H}$, as long as $\vec{E}$ is zero. We also restrict our attention from now on to stationary solutions of (1). We take the Fermi level as the zero of energy and write f in the form

$$f(\vec{k})=1(e^{\beta W(\vec{k})}+1)^{-1}+g(\vec{k})\,. \tag{5}$$

$g(\vec{k})$ must be thought of as proportional to E. If we substitute this into (1) and retain only linear terms in E, we get

$$-\left(\beta e\,\vec{E}\cdot\frac{\partial W}{\partial\vec{k}}\Big/4\hbar\cosh^2\tfrac{1}{2}\beta W\right)-\frac{e}{\hbar^2c}\,\vec{H}\cdot\left(\frac{\partial W}{\partial\vec{k}}\times\frac{\partial g}{\partial\vec{k}}\right)$$
$$+\int\frac{R(\vec{k},\vec{k}')}{(1+e^{-\beta W})(1+e^{-\beta W'})}(4g\cosh^2\tfrac{1}{2}\beta W-4g'\cosh^2\tfrac{1}{2}\beta W')d\vec{k}'=0\,. \tag{6}$$

Similarly, the entropy production (4) reduces to a quadratic expression in E:

$$\frac{1}{k_B}\frac{dS}{dt}=\frac{2V}{\pi^3}\iint\frac{R(\vec{k},\vec{k}')}{(1+e^{-\beta W})(1+e^{-\beta W'})}$$
$$\times(g\cosh^2\tfrac{1}{2}\beta W-g'\cosh^2\tfrac{1}{2}\beta W')^2d\vec{k}\,d\vec{k}'\,. \tag{7}$$

To get the behavior of the system as a function of the magnetic field we differentiate both (6) and (7) with respect to it. We define

$$h=\frac{\partial g}{\partial H}=\frac{\partial f}{\partial H} \tag{8a}$$

or, more precisely,

$$h=\frac{1}{H}\,\vec{H}\cdot\frac{\partial g}{\partial\vec{H}} \tag{8b}$$

The derivative of (7) reads

$$\frac{d}{dH}\left(\frac{1}{k_B}\frac{dS}{dt}\right) = \frac{4V}{\pi^3}\iint \frac{R(\vec{k},\vec{k}')}{(1+e^{-\beta W})(1+e^{-\beta W'})} \times\left(g\cosh^2\tfrac{1}{2}\beta W - g'\cosh^2\tfrac{1}{2}\beta W'\right) \times\left(h\cosh^2\tfrac{1}{2}\beta W - h'\cosh^2\tfrac{1}{2}\beta W'\right)d\vec{k}\,d\vec{k}' \qquad (9)$$

and of (6) reads

$$-\frac{e}{\hbar^2 c}\frac{\vec{H}}{H}\cdot\left(\frac{\partial W}{\partial\vec{k}}\times\frac{\partial g}{\partial\vec{k}}\right) - \frac{e}{\hbar^2 c}\vec{H}\cdot\left(\frac{\partial W}{\partial\vec{k}}\times\frac{\partial h}{\partial\vec{k}}\right) + 4\int\frac{R(\vec{k},\vec{k}')}{(1+e^{-\beta W})(1+e^{-\beta W'})} \times\left(h\cosh^2\tfrac{1}{2}\beta W - h'\cosh^2\tfrac{1}{2}\beta W'\right)d\vec{k}' = 0\,. \qquad (10)$$

We now extract a pseudo-H-theorem from (10) and link this result with the field derivative of the entropy production. Multiply with $h\cosh^2\frac{1}{2}\beta W$ and integrate. The second term disappears:

$$\frac{e}{\hbar^2 c}\frac{\vec{H}}{H}\cdot\int h\cosh^2\tfrac{1}{2}\beta W\left(\frac{\partial W}{\partial\vec{k}}\times\frac{\partial g}{\partial\vec{k}}\right)d\vec{k} = 2\iint\frac{R(\vec{k},\vec{k}')}{(1+e^{-\beta W})(1+e^{-\beta W'})} \times\left(h\cosh^2\tfrac{1}{2}\beta W - h'\cosh^2\tfrac{1}{2}\beta W'\right)^2 d\vec{k}\,d\vec{k}'\,.$$

The left-hand side above allows an interesting transformation. It is of the form

$$\int h\,\frac{\partial\varphi}{\partial\vec{k}}\times\frac{\partial g}{\partial\vec{k}}\,d\vec{k}\,,$$

where φ is a function of W. Because of the structure of the cross product this can be integrated by parts on g and h without touching φ: The second derivatives of φ cancel. We have therefore the alternative form

$$\frac{e}{\hbar^2 c}\frac{\vec{H}}{H}\cdot\int g\cosh^2\tfrac{1}{2}\beta W\left(\frac{\partial W}{\partial\vec{k}}\times\frac{\partial h}{\partial\vec{k}}\right)d\vec{k} = -2\iint\frac{R(\vec{k},\vec{k}')}{(1+e^{-\beta W})(1+e^{-\beta W'})} \times\left(h\cosh^2\tfrac{1}{2}\beta W - h'\cosh^2\tfrac{1}{2}\beta W'\right)^2 d\vec{k}\,d\vec{k}'\,. \qquad (11)$$

Now we multiply (10) with $g\cosh^2\frac{1}{2}\beta W$ and integrate. The first term now disappears, and we are left with

$$\frac{e}{\hbar^2 c}\vec{H}\cdot\int g\cosh^2\tfrac{1}{2}\beta W\left(\frac{\partial W}{\partial\vec{k}}\times\frac{\partial h}{\partial\vec{k}}\right)d\vec{k} = 2\iint\frac{R(\vec{k},\vec{k}')}{(1+e^{-\beta W})(1+e^{-\beta W'})} \times\left(g\cosh^2\tfrac{1}{2}\beta W - g'\cosh^2\tfrac{1}{2}\beta W'\right)\left(h\cosh^2\tfrac{1}{2}\beta W - h'\cosh^2\tfrac{1}{2}\beta W'\right)d\vec{k}\,d\vec{k}'\,.$$

In this formula, the right-hand side appears in (9), the left-hand side in (11). Putting this together, we find, using (8a),

$$\frac{d}{dH}\left(\frac{1}{k_B}\frac{dS}{dt}\right) = -\frac{4VH}{\pi^3}\iint\frac{R(\vec{k},\vec{k}')}{(1+e^{-\beta W})(1+e^{-\beta W'})}\left(\frac{\partial f}{\partial H}\cosh^2\tfrac{1}{2}\beta W - \frac{\partial f'}{\partial H}\cosh^2\tfrac{1}{2}\beta W'\right)^2 d\vec{k}\,d\vec{k}'\,. \qquad (12)$$

This is the desired result. Entropy production here is at constant E and, incidentally, $\partial f/\partial H$ is proportional to E. So the left-hand side is shown to be proportional to E^2 and negative. This means a conductivity which is monotonically nonincreasing with H. Incidentally when the magnetoconductivity tends to be constant, Eq. (12) contains a statement on the functional form of the distribution function.

The extension of the proof given to band systems is automatic. Wherever $\vec{k}$ appears, a band index must appear also, and wherever $\vec{k}$ is integrated over, there is also a sum over a band index; interchange of k and k' must be accompanied by interchange of the band indices. The relaxation rate becomes a function $R_{n,n'}(k,k')$; it is still symmetric provided the band indices are interchanged simultaneously with the wave vectors. The end result will be

$$\frac{d}{dH}\left(\frac{1}{k_B}\frac{dS}{dt}\right) = -\frac{4VH}{\pi^3}\sum_{n,n'}\iint\frac{R_{n,n'}(\vec{k},\vec{k}')}{(1+e^{-\beta W_n(\vec{k})})(1+e^{-\beta W_{n'}(\vec{k}')})} \times\left(\frac{\partial f_n(\vec{k})}{\partial H}\cosh^2\tfrac{1}{2}\beta W_n(\vec{k}) - \frac{\partial f_{n'}(\vec{k}')}{\partial H}\cosh^2\tfrac{1}{2}\beta W_{n'}(\vec{k}')\right)^2 d\vec{k}\,d\vec{k}'\,. \qquad (13)$$

The previous conclusions are not modified by this more general result.

There are indications in the literature that the statement just proved does not hold for certain metals containing paramagnetic impurities.[2] The cause for this failure is almost certainly that the scattering is dependent on the magnetic field. This renders the given proof invalid.

[1] A. B. Pippard, *The Dynamics of Conduction Electrons* (Gordon and Breach, London, 1965), p. 92.

[2] G. Williams, G. A. Swallow, and J. W. Loran, Phys. Rev. 3, 3863 (1971).

PHYSICAL REVIEW B VOLUME 5, NUMBER 10 15 MAY 1972

Different Types of Phase-Shift Pseudopotential with Application to the Alkali Metals and Copper

Martin J. G. Lee*
James Franck Institute and Department of Physics, University of Chicago, Chicago, Illinois 60637

and

Volker Heine†
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 19 August 1971)

The total pseudopotential in a metal can be expressed in many ways as a sum of atomic pseudopotentials. One way involves the usual "linear-screening" potential and another a "minimum-perturbation" potential. These different types of pseudopotential can be constructed by fitting experimental Fermi-surface data in terms of phase shifts within the formalism of the augmented-plane-wave method of band-structure calculation. An investigation is made of the effect of choosing different values of the "Fermi energy parameter" which defines the mean interstitial potential relative to the absolute Fermi level. Pseudopotential form factors calculated from the empirical phase shifts are presented for the alkali metals and copper.

I. INTRODUCTION

There has been a trend in recent years[1–6] to express the band structures of nearly free-electron solids in terms of scattering phase shifts η_l. This approach seems to be more effective than others when d-band effects are important, even in the alkali metals.[5] In particular, the Fermi surfaces of the alkali metals[5] and copper[6] have been fitted in this way by using the formalism of the augmented-plane-wave (APW) method[7] of band-structure calculation. The phase shifts describe the interaction of a conduction electron with the atom concerned, and, in order make use of this information to describe the electron-phonon interaction and a variety of physical properties, one needs to deduce the appropriate pseudopotential. The term pseudopotential is used here in its current wide sense,[7,8] and includes, for example, the APW form factor and the Korringa-Kohn-Rostoker-Ziman (KKRZ)[9] expression.

However, it is necessary to resolve one ambiguity first.[2,10,11] In fitting Fermi surfaces within the APW formalism, one has to choose a value of the Fermi energy parameter E_F, which is the measure of the Fermi energy relative to the muffin-tin constant. It is not a fitting parameter in the usual sense, because for any chosen E_F (within wide limits) one can obtain a corresponding set of phase shifts that reproduces the measured Fermi surface. The first purpose of this paper is to explore the effect of changing the E_F parameter and what it corresponds to physically. Secondly, we present phase-shift pseudopotentials for the alkali metals and copper. The calculation of various physical properties and comparison with other pseudopotentials is deferred to the following paper.

The nonuniqueness of E_F can be looked at from a physical point of view. Suppose one is given the total potential (or pseudopotential) $V(\vec{r})$ in a crystal. It can be expressed as a sum of atomic potentials $v(\vec{r}-\vec{R}_\alpha)$ associated with the sites $\vec{R}_\alpha$ in an infinite variety of ways (Fig. 1), and from Poisson's equation one can associate with each v a corresponding distribution of conduction electrons. In pseudopotential calculations the electrical neutrality is usually treated by linear-screening theory with overlapping charge clouds.[12–14] But this is not the only way to allocate the conduction electrons. Other formulations have appeared occasionally[4,15,16] and we think that there is a need to relate these to one another and also to the screening method. Thus by way of an extended introduction we try to classify these approaches in Sec. II. In particular, what we have called[11] the minimum-perturbation pseudopotential is stated more precisely than usual.

II. DEFINITION OF VARIOUS PSEUDOPOTENTIALS

We consider a system of N identical atoms at arbitrary positions $\vec{R}_\alpha$ in a volume $N\Omega$ with periodic boundary conditions applied at the surface of the box. The total pseudopotential $V(\vec{r})$ is expressed in