Changes in the Electrical, Thermal, and Thermoelectrical Properties of Monovalent Metals by Lattice Distortions*

A. W. SÁENZ
Applied Mathematics Branch, Mechanics Division, Naval Research Laboratory, Washington, D. C.
(Received February 18, 1953)

In this paper we study theoretically the effect of static lattice distortions on the electrical resistivity, electronic thermal conductivity, and absolute thermoelectric power of monovalent metals. We base our work on a transport equation which follows from straightforward quantum-statistical arguments. Employing an iteration method, we reduce this equation to a set of integral equations in one independent variable, and solve this set explicitly for $T \gg \Theta$. We are thus able to study the three effects of interest for a distorted metallic lattice at high temperatures, and to obtain information concerning the anisotropy of a metal, containing certain types of imperfections, in a much wider temperature range. We prove the striking result that our transport equation yields the same results as the simplified one employed by Mackenzie and Sondheimer, provided that $T \gg \Theta$ and that the effect of the lattice distortions on the three properties mentioned above is small. To illustrate our general formulas, we treat in detail the case of an array of parallel edge dislocations. We express our results in terms of a quantity Q, which is proportional to the ratio of the changes in absolute thermoelectric power and electrical resistivity. For plastically deformed noble metals, the observed values of Q are appreciably larger than the corresponding theoretical values for dislocation arrays of the type mentioned above.

1. INTRODUCTION

THE purpose of this investigation is the theoretical study of the effect of static lattice distortions on the electrical resistivity, electronic thermal conductivity, and absolute thermoelectric power of monovalent metals. We shall pay particular attention to the important special case of edge dislocations, although the effect of impurities and vacancies on the three properties cited above could be dealt with equally well within the framework of this paper.

Before summarizing our results, we shall present a critical review of previous theoretical studies in this field, which will demonstrate the need for a theory based on sounder foundations.

Several authors[1–5] have calculated the tensor $\delta\boldsymbol{\varrho}$,[6] describing the change in electrical resistivity of a metal containing an array of Burgers edge dislocations.

In essence, their calculations are based on two assumptions:

(1) They suppose that it is possible to describe transport phenomena in a lattice by means of a Boltzmann equation having the simple structure

$$[\partial f/\partial t]_{\text{fields}}+[\partial f/\partial t]_{\text{coll}}=0; \qquad [\partial f/\partial t]_{\text{coll}}\equiv-(f-f_0)/\tau+[\partial f/\partial t]_{\text{def}}; \tag{1.1}$$

where f_0 is the equilibrium Fermi-Dirac distribution function for the conduction electrons; f is the corresponding perturbed function when an electric field, a thermal gradient, or both, are present; τ is the so-called relaxation time associated with the electron-phonon interaction energy H_1, and is supposed to depend only on $K\equiv|\mathbf{K}|$, where $\mathbf{K}$ is the electronic wave vector; $[\partial f/\partial t]_{\text{fields}}$ is an abbreviation for the streaming terms in Boltzmann's equation; and $[\partial f/\partial t]_{\text{def}}$ is the contribution to the collision integral $[\partial f/\partial t]_{\text{coll}}$ due to the interaction of the conduction electrons with the static deformations of the crystal, it being supposed that the latter scatter the former in an elastic, but nonisotropic, manner.[7]

(2) They calculate the matrix elements $\langle\mathbf{K}'|H_2|\mathbf{K}\rangle$ of the interaction energy H_2 between electrons and lattice defects for edge dislocations.[8] This allows them to find $[\partial f/\partial t]_{\text{coll}}$ and to evaluate $\delta\boldsymbol{\varrho}$ on the basis of the solution of Eq. (1.1) for this special case, coupled with the use of Matthiessen's rule.

Although it would superficially appear that Eq. (1.1) holds for temperatures T for which a time of relaxation τ can be defined, *viz.*, when T is much larger than the Debye temperature Θ of the lattice, this is not true. In fact, we shall prove in Sec. 2 that a set of quite general and plausible hypotheses, in conjunction with elementary principles of quantum statistics, lead us to a transport equation which is *different* from Eq. (1.1) for *all* T, if the scattering of electrons by the lattice

* This work was performed under a contract between Indiana University and the U. S. Office of Naval Reserach.

[1] J. S. Koehler, Phys. Rev. **75**, 106 (1946). A partial survey of the corresponding experimental literature is contained therein.

[2] J. K. Mackenzie and E. H. Sondheimer, Phys. Rev. **77**, 264 (1950). Their collision integral corresponding to dislocational scattering is too large by a factor of 2, as is pointed out in reference 4.

[3] R. Landauer, Phys. Rev. **82**, 520 (1951).

[4] D. L. Dexter, Phys. Rev. **86**, 770 (1952).

[5] T. Hirone and K. Adachi, Science Repts. Research Insts. Tohôku Univ. **A3**, 454 (1951).

[6] We shall employ boldface letters to designate second-rank Cartesian tensors, having indices which run from 1 to 3. Thus $\delta\boldsymbol{\varrho}$ is a tensor with components $(\delta\boldsymbol{\varrho})_{ij}$, where $i, j=1, 2, 3$.

[7] The scattering of conduction electrons is said to be isotropic when the absolute value of the matrix elements of the perturbing Hamiltonian, taken between states $\mathbf{K}'$ and $\mathbf{K}$, depends on $|\mathbf{K}'-\mathbf{K}|$ only.

[8] They employ one of two standard methods, or minor variations thereof, viz., the rigid-ion model of L. Nordheim, Ann. Physik (5) **9**, 607 (1931), or the deformation-potential procedure of J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950). For a proof of the equivalence of these methods in the limit of perfect ionic shielding, see reference 4.

defects is nonisotropic. Since the authors cited in references 1 to 5 are concerned with precisely this situation, we conclude that their use of Eq. (1.1) is unjustified. However, we shall show that our transport equation leads to the same results as Eq. (1.1) under the conditions stated in the concluding paragraphs of this section.

We now turn our attention to previous investigations on the changes in electronic thermal conductivity $\delta\kappa$ and absolute thermoelectric power $\delta\mathbf{S}$ in plastically deformed metals. No detailed theoretical work regarding $\delta\kappa$ is available. With regard to $\delta\mathbf{S}$, we mention the early attempt of Nordheim and Gorter[9] to compute this quantity for metals with impurities and randomly oriented deformations, for which corresponding mean free paths can be defined, as well as the later papers of Kohler[10] on related topics. The only calculation of $\delta\mathbf{S}$ for the case of edge dislocations is due to Hirone and Adachi.[5] Unfortunately, they base their work on Eq. (1.1) and a rather uncritical use of free-electron theory and Matthiessen's rule. Moreover, their final formula for $\delta\mathbf{S}$ contains a serious error, which is equivalent to neglecting $\mathbf{S}^{(1)}$ with regard to $\mathbf{S}^{(0)}$ in Eq. (4.13) of the present paper, these two quantities being of the same order of magnitude for edge dislocations.

To our best knowledge, no systematic experimental work has been carried out to determine the value of $\delta\kappa$ for cold-worked metals. We have a wealth of empirical information concerning $\delta\mathbf{S}$ for plastically deformed metals in the polycrystalline state,[11,12] but little or no data for single crystals.

We now outline the content of the succeeding sections of the present paper, in which we employ no semiempirical formulas, such as Matthiessen's rule.

In Sec. 2, we derive a transport equation for the distribution of conduction electrons in monovalent metals with static lattice distortions, employing four simple assumptions regarding H_1 and H_2. We do not use a detailed model for H_1 throughout this paper. As to H_2, we do not specialize its form until Sec. 5, and then merely to provide an illustration of the general theory.

In Sec. 3, we introduce an iteration method, which should converge rapidly for $T\gg T_0$, where T_0 is a temperature at which the eigenvalues of $\delta\varrho$, $\delta\kappa$, and $\delta\mathbf{S}$ are of the same order of magnitude as the electrical resistivity, thermal conductivity, and absolute thermoelectric power of the corresponding undeformed metal.[13] This procedure reduces our transport equation to a set of integral equations in one independent variable, which we solve explicitly for $T\gg\Theta$. We remark that, for the cases of interest in this paper, T_0 is considerably smaller than Θ, so that the condition $T\gg T_0$ is much less restrictive than $T\gg\Theta$.[13]

In Sec. 4, we develop general expressions for $\delta\varrho$, $\delta\kappa$, and $\delta\mathbf{S}$ for $T\gg T_0$. Employing these results and those of the previous section, we arrive at explicit formulas for the above tensors in the high-temperature range. We also consider the case when $(\tau)^{-1}=p(\epsilon)\mathfrak{A}$, where $p(\epsilon)$ is a scalar function of the electronic energy ϵ, and $\mathfrak{A}$ is a symmetric tensor of the second rank independent of ϵ and T, obtaining an interesting theorem relative to the anisotropy ratios of $\delta\varrho$, $\delta\kappa$, $\delta\mathbf{S}$ for $T\gg T_0$.

In Sec. 5, we compute $\delta\varrho$, $\delta\kappa$, and $\delta\mathbf{S}$ for a metal with $T\gg\Theta$ having an array of parallel positive-negative edge dislocations, by using the theory in the last section in conjunction with the formula for $|\langle\mathbf{K}'|H_2|\mathbf{K}\rangle|^2$ in reference 4. For free electrons, our result for $\delta\varrho$ coincides with that obtained in the above reference, and we shall presently see that this agreement is not fortuitous. By exploiting the theorem of Sec. 4 mentioned previously, we also succeed in showing that the anisotropy ratios of $\delta\varrho$, $\delta\kappa$, and $\delta\mathbf{S}$ are the same and are independent of T, for $T\gg T_0$. We conclude this section by a brief comparison of our theory with experiment.

Finally, we prove the following striking result in the Appendix:

The computation of $\delta\varrho$, $\delta\kappa$, and $\delta\mathbf{S}$ for $T\gg\Theta$ on the basis of either the simplified Eq. (1.1) or of the transport Eq. (2.9) employed in this paper yields the same results, provided only first-order terms[14] are retained in both cases.

2. TRANSPORT EQUATION FOR ELECTRONS IN DISTORTED LATTICES

In this section we shall derive a transport equation for the conduction electrons in a statically deformed monovalent metal.

We denote by $W_1(\mathbf{K}', \mathbf{K})$ and $W_2(\mathbf{K}', \mathbf{K})$ the transition probabilities per unit time for one of the two electrons with wave vector $\mathbf{K}$ to go to a state characterized by the wave vector $\mathbf{K}'$, due to the action of H_1 and H_2, respectively. We designate by $W_1(\mathbf{K}, \mathbf{K}')$ and $W_2(\mathbf{K}, \mathbf{K}')$ the transition probabilities for the corresponding inverse processes.

We shall base our further considerations on the four hypotheses stated below:

(a) the initial and final electronic energies ϵ and ϵ'

[9] L. Nordheim and C. G. Gorter, Physica **2**, 383 (1935). References to earlier work of Nordheim on this topic are contained therein.

[10] M. Kohler, Z. Physik **126**, 481 (1949). A list of previous papers by Kohler on this subject is given here.

[11] See, for example, the references in the article by G. Borelius in *Handbuch der Metall Physik* (Akademische Verlagsgesellschaft M.B.H., Leipzig, 1935), vol. 1, p. 418.

[12] C. Crussard, *Report of the 1947 Bristol Conference of the Strength of Solids* (Physical Society, London, 1948), p. 119.

[13] As is generally known, the percentage increase in resistivity is of the order of 1 percent at room temperature for heavily cold-worked metals. The paper of J. Molenaar and W. A. Aarts, Nature **166**, 690 (1950), shows that the percentage increase in resistivity is nearly 6 percent for Cu and 8 percent for Ag, for strains of 10 percent at liquid air temperatures. From these data and the rough rule that the percentage changes in the three effects considered here are of the same order of magnitude, we estimate that T_0 can be taken as 100°K for the noble metals, subjected to strains comparable to those reported by Molenaar and Aarts.

[14] The meaning of these "first-order terms" will become clear to the reader in Sec. 3 and in the Appendix.

depend solely on K and K', respectively,

$$\epsilon=\epsilon(K), \quad \epsilon'=\epsilon(K'); \tag{2.1}$$

(*b*) the total scattering potential H is thus

$$H=H_1+H_2; \tag{2.2}$$

(*c*) the scattering due to H_1 is isotropic at all T and elastic at $T\gg\Theta$,[15] and $W_1(\mathbf{K}', \mathbf{K})$ satisfies the usual stationary condition, *viz.*,

$$\begin{aligned} &W_1(\mathbf{K}, \mathbf{K}')=F(K, K'; |\mathbf{K}-\mathbf{K}'|), \textit{ all } T; \\ &W_1(\mathbf{K}, \mathbf{K}')=M(|\mathbf{K}'-\mathbf{K}|)\delta(\epsilon'-\epsilon), \ T\gg\Theta; \end{aligned} \tag{2.3a}$$

$$W_1(\mathbf{K}', \mathbf{K})f_0(\epsilon)[1-f_0(\epsilon')] - W_1(\mathbf{K}, \mathbf{K}')f_0(\epsilon')[1-f_0(\epsilon)]=0; \tag{2.4}$$

where

$$f_0(\epsilon)\equiv 1/(e^{(\epsilon-\zeta)/kT}+1), \tag{2.5}$$

ζ being the Fermi energy, k Boltzmann's constant, $F(K, K'; |\mathbf{K}-\mathbf{K}'|)$ a non-negative function, and $M(|\mathbf{K}'-\mathbf{K}|)$ a continuous and non-negative function of $\mathbf{K}$ and $\mathbf{K}'$.

(*d*) H_2 is independent of the coordinates of the lattice.

The detailed forms of $F(K, K', |\mathbf{K}-\mathbf{K}'|)$ and of $M(|\mathbf{K}-\mathbf{K}'|)$ are irrelevant for our present purpose. We also remark that Eqs. (2.3a) should hold satisfactorily for the monovalent metals, which are isotropic with respect to the three properties considered in this paper, when in a pure and undeformed state. These equations are satisfied exactly by the Sommerfeld-Bethe[16] deformable-ion model, and hold approximately in the case of Bardeen's[17] theory of electron-phonon interaction.

Employing the well-known selection rules for electronic transitions in a metallic lattice,[18] assumption (*d*) above, and a simple statistical argument, we conclude that

$$\begin{aligned} &W(\mathbf{K}', \mathbf{K})=W_1(\mathbf{K}', \mathbf{K})+W_2(\mathbf{K}', \mathbf{K}); \\ &W(\mathbf{K}, \mathbf{K}')=W_1(\mathbf{K}, \mathbf{K}')+W_2(\mathbf{K}, \mathbf{K}'); \end{aligned} \tag{2.6}$$

where $W(\mathbf{K}', \mathbf{K})$ is the probability per unit time for an electron to go from $\mathbf{K}$ to $\mathbf{K}'$ due to H, and $W(\mathbf{K}, \mathbf{K}')$ is the probability of the inverse process.

Hypothesis (*d*) also implies the equation

$$W_2(\mathbf{K}, \mathbf{K}')=W_2(\mathbf{K}', \mathbf{K}) = (2\pi/\hbar)|\langle\mathbf{K}'|H_2|\mathbf{K}\rangle|^2\delta(\epsilon'-\epsilon) \tag{2.3b}$$

which states that the collisions between electrons and lattice imperfections are elastic for arbitrary T.

[15] See F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), first edition, p. 524, for a justification of this assumption of elastic scattering for metals at $T\gg\Theta$.

[16] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (J. Springer, Berlin, 1933), 24_2, chap. 3.

[17] J. Bardeen, Phys. Rev. **52**, 688 (1937).

[18] See, for example, H. A. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1936), p. 119, Eq. (3.08).

We shall now derive the linearized equation of transport on which the present investigation is based. We begin by writing the familiar Boltzmann equation for the conduction electrons in a distorted metal, which is subjected to an electric field $\mathbf{E}$ and to a thermal gradient $\nabla_r T$,[19]

$$\begin{aligned} &\frac{1}{\hbar}\nabla_k\epsilon\cdot\nabla_r f+\frac{e\mathbf{E}}{\hbar}\cdot\nabla_k f \\ &=\frac{\Omega}{(2\pi)^3}\int\int\int d\mathbf{K}'\{W(\mathbf{K}, \mathbf{K}')f(\mathbf{K}')[1-f(\mathbf{K})] \\ &\qquad -W(\mathbf{K}', \mathbf{K})f(\mathbf{K})[1-f(\mathbf{K}')]\}; \end{aligned} \tag{2.7}$$

where $e=-|e|$ is the electronic charge and Ω is the volume of the metal.

Following a standard procedure,[19] we introduce an auxiliary function $\Phi(\mathbf{K})$ by the equation

$$f(\mathbf{K})=f_0(\epsilon)-[\partial f_0(\epsilon)/\partial\epsilon]\Phi(\mathbf{K}). \tag{2.8}$$

Employing Eqs. (2.1), (2.3b), (2.4), (2.5), (2.6), and (2.8) and retaining only linear terms in $\Phi(\mathbf{K})$, we can reduce Eq. (2.7) to the form

$$\mathfrak{L}_0\{\Phi\}+\mathfrak{L}_1\{\Phi\}=-\frac{1}{\hbar}\frac{d\epsilon}{dK}\xi\cdot\{\mathfrak{M}+\epsilon\mathfrak{N}\};$$

where

$$\xi\equiv\mathbf{K}/K,$$

$$\mathfrak{L}_0\{G\}\equiv-\frac{\Omega}{(2\pi)^3}\int\int\int d\mathbf{K}'\frac{f_0(\epsilon')}{f_0(\epsilon)}W_1(\mathbf{K}', \mathbf{K}) \times\{G(\mathbf{K}')-G(\mathbf{K})\}, \tag{2.9}$$

$$\mathfrak{L}_1\{G\}\equiv-\frac{\Omega}{4\pi^2\hbar}\frac{K^2}{(d\epsilon/dK)}\int\int d\omega'|\langle\mathbf{K}'|H_2|\mathbf{K}\rangle|^2 \times\{G(\mathbf{K}')-G(\mathbf{K})\},$$

$$\mathfrak{M}\equiv e\mathbf{E}-T(d/dT)(\zeta/T)\nabla_r T, \quad \mathfrak{N}\equiv-(1/T)\nabla_r T;$$

where $d\omega'$ is an elementary solid angle about $\mathbf{K}'$, the corresponding integration extends over the sphere $|\mathbf{K}'|=|\mathbf{K}|$, and $G(\mathbf{K})$ is an arbitrary function of $\mathbf{K}$. We are, of course, excluding the case $(d\epsilon/dK)=0$.

3. ELIMINATION OF ANGULAR VARIABLES IN THE TRANSPORT EQUATION. EXPLICIT SOLUTION FOR $T\gg\Theta$

In order to eliminate the angular variables from (2.9), we shall require the following two properties of $\mathfrak{L}_0$.

I. Let $F(\mathbf{K})$ be a function admitting the expansion

$$F(\mathbf{K})=\sum_{L=0}^{\infty}\sum_{|M|\leq L}F_{LM}(K)Y_{LM}(\Theta, \Phi) \tag{3.1}$$

[19] See, for example, Nordheim, reference 8, or Kohler, Ann. Physik (5)**40**, 601 (1940), Part 1.

in terms of the complete set of spherical harmonics $Y_{LM}(\Theta,\Phi)$ normalized over the unit sphere, where Θ and Φ are the polar and azimuthal angles of $\mathbf{K}$ with respect to a Cartesian coordinate system x_1, x_2, and x_3, fixed in the crystal. Then

$$\mathfrak{L}_0\{F(\mathbf{K})\}=\sum_{L=0}^{\infty}\sum_{|M|\leq L}\Lambda_L\{F_{LM}(K)\}Y_{LM}(\Theta,\Phi), \quad (3.2)$$

where Λ_L is a linear integral operator which acts only on K, and whose structure depends solely on $\mathfrak{L}_0$ and L.

Proof. We shall carry out our proof in two steps.

First, we remark that, according to Eq. (2.3a), $W_1(\mathbf{K},\mathbf{K}')$ depends solely on K and K', and $\cos\theta$, where θ is the angle between $\mathbf{K}$ and $\mathbf{K}'$. Supposing that the angular dependence of $W_1(\mathbf{K},\mathbf{K}')$ is regular enough, we may thus write

$$W_1(\mathbf{K},\mathbf{K}')=\sum_{L=0}^{\infty}w_L(K,K')P_L(\cos\theta), \quad (3.3)$$

where we consider $P_L(\cos\theta)$ to be normalized over the surface of the unit sphere.

Second, we employ Eqs. (2.9), (3.1), (3.3), and the addition theorem for spherical harmonics. The result of this calculation is given below:

$$\mathfrak{L}_0\{F(\mathbf{K})\}=-\frac{\Omega}{4\pi^{5/2}}\sum_{L=0}^{\infty}\sum_{|M|\leq L}\int_0^{\infty}dK'K'^2\frac{f_0(\epsilon')}{f_0(\epsilon)}\cdot\left\{\frac{w_L(K,K')}{(2L+1)^{\frac{1}{2}}}F_{LM}(K')-w_0(K,K')F_{LM}(K)\right\}\times Y_{LM}(\Theta,\Phi); \quad (3.4)$$

where $F(\mathbf{K})$ is a function of $\mathbf{K}$ admitting the expansion Eq. (3.2).

Defining the linear integral operator Λ_L by the equation

$$\Lambda_L\{g(K)\}\equiv-\frac{\Omega}{4\pi^{5/2}}\int_0^{\infty}dK'K'^2\frac{f_0(\epsilon')}{f_0(\epsilon)}\cdot\left\{\frac{w_L(K,K')}{(2L+1)^{\frac{1}{2}}}g(K')-w_0(K,K')g(K)\right\}, \quad (3.5)$$

for any function $g(K)$ of K, we immediately recognize that (3.4) is equivalent to Eq. (3.2), which completes the proof.

II. Let

$$K,\ d\epsilon/dK\neq 0;\quad M(|\mathbf{K}'-\mathbf{K}|)\not\equiv 0. \quad (3.6)$$

Then

$$\Lambda_L\{g(\mathbf{K})\}=g(K)/\tau_L(\epsilon)\ (L\geq 1), \quad (3.7)$$

for $T\gg\Theta$, where $g(K)$ is an arbitrary function of K, and $\tau_L(\epsilon)$ depends only on ϵ and Λ_L, and satisfies the inequality

$$\tau_L(\epsilon)d\epsilon/dK>0,\quad (L\geq 1). \quad (3.8)$$

Proof. We find it convenient to introduce the notation,

$$(P(\mathbf{K}'),Q(\mathbf{K}'))\equiv\int\int d\omega' P^*(\mathbf{K}')Q(\mathbf{K}'), \quad (3.9)$$

where $P(\mathbf{K}')$ and $Q(\mathbf{K}')$ are two functions of $\mathbf{K}'$, $P^*(\mathbf{K}')$ designates the complex conjugate of $P(\mathbf{K}')$, $d\omega'$ is an element of solid angle about $\mathbf{K}'$, and the integration extends over the surface of the sphere $|\mathbf{K}'|=K$.

Taking into account the circumstance that ϵ and ϵ' depend solely on K and K', respectively, because of Eq. (2.1), and invoking Eq. (2.3a), we have

$$W_1(\mathbf{K},\mathbf{K}')=\delta(\epsilon'-\epsilon)\sum_{L=0}^{\infty}M_L(K,K')P_L(\cos\theta);\qquad M_L(K,K')\equiv(P_L(\cos\theta),M(|\mathbf{K}'-\mathbf{K}|)). \quad (3.10)$$

Comparing coefficients of $P_L(\cos\theta)$ in Eqs. (3.3) and (3.10), we find

$$w_L(K,K')=M_L(K,K')\delta(\epsilon'-\epsilon). \quad (3.11)$$

Substituting Eq. (3.11) into Eq. (3.5), and changing the variable of integration therein from K' to ϵ', we get Eq. (3.7), where $\tau_L(\epsilon)$ is given by the formula

$$\frac{1}{\tau_L(\epsilon)}=-\frac{\Omega}{4\pi^{5/2}}\frac{K^2}{(d\epsilon/dK)}\left\{\frac{M_L(K,K)}{(2L+1)^{\frac{1}{2}}}-M_0(K,K)\right\},\quad (L\geq 1). \quad (3.12)$$

The properties of $M(|\mathbf{K}-\mathbf{K}'|)$ in (*c*) and Eq. (3.6), and the elementary inequality

$$P_L(\cos\theta)\leq[(2L+1)/4\pi]^{\frac{1}{2}},$$

where the equal sign holds at a finite number of points of the interval $0\leq\theta\leq\pi$ for $L\neq 0$, imply that the quantity inside the curly brackets in Eq. (3.12) is *negative*. Combining this result with the first two inequalities, Eq. (3.6), we readily obtain Eq. (3.8).

The quantities $\tau_L(\epsilon)$ have the dimensions of time. We shall presently see that $\tau_1(\epsilon)$ is the ordinary electron-phonon time of relaxation for a monovalent metal. To conform with the current nomenclature of conductivity theory, we shall call it $\tau(\epsilon)$ from now on.

It is clear that if $\mathbf{X}^{(n)}(\mathbf{K})$ is a solution of

$$(\mathfrak{L}_0+\mathfrak{L}_1)\{\mathbf{X}^{(n)}(\mathbf{K})\}=\frac{1}{n\hbar}\frac{d}{dK}(\epsilon^n)\xi, \quad (3.13)$$

then a solution of Eq. (2.9) is given by

$$\Phi(\mathbf{K})=\mathfrak{M}\cdot\mathbf{X}^{(1)}(\mathbf{K})+\mathfrak{N}\cdot\mathbf{X}^{(2)}(\mathbf{K}), \quad (3.14)$$

because of the linearity of the operators $\mathfrak{L}_0$ and $\mathfrak{L}_1$.[20] We thus concentrate our attention on Eq. (3.13).

In what follows, we suppose that $T\gg T_0$ [see Sec. 1],

[20] Compare with reference 18, Sec. 6.5.

so that $\mathcal{L}_1$ may be regarded as a perturbation with respect to $\mathcal{L}_0$. This suggests that we develop $\mathbf{X}^{(n)}$ in the following manner:

$$\mathbf{X}^{(n)}=\sum_{r=0}^{\infty}\mathbf{X}^{(n,r)}, \tag{3.15}$$

where the $\mathbf{X}^{(n,r)}$'s satisfy the set of integral equations,

$$\begin{aligned}&\mathcal{L}_0\{\mathbf{X}^{(n,0)}\}=\frac{1}{\hbar n}\frac{d}{dK}(\epsilon^n)\xi;\\ &\mathcal{L}_0\{\mathbf{X}^{(n,r)}\}=-\mathcal{L}_1\{\mathbf{X}^{(n,r-1)}\},\quad (r\geq 1).\end{aligned} \tag{3.16}$$

It is easy to see that the series Eq. (3.15) is a (formal) solution of Eq. (3.13), provided that the $\mathbf{X}^{(n,r)}$'s satisfy Eq. (3.16).

In order to solve the set Eq. (3.16), we expand $\mathbf{X}^{(n,r)}$ thus:

$$\mathbf{X}^{(n,r)}(\mathbf{K})=\sum_{L=0}^{\infty}\sum_{|M|\leq L}\mathbf{X}_{LM}{}^{(n,r)}(\epsilon)Y_{LM}(\Theta,\Phi). \tag{3.17}$$

Equations (3.2), (3.16), and (3.17) together with the orthogonality of the Y_{LM}'s, lead us to the result

$$\Lambda_L\{\mathbf{X}_{LM}{}^{(n,0)}(\epsilon)\}=\frac{1}{\hbar n}\frac{d}{dK}(\epsilon^n)(Y_{LM}(\Theta,\Phi),\xi); \tag{3.18a}$$

$$\Lambda_L\{\mathbf{X}_{LM}{}^{(n,r)}(\epsilon)\}=-(Y_{LM}(\Theta,\Phi),\mathcal{L}_1\{\mathbf{X}^{(n,r-1)}\}),\quad (r\geq 1); \tag{3.18b}$$

where we employ the notation in Eq. (3.9) in the sense that the scalar products in Eq. (3.18) represent integrations over the unit sphere $|\xi|=1$.

Since

$$(Y_{LM}(\Theta,\Phi),\xi)=0,\quad L\neq 1,$$

Eq. (3.18a) can be satisfied by placing

$$\mathbf{X}_{LM}{}^{(n,0)}(\epsilon)=0,\quad L\neq 1,$$

which implies, according to (3.17),

$$\mathbf{X}^{(n,0)}=\sum_{|M|\leq 1}\mathbf{X}_{1M}{}^{(n,0)}Y_{1M}(\Theta,\Phi). \tag{3.19}$$

We now turn to the case of high temperatures, *viz.*, $T\gg\Theta$. Under these circumstances, we can make use of Eq. (3.7) to reduce the integral equations (3.18) to a set of algebraic equations, which express $\mathbf{X}^{(n,r)}$ in terms of $\mathbf{X}^{(n,r-1)}$, *viz.*,

$$\mathbf{X}_{LM}{}^{(n,0)}(\epsilon)=\frac{\tau_L(\epsilon)}{\hbar n}\frac{d}{dK}(\epsilon^n)(Y_{LM}(\Theta,\Phi),\xi),\quad (L\geq 1); \tag{3.20a}$$

$$\mathbf{X}_{LM}{}^{(n,r)}(\epsilon)=-\tau_L(\epsilon)(Y_{LM}(\Theta,\Phi),\mathcal{L}_1\{\mathbf{X}^{(n,r-1)}\}),\quad (r\geq 1, L\geq 1). \tag{3.20b}$$

In principle, we could construct $\mathbf{X}_{LM}{}^{(n,r)}$ explicitly for *any* r of interest and $L\geq 1$ by means of (3.20). However, we shall treat only the case when the percentage changes in electrical resistivity, thermal conductivity, and absolute thermoelectric power due to lattice defects are small enough to justify the neglect of terms with $r>1$. This approximation is a good one for cold-worked monovalent metals at high temperatures.

Another fortunate circumstance arises from the fact that the only terms in Eq. (3.17) which contribute to the thermal and electrical currents, i.e., to the three effects studied in this paper, are those with $L=1$, as the reader can verify by elementary orthogonality arguments.

The explicit solution of Eq. (3.16) for $L=1$ and $r=0, 1$ can be written in an extremely compact and convenient form by means of the vectors $\boldsymbol{\varphi}_i{}^{(n,r)}$ $(i=1, 2, 3)$ defined below:

$$\begin{aligned}&\boldsymbol{\varphi}_1{}^{(n,r)}(\epsilon)\equiv(3/8\pi)^{\frac{1}{2}}[\mathbf{X}_{11}{}^{(n,r)}(\epsilon)+\mathbf{X}_{1-1}{}^{(n,r)}(\epsilon)];\\ &\boldsymbol{\varphi}_2{}^{(n,r)}(\epsilon)\equiv i(3/8\pi)^{\frac{1}{2}}[\mathbf{X}_{11}{}^{(n,r)}(\epsilon)-\mathbf{X}_{1-1}{}^{(n,r)}(\epsilon)];\\ &\boldsymbol{\varphi}_3{}^{(n,r)}(\epsilon)\equiv i(3/4\pi)^{\frac{1}{2}}\mathbf{X}_{10}{}^{(n,r)}(\epsilon).\end{aligned} \tag{3.21}$$

To find this solution, let us first calculate the jth component, $\varphi_{i,j}{}^{(n,0)}$, of $\boldsymbol{\varphi}_i{}^{(n,0)}$ with respect to the Cartesian coordinates x_1, x_2, x_3 mentioned in I, by means of Eq. (3.20a) and Eq. (3.21). We obtain

$$\varphi_{i,j}{}^{(n,0)}(\epsilon)=\frac{1}{\hbar n}\frac{d}{dK}(\epsilon^n)\tau(\epsilon)\delta_{ij}, \tag{3.22a}$$

where we have replaced $\tau_1(\epsilon)$ by $\tau(\epsilon)$.

Second, let us combine Eqs. (3.19), (3.21), and (3.22a) to express the jth component, $\chi_j{}^{(n,0)}(\mathbf{K})$, of $\mathbf{X}^{(n,0)}(\mathbf{K})$ in terms of $\varphi_{i,j}{}^{(n,0)}(\epsilon)$. Our final result is

$$\chi_j{}^{(n,0)}(\mathbf{K})=\frac{1}{\hbar n}\frac{d}{dK}(\epsilon^n)\tau(\epsilon)\xi_j. \tag{3.22b}$$

From Eqs. (3.20b), (3.21), and (3.22b), we conclude that

$$\varphi_{i,j}{}^{(n,1)}(\epsilon)=-\frac{1}{\hbar n}\frac{d}{dK}(\epsilon^n)\tau^2(\epsilon)(\boldsymbol{\tau}^{-1}(\epsilon))_{ij};$$

where (3.22c)

$$\boldsymbol{\tau}(\epsilon)\equiv\left\|\frac{3}{4\pi}(\xi_k,\mathcal{L}_1\{\xi_l\})\right\|^{-1},\quad (k,l=1,2,3).$$

The tensor $\boldsymbol{\tau}$ is of the dimension of time. From its definition in Eq. (3.22c) and that of $\mathcal{L}_1$ in Eq. (2.9) we deduce: *The tensor $\boldsymbol{\tau}$ is symmetric and the eigenvalues of $(d\epsilon/dK)\boldsymbol{\tau}$ are positive, provided that $K>0$, $d\epsilon/dK\neq 0$, and $\langle\mathbf{K}'|H_2|\mathbf{K}\rangle\not\equiv 0$.* These properties of $\boldsymbol{\tau}$ have important physical consequences, which we shall point out in Sec. 4. We omit their proof, which is essentially contained in the work of Kohler.[21]

[21] The reader will encounter no difficulties in supplying a proof if he employs definition (3.22c) together with Eqs. (3a), (3b) in Kohler, reference 19.

We conclude this Section by stating the equations satisfied by $\varphi_{i,j}^{(n,0)}$ and $\varphi_{i,j}^{(n,1)}$ for abitrary T, which we shall require in Secs. 4 and 5. Since this proof, which rests on Eqs. (3.18), (3.19), and (3.21), runs parallel to those of Eq. (3.22a) and (3.22c), we shall simply give the final results

$$\varphi_{i,j}^{(n,0)}(\epsilon)=\Psi^{(n)}(\epsilon)\delta_{ij}; \tag{3.23a}$$

$$\Lambda_1\{\varphi_{i,j}^{(n,1)}(\epsilon)\}=-\Psi^{(n)}(\epsilon)(\tau^{-1}(\epsilon))_{ij}; \tag{3.23b}$$

where $\Psi^{(n)}(\epsilon)$ satisfies the integral equation,

$$\Lambda_1\{\Psi^{(n)}(\epsilon)\}=\frac{1}{\hbar n}\frac{d}{dK}(\epsilon^n). \tag{3.23c}$$

For high temperatures, Eqs. (3.7) and (3.23c) imply

$$\Psi^{(n)}(\epsilon)=\frac{1}{\hbar n}\frac{d}{dK}(\epsilon^n)\tau(\epsilon),$$

from which it easily follows that Eq. (3.23a) reduces to Eq. (3.22a), and Eq. (3.23b) to (3.22c), for $T\gg\Theta$.

4. GENERAL FORMULAS FOR $\delta\varrho$, $\delta\kappa$, AND $\delta\mathbf{S}$

In this section, we shall develop general expressions for $\delta\varrho$, $\delta\kappa$, and $\delta\mathbf{S}$, valid for a degenerate electron gas to the first nonvanishing order of the degeneracy parameter kT/ζ and for $r\leq 1$. Since our calculations follow a pattern which arises in the theory of perfect metallic lattices, we shall omit most of the intermediate steps.

We begin by introducing the tensors $\mathbf{A}^{(r)}$, $\mathbf{B}^{(r)}$, $\mathbf{C}^{(r)}$ $(r=0, 1, \cdots)$, by the following matrix schemes

$$\mathbf{A}^{(r)}\equiv\left\|-\frac{1}{3\pi^2\hbar}\int_0^\infty d\epsilon K^2\frac{\partial f_0}{\partial\epsilon}\varphi_{i,k}^{(1,r)}(\epsilon)\right\|;$$

$$\mathbf{B}^{(r)}\equiv\left\|-\frac{1}{3\pi^2\hbar}\int_0^\infty d\epsilon K^2\frac{\partial f_0}{\partial\epsilon}\varphi_{i,k}^{(2,r)}(\epsilon)\right\|; \tag{4.1}$$

$$\mathbf{C}^{(r)}\equiv\left\|-\frac{1}{3\pi^2\hbar}\int_0^\infty d\epsilon\epsilon K^2\frac{\partial f_0}{\partial\epsilon}\varphi_{i,k}^{(2,r)}(\epsilon)\right\|.$$

We shall also require the tensors

$$\mathbf{A}\equiv\sum_{r=0}^{\infty}\mathbf{A}^{(r)};\quad \mathbf{B}\equiv\sum_{r=0}^{\infty}\mathbf{B}^{(r)};\quad \mathbf{C}\equiv\sum_{r=0}^{\infty}\mathbf{C}^{(r)}; \tag{4.2}$$

which satisfy the equations[22]

$$\mathbf{A}^T=\mathbf{A};$$

$$\mathbf{B}^T=\left\|-\frac{1}{3\pi^2\hbar}\int_0^\infty d\epsilon K^2\epsilon\frac{\partial f_0}{\partial\epsilon}\varphi_{i,k}^{(1,r)}(\epsilon)\right\|; \tag{4.3}$$

$$\mathbf{C}^T=\mathbf{C};$$

where $\mathbf{A}^T$, $\mathbf{B}^T$, and $\mathbf{C}^T$ denote the transposes of $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$, respectively.

Denoting by $\boldsymbol{\sigma}^{(0)}$, $\boldsymbol{\kappa}^{(0)}$, and $\mathbf{S}^{(0)}$ the electrical conductivity, thermal conductivity, and absolute thermoelectric power of a perfect metallic lattice; and by $\boldsymbol{\sigma}$, $\boldsymbol{\kappa}$, and $\mathbf{S}$ the corresponding quantities for a distorted lattice, we may write[23]

$$\begin{aligned}&\boldsymbol{\sigma}^{(0)}\equiv e^2\mathbf{A}^{(0)};\\ &\boldsymbol{\kappa}^{(0)}\equiv T^{-1}\{\mathbf{C}^{(0)}-\mathbf{B}^{(0)}(\mathbf{A}^{(0)})^{-1}(\mathbf{B}^{(0)})^T\};\\ &\mathbf{S}^{(0)}\equiv e^{-1}T^{-1}\{(\mathbf{A}^{(0)})^{-1}(\mathbf{B}^{(0)})^T-\zeta\mathbf{1}\};\end{aligned} \tag{4.4a}$$

$$\begin{aligned}&\boldsymbol{\sigma}\equiv e^2\mathbf{A};\\ &\boldsymbol{\kappa}\equiv T^{-1}\{\mathbf{C}-\mathbf{B}\mathbf{A}^{-1}\mathbf{B}^T\};\\ &\mathbf{S}\equiv e^{-1}T^{-1}\{\mathbf{A}^{-1}\mathbf{B}^T-\zeta\mathbf{1}\};\end{aligned} \tag{4.4b}$$

where $\mathbf{1}$ is the unit tensor, with components δ_{ij}, $(\mathbf{B}^{(0)})^T$ is the transpose of $\mathbf{B}^{(0)}$, and all products are to be interpreted as matrix multiplications.

Employing Eqs. (4.1) to (4.4), together with the well-known asymptotic expansions for integrals involving $\partial f_0/\partial\epsilon$, we obtain the following formulas, valid to the first nonvanishing order in kT/ζ:

$$\boldsymbol{\sigma}^{(0)}=\frac{e^2}{3\pi^2\hbar}\{K^2\boldsymbol{\varphi}^{(1,0)}(\epsilon)\}_{\epsilon=\zeta};$$

$$\boldsymbol{\kappa}^{(0)}=\frac{k^2T}{9\hbar}\left\{\frac{d}{d\epsilon}(K^2\boldsymbol{\varphi}^{(2,0)}(\epsilon))-\epsilon\frac{d}{d\epsilon}(K^2\boldsymbol{\varphi}^{(1,0)}(\epsilon))\right\}_{\epsilon=\zeta}; \tag{4.5a}$$

$$\mathbf{S}^{(0)}=\frac{\pi^2k^2T}{3e}\left\{(K^2\boldsymbol{\varphi}^{(1,0)}(\epsilon))^{-1}\frac{d}{d\epsilon}(K^2\boldsymbol{\varphi}^{(1,0)}(\epsilon))\right\}_{\epsilon=\zeta};$$

$$\boldsymbol{\sigma}=\frac{e^2}{3\pi^2\hbar}\{K^2\boldsymbol{\varphi}^{(1)}\}_{\epsilon=\zeta};$$

$$\boldsymbol{\kappa}=\frac{k^2T}{9\hbar}\left\{\frac{d}{d\epsilon}(K^2\boldsymbol{\varphi}^{(2)})-\epsilon\frac{d}{d\epsilon}(K^2\boldsymbol{\varphi}^{(1)})\right\}_{\epsilon=\zeta}; \tag{4.5b}$$

$$\mathbf{S}=\frac{\pi^2k^2T}{3e}\left\{(K^2\boldsymbol{\varphi}^{(1)})^{-1}\frac{d}{d\epsilon}(K^2\boldsymbol{\varphi}^{(1)})\right\}_{\epsilon=\zeta};$$

where all products are to be interpreted as above, and where we have employed the notation

$$\boldsymbol{\varphi}^{(n,r)}(\epsilon)\equiv\|\varphi_{i,k}^{(n,r)}(\epsilon)\|;\quad \boldsymbol{\varphi}^{(n)}(\epsilon)\equiv\sum_{r=0}^{\infty}\boldsymbol{\varphi}^{(n,r)}(\epsilon), \tag{4.6}$$
$$(r=0, 1, \cdots).$$

Since $\boldsymbol{\varphi}^{(n,0)}$ is a multiple of $\mathbf{1}$, by Eq. (3.22a), we can write $\boldsymbol{\sigma}^{(0)}$, $\boldsymbol{\kappa}^{(0)}$, and $\mathbf{S}^{(0)}$ in terms of scalars $\sigma^{(0)}$, $\kappa^{(0)}$, and

[22] For a proof of Eqs. (4.3), the reader may consult reference 18, Sec. 548, or Kohler, reference 19, p. 607, Eqs. (6a), (6b).

[23] In terms of the definitions in Eq. (4.4) the rate dH/dt at which heat accumulates per unit volume in a distorted metal simultaneously carrying an electrical current j_i and a thermal current w_i, due to the presence of an electric field E_k and a thermal gradient $\partial T/\partial x_k$ is as follows:

$$dH/dt=(\boldsymbol{\sigma}^{-1})_{ik}j_ij_k-\partial/\partial x_k(j_i(\mathbf{S})_{ik})+\partial/\partial x_i((\boldsymbol{\kappa})_{ik}\partial T/\partial x_k),$$

where we sum from 1 to 3 over all repeated indices.

$S^{(0)}$, thus:

$$\boldsymbol{\sigma}^{(0)}=\sigma^{(0)}\mathbf{1};\quad \boldsymbol{\kappa}^{(0)}=\kappa^{(0)}\mathbf{1};\quad \mathbf{S}^{(0)}=S^{(0)}\mathbf{1};\qquad (4.5c)$$

viz., our undeformed lattice is isotropic with respect to the three effects studied in this paper. This property of isotropy is a consequence of Eq. (2.3a).

Neglecting all terms of the form $\boldsymbol{\varphi}^{(n_1,r_1)}\cdots\boldsymbol{\varphi}^{(n_s,r_s)}$ with $r_1+\cdots+r_s>1$, Eqs. (4.5a) and (4.5b) yield the following formulas for the changes $\delta\boldsymbol{\sigma}$, $\delta\boldsymbol{\kappa}$, and $\delta\mathbf{S}$ of $\boldsymbol{\sigma}^{(0)}$, $\boldsymbol{\kappa}^{(0)}$, and $\mathbf{S}^{(0)}$ due to static lattice deformations:

$$\delta\boldsymbol{\sigma}=\boldsymbol{\sigma}-\boldsymbol{\sigma}^{(0)}=\frac{e^2}{3\pi^2\hbar}\{K^2\boldsymbol{\varphi}^{(1,1)}(\epsilon)\}_{\epsilon=\zeta};$$

$$\delta\boldsymbol{\kappa}=\boldsymbol{\kappa}-\boldsymbol{\kappa}^{(0)}=\frac{k^2T}{9\hbar}\left\{\frac{d}{d\epsilon}(K^2\boldsymbol{\varphi}^{(2,1)}(\epsilon))-\epsilon\frac{d}{d\epsilon}(K^2\boldsymbol{\varphi}^{(1,1)}(\epsilon))\right\}_{\epsilon=\zeta};\qquad (4.7)$$

$$\delta\mathbf{S}=\mathbf{S}-\mathbf{S}^{(0)}=\frac{\pi^2k^2T}{3e}\left\{\frac{d}{d\epsilon}[(K^2\boldsymbol{\varphi}^{(1,0)}(\epsilon))^{-1}\times(K^2\boldsymbol{\varphi}^{(1,1)}(\epsilon))]\right\}_{\epsilon=\zeta}.$$

We emphasize the fact that Eqs. (4.7) hold for $T\gg T_0$.

Before discussing the case $T\gg\Theta$, we pause to derive a theorem which we shall find useful in Sec. 5.

Let T be such that the eigenvalues $(\delta\sigma)_i$, $(\delta\kappa)_j$, $(\delta\mathbf{S})_k$ $(i,j,k=1,2,3)$ of $\delta\boldsymbol{\sigma}$, $\delta\boldsymbol{\kappa}$, and $\delta\mathbf{S}$ are small compared to $\boldsymbol{\sigma}^{(0)}$, $\boldsymbol{\kappa}^{(0)}$, $\mathbf{S}^{(0)}$, respectively, *viz.*, $T\gg T_0$, and let

$$(\boldsymbol{\tau}(\epsilon))^{-1}=p(\epsilon)\boldsymbol{\lambda},\qquad (4.8)$$

where $p(\epsilon)$ is a scalar function of ϵ, and $\boldsymbol{\lambda}$ is a symmetric tensor independent of ϵ and T. We then have

(1) The principal directions of $\delta\boldsymbol{\sigma}$, $\delta\boldsymbol{\kappa}$, and $\delta\mathbf{S}$ are the same as those of $\boldsymbol{\lambda}$; they do not depend on T.

(2) The eigenvalues of $\delta\boldsymbol{\sigma}$, $\delta\boldsymbol{\kappa}$, and $\delta\mathbf{S}$ are proportional to the eigenvalues λ_i of $\boldsymbol{\lambda}$,

$$(\delta\boldsymbol{\sigma})_i/(\delta\boldsymbol{\sigma})_j=(\delta\boldsymbol{\kappa})_i/(\delta\boldsymbol{\kappa})_j=(\delta\mathbf{S})_i/(\delta\mathbf{S})_j=\lambda_i/\lambda_j,\qquad (4.9)$$

for $i,j=1,2,3$, i.e., the anisotropy ratios $(\delta\boldsymbol{\sigma})_i/(\delta\boldsymbol{\sigma})_j$, $(\delta\boldsymbol{\kappa})_i/(\delta\boldsymbol{\kappa})_j$, $(\delta\mathbf{S})_i/(\delta\mathbf{S})_j$ are equal and independent of T.

Proof: Eqs. (3.23b), (4.6), and (4.8) imply

$$\Lambda_1\{\boldsymbol{\varphi}^{(n,1)}(\epsilon)\}=-\Psi^{(n)}(\epsilon)p(\epsilon)\boldsymbol{\lambda}.$$

In virtue of the linearity of Λ_1, this equation shows that $\boldsymbol{\varphi}^{(n,1)}(\epsilon)$ is a scalar multiple of $\boldsymbol{\lambda}$, since the latter does not depend on ϵ by the hypotheses of our theorem. Coupling this result with the fact that $\boldsymbol{\varphi}^{(n,0)}$ is a multiple of $\mathbf{1}$, we conclude from Eq. (4.7):

$$\delta\boldsymbol{\sigma}=\alpha(T)\boldsymbol{\lambda};\quad \delta\boldsymbol{\kappa}=\beta(T)\boldsymbol{\lambda};\quad \delta\mathbf{S}=\gamma(T)\boldsymbol{\lambda};\qquad (4.10)$$

where the scalars α, β, γ depend on T. Assertions (1) and (2) of our theorem are immediate consequences of Eq. (4.10) and the assumption that $\boldsymbol{\lambda}$ is independent of T, which completes the proof.

Let us now turn to the case $T\gg\Theta$. In this region, we can use Eqs. (3.22a), (3.22c), and (4.7) to prove that

$$\delta\boldsymbol{\sigma}=-\frac{e^2}{3\pi^2\hbar}\left\{K^2\frac{d\epsilon}{dK}\tau^2(\epsilon)\boldsymbol{\tau}^{-1}(\epsilon)\right\}_{\epsilon=\zeta};$$

$$\delta\boldsymbol{\kappa}=\frac{\pi^2e^2T}{3e^2}\delta\boldsymbol{\sigma};\qquad (4.11)$$

$$\delta\mathbf{S}=-\frac{\pi^2k^2T}{3e}\left\{\frac{d}{d\epsilon}(\tau(\epsilon)\boldsymbol{\tau}^{-1}(\epsilon))\right\}_{\epsilon=\zeta}.$$

From Eq. (4.11), we see that $\delta\boldsymbol{\kappa}$ and $\delta\boldsymbol{\sigma}$ satisfy the Wiedemann-Franz law if $T\gg\Theta$.[24] This circumstance simplifies the remaining calculations in this temperature range, because it reduces our task to the computation of $\delta\boldsymbol{\sigma}$ and $\delta\mathbf{S}$.

To calculate the change in resistivity, $\delta\boldsymbol{\varrho}$, we exploit the fact that $(\delta\boldsymbol{\sigma})_i\ll\boldsymbol{\sigma}^{(0)}$ for $T\gg T_0$, which implies to first order that

$$\delta\boldsymbol{\varrho}\equiv\boldsymbol{\varrho}-\boldsymbol{\varrho}^{(0)}=-(\boldsymbol{\varrho}^{(0)})^2\delta\boldsymbol{\sigma}\quad(T\gg T_0);\qquad (4.12)$$

where $\boldsymbol{\varrho}^{(0)}\equiv\rho^{(0)}\mathbf{1}$, $\rho^{(0)}\equiv1/\sigma^{(0)}$, and $\boldsymbol{\varrho}\equiv(\boldsymbol{\sigma})^{-1}$.

If $T\gg\Theta$, Eqs. (4.11) and (4.12) permit us to write, after a straightforward calculation,[25]

$$\delta\boldsymbol{\varrho}=\frac{3\pi^2\hbar^2}{e^2}\left\{K^{-2}\left(\frac{d\epsilon}{dK}\right)^{-1}\boldsymbol{\tau}^{-1}(\epsilon)\right\}_{\epsilon=\zeta};$$

$$\delta\mathbf{S}=-(\boldsymbol{\varrho}^{(0)})^{-1}\delta\boldsymbol{\varrho}\{\mathbf{S}^{(0)}+\mathbf{S}^{(1)}\};\qquad (4.13)$$

where

$$\mathbf{S}^{(1)}\equiv\frac{\pi^2k^2T}{3e}\left\{\left(K^2\frac{d\epsilon}{dK}\boldsymbol{\tau}(\epsilon)\right)\frac{d}{d\epsilon}\left(K^2\frac{d\epsilon}{dK}\boldsymbol{\tau}(\epsilon)\right)^{-1}\right\}_{\epsilon=\zeta}.$$

We now make two remarks of a general nature concerning $\delta\boldsymbol{\varrho}$, $\delta\boldsymbol{\kappa}$, and $\delta\mathbf{S}$ for $T\gg\Theta$.

Provided (3.6) holds for $\epsilon=\zeta$ and that we exclude the trivial case $\langle\mathbf{K}'|H_2|\mathbf{K}\rangle\equiv0$, we may employ the inequality (3.8) and the result on the eigenvalues of $\boldsymbol{\tau}$ in Sec. 3 to conclude that

$$(\delta\boldsymbol{\varrho})_i>0,\quad T\gg\Theta.\qquad (4.14)$$

This inequality provides a check of our theory in the high-temperature region, since it is well-known experimentally that the types of lattice imperfections considered here always lead to an increase of the electrical resistivity of the metal in which they are embedded.

Second, the temperature dependence of $\delta\boldsymbol{\varrho}$ for $T\gg\Theta$ can be deduced solely from Eq. (4.13) and the definition (3.22c) of $\boldsymbol{\tau}$. However, to find how $\delta\boldsymbol{\kappa}$ and $\delta\mathbf{S}$ vary

[24] This result is in agreement with a general theorem derived by Kohler. See reference 19, pp. 613–615. *Note added in proof:*— It is also in good agreement with experiment for cold-worked metals, as shown by the work of G. Tammann and W. Boehme, Ann. Physik (5) **22**, 500 (1935).

[25] Compare the second Eq. (4.13) with Eq. (9), p. 385, reference 9, which holds when the lattice imperfections scatter electrons isotropically.

with temperature in this region it is essential to know how τ depends on T. Taking $\tau \propto T^{-1}$ for $T \gg \Theta$, in accordance with the theories of Sommerfeld-Bethe,[16] Nordheim,[8] and Bardeen,[17] Eqs. (3.22c), (4.11), and (4.13) lead to the results

$$\delta\varrho, \delta\mathbf{S}: \text{independent of } T; \quad \delta\kappa \propto 1/T; \quad (4.15)$$

for $T \gg \Theta$.

Let us compare Eq. (4.15) with the empirical results for cold-worked metals. If $T \gg \Theta$ and T is such that no appreciable annealing takes place, the changes in electrical conductivity[26] and absolute thermoelectric power[12,27] do not vary with T, while those in thermal conductivity[24] are inversely proportional to T, in agreement with Eq. (4.15), in whose derivation we implicitly assumed that the lattice deformations were independent of T.

5. CHANGES IN THE ELECTRICAL, THERMAL, AND THERMOELECTRIC PROPERTIES OF ISOTROPIC METALS BY BURGERS DISLOCATIONS

To provide an illustration of the usefulness of the general formulas in Sec. 4, we compute $\delta\varrho$, $\delta\kappa$, and $\delta\mathbf{S}$ for the idealized situation of an elastically isotropic metal having an array of parallel positive-negative pairs of Burgers edge dislocations. The assumption of elastic isotropy is not essential; it is made solely to simplify our calculations.

In terms of a Cartesian coordinate system x_1, x_2, x_3, fixed in the crystal of interest, let us consider a positive and a negative edge dislocation, having their singular lines at $x_1=0$, $x_2=R/2$, and $x_1=0$, $x_2=-R/2$, respectively, where $R\{K\}_{\epsilon=\zeta} \gg 1$. Then it follows from the work of Dexter[4] that

$$|\langle \mathbf{K}'|H_2|\mathbf{K}\rangle|^2 = \frac{D^2 \sin^2(\bar{K}_3\Omega^{\frac{1}{3}}/2)\bar{K}_2^2}{(1+\bar{K}^2/q^2)\bar{K}_3^2\bar{K}_s^4}; \qquad D^2 \equiv \frac{128\pi^2 Z^2 e^4 \lambda^2}{\Delta^2\Omega^2 q^4}\left(\frac{1-2\nu}{1-\nu}\right); \quad (5.1)$$

where $\bar{K}_i \equiv K_i' - K_i$ $(i=1, 2, 3)$, $\bar{K}_s^2 \equiv \bar{K}_1^2 + \bar{K}_2^2$, q is a screening constant of the order of 10^8 cm^{-1}, Z is the effective nuclear charge, Δ is the atomic volume, ν is Poisson's ratio, and λ is the unit crystallographic slip distance.

From Eq. (3.22c) and Eq. (5.1) we obtain the following values for the nonvanishing components of $(\tau)^{-1}$, by direct computation:

$$(\tau^{-1})_{11} = \frac{3}{64}\frac{\Omega^{4/3}D^2}{\hbar q(d\epsilon/dK)}a^2\left(\cot^{-1}a + \frac{a}{1+a^2}\right); \qquad (\tau^{-1})_{22} = 3(\tau^{-1})_{11}; \quad (5.2)$$

where $a \equiv q/2K$.

In order to avoid ambiguities, we employ $\delta\varrho^{(1)}$, $\delta\kappa^{(1)}$, and $\delta\mathbf{S}^{(1)}$ to designate the changes in electrical resistivity, thermal conductivity, and absolute thermoelectric power of a metal of volume Ω, which contains exactly one dislocation pair in its interior. If N pairs per unit area are present, we denote the corresponding changes by $\delta\varrho^{(N)}$, $\delta\kappa^{(N)}$, $\delta\mathbf{S}^{(N)}$. If we are dealing with a parallel array of positive-negative edge dislocations, such that the distances between the dislocation pairs are large enough so that no appreciable interference effects arise, we may write

$$\delta\varrho^{(N)} = \Omega^{\frac{2}{3}}N\delta\varrho^{(1)}; \quad \delta\kappa^{(N)} = \Omega^{\frac{2}{3}}N\delta\kappa^{(1)}; \quad \delta\mathbf{S}^{(N)} = \Omega^{\frac{2}{3}}N\delta\mathbf{S}^{(1)}. \quad (5.3)$$

A straightforward calculation based on Eq. (4.13), where we replace $\delta\varrho$ by $\delta\varrho^{(1)}$, Eqs. (5.2), and (5.3), leads to the result,

$$(\delta\varrho^{(N)})_{11} = \frac{36\pi^4\hbar Z^2 e^2 \lambda^2 N}{\Delta^2 q^6}\left(\frac{1-2\nu}{1-\nu}\right)^2 \cdot \left\{\frac{a^3}{K(d\epsilon/dK)^2}\left(\cot^{-1}a + \frac{a}{1+a^2}\right)\right\}_{\epsilon=\zeta}; \quad (5.4a)$$

$$(\delta\varrho^{(N)})_{22} = 3(\delta\varrho^{(N)})_{11};$$

all other components vanishing.

For the important special case of free electrons, *viz.*,

$$\epsilon = \hbar^2 K^2/2m^*, \quad (5.5)$$

where m^* is the effective mass, we obtain the following explicit expression for $(\delta\varrho^{(N)})_{11}$:

$$(\delta\varrho^{(N)})_{11} = \frac{12\pi^2 Z^2 e^2 m^{*2} \lambda^2 N}{\hbar^3 \Delta^2 q^6 n_0}\left(\frac{1-2\nu}{1-\nu}\right)^2 \cdot \left\{a^3\left[\cot^{-1}a + \frac{a}{1+a^2}\right]\right\}_{\epsilon=\zeta}; \quad (5.4a)'$$

where n_0 is the effective number of free electrons per unit volume at $\epsilon=\zeta$.

The second Eq. (5.4a) and Eq. (5.4a)′ coincide with the results derived by Dexter[4] from Eqs. (1.1) and (5.1). This agreement is not fortuitous, as we shall see in the Appendix.

Equations (4.11), (4.12), (4.13), (5.2), and (5.4a) lead us to the following formulas for the nonvanishing components of $\delta\kappa^{(N)}$ and $\delta\mathbf{S}^{(N)}$, by calculations similar

[26] G. Tammann and K. L. Dreyer, Ann. Physik (5) **16**, 111 (1933). It is difficult to decide whether the experiments of W. J. Rutter and J. Reekie, Phys. Rev. **78**, 70 (1950), which show that $\delta\varrho$ depends on T for severely cold-worked polycrystalline Cu and Al, contradict Eq. (4.15), which is based on the assumption that the microscopic strain field does not vary with T, or whether they can be explained in terms of a variation of the lattice strains with T. *Note added in proof:*—The work of Rutter and Reekie is in disagreement with recent experiments of C. W. Berghout, Physica **18**, 978 (1953).

[27] G. Tammann and G. Bandel, Ann. Physik (5) **16**, 120 (1933).

to those employed to derive (5.4a):

$$(\delta\kappa^{(N)})_{11}=-\frac{\pi^2k^2}{3e^2}T(\rho^{(0)})^{-2}(\delta\varrho^{(N)})_{11}; \tag{5.4b}$$

$$(\delta\kappa^{(N)})_{22}=3(\delta\kappa^{(N)})_{11};$$

$$(\delta\mathbf{S}^{(N)})_{11}=\frac{\pi^2k^2T}{3e}\left\{\frac{d}{d\epsilon}\log\left(\frac{K^2(d\epsilon/dK)}{\tau(\epsilon)}\right)-\frac{2}{K}\frac{dK}{d\epsilon}f(a)\right\}_{\epsilon=\zeta}(\varrho^{(0)})^{-1}(\delta\varrho^{(N)})_{11}; \tag{5.4c}$$

$$(\delta\mathbf{S}^{(N)})_{22}=3(\delta\mathbf{S})_{11};$$

where

$$f(a)\equiv\frac{a^3}{(1+a^2)^2}\left(\cot^{-1}a+\frac{a}{1+a^2}\right)^{-1}.$$

The fact that for edge dislocations τ satisfies Eq. (4.8), coupled with Eqs. (4.12), (5.4a), (5.4b), and (5.4c), allows us to conclude for $T\gg T_0$:

(1)′ The principal directions of $\delta\varrho^{(N)}$, $\delta\kappa^{(N)}$, and $\delta\mathbf{S}^{(N)}$ are parallel to the x_1, x_2, and x_3 axes.

(2)′ The anisotropy ratios for the nonvanishing eigenvalues of these tensors are thus

$$(\delta\varrho)_{11}/(\delta\varrho)_{22}=(\delta\kappa)_{11}/(\delta\kappa)_{22}=(\delta\mathbf{S})_{11}/(\delta\mathbf{S})_{22}=\tfrac{1}{3}. \tag{5.5}$$

Let us now compare the results of this section with the corresponding experimental data for monovalent metals. The comparison between the observed and calculated changes in electrical resistivity due to cold work has been carried out in reference 4. We shall limit our attention to the effect of plastic deformations on the thermoelectric power of monovalent metals.

Since the majority of the experiments have been carried out with polycrystalline materials, we shall assume that the cold-working process creates N pairs of edge dislocations, whose surfaces of discontinuity (slip planes) are oriented at random. We may then write for the changes $\delta\rho$ and δS in electrical resistivity and thermoelectric power,

$$\begin{aligned}\delta\rho&=\tfrac{1}{3}\{(\delta\varrho^{(N)})_{11}+(\delta\varrho^{(N)})_{22}\};\\ \delta S&=\tfrac{1}{3}\{(\delta\mathbf{S}^{(N)})_{11}+(\delta\mathbf{S}^{(N)})_{22}\}.\end{aligned} \tag{5.6}$$

From now on, we shall focus our attention on the ratio

$$Q\equiv(\rho^{(0)}/T)(\delta S/\delta\rho), \tag{5.7}$$

which is independent of T and N for $T\gg\Theta$, by virtue of (4.15), (5.6), and the fact that $\rho^{(0)}\propto T$ for $T\ll\Theta$.

The only monovalent metals for which Q has been measured are the noble metals, and the results may be stated thus, for $T\gg\Theta$:[28]

$$Q\sim+10^{-8}\ \text{volt}/(^\circ\text{K})^2. \tag{5.8}$$

[28] We arrived at Eq. (5.8) by employing the data on δS in references 12 and 27, coupled with that on $(\delta\rho/\rho^{(0)})$ in reference 26.

In the present state of the theory of metals, it is not possible to predict Eq. (5.8) from first principles, because of our lack of knowledge concerning the energy dependence of τ and $d\epsilon/dK$ near $\epsilon=\zeta$. The following statements are therefore of a preliminary character.

From Eqs. (5.4c) and (5.6), we find that our theory implies for edge dislocations

$$Q=\frac{\pi^2k^2}{3e}\left\{\frac{d}{d\epsilon}\log\left(\frac{K^2(d\epsilon/dK)}{\tau(\epsilon)}\right)-\frac{2}{K}\frac{dK}{d\epsilon}f(a)\right\}_{\epsilon=\zeta}. \tag{5.9}$$

According to both the Sommerfeld-Bethe[16] and the Bardeen[17] theories of conductivity,

$$K^2(d\epsilon/dK)/\tau(\epsilon)\propto C^2, \tag{5.10}$$

where C is a *positive* number, the so-called Sommerfeld-Bethe "constant," which is proportional to the mean kinetic energy of a conduction electron in state $\mathbf{K}$.[16] It is thus plausible to suppose

$$(1/C)(dC/d\epsilon)\geq 0. \tag{5.11}$$

Since $dK/d\epsilon$ is presumably *positive* at $\epsilon=\zeta$, we see from Eq. (5.9) and Eq. (5.11) that

$$Q\leq\frac{2\pi^2k^2}{3|e|}\left\{\frac{1}{K}\frac{dK}{d\epsilon}f(a)\right\}_{\epsilon=\zeta}. \tag{5.12}$$

the equality sign corresponding to $\{dC/d\epsilon\}_{\epsilon=\zeta}=0$.

For order-of-magnitude purposes, we may write

$$\left\{\frac{2}{K}\frac{dK}{d\epsilon}\right\}_{\epsilon=\zeta}\approx\frac{1}{\zeta}, \tag{5.13}$$

so that Eq. (5.12) becomes

$$Q\lesssim(\pi^2k^2/3|e|\zeta)\{f(a)\}_{\epsilon=\zeta}. \tag{5.14}$$

Let us evaluate the right-hand side of (5.14) for the typical case of Cu, where we put $a=0.8$ for $\epsilon=\zeta$.[4] We then have

$$Q\lesssim 5\times10^{-10}\ \text{volt}/(^\circ\text{K})^2. \tag{5.15}$$

For the optimum case when $\{dC/d\epsilon\}_{\epsilon=\zeta}=0$, we see from Eq. (5.15) that Q has the correct sign but that it is considerably smaller than the corresponding experimental value in Eq. (5.8).

In spite of the many simplifications which we have introduced into our calculation, we are of the opinion that this result means that *edge dislocations do not account for the observed Q in plastically deformed monovalent metals*, contrary to the views put forward in reference 5.

It is believed that vacancies are responsible for a substantial amount of the residual electrical resistivity in plastically deformed metals.[29] We are now calculating

[29] N. F. Mott, Phil. Mag. 43, 1167 (1952).

Q for lattice defects of this type by the methods of Sec. 4, in order to determine whether the discrepancy between our preliminary theory and experiment can be removed in this manner.

It is a pleasure to thank Professor D. L. Dexter for his stimulating discussions during the course of this work. The author also wishes to thank his colleagues, Mr. D. M. Chase, Dr. J. R. DeLaunay, Dr. E. W. Kammer, Mr. T. E. Pardue, and Dr. E. I. Salkovitz for their friendly interest in the present investigation.

APPENDIX

We shall now prove that the formulas for $\delta\sigma$, $\delta\kappa$, and $\delta\mathbf{S}$, derived from the simple transport Eq. (1.1) are identical to the corresponding expressions in Sec. 4, provided that $T\gg\Theta$ and that only terms of order $r\leq 1$ are retained, in the sense of Secs. 3 and 4.

We begin by introducing the notation

$$f(\mathbf{K})=f(\epsilon)-(\partial f_0/\partial\epsilon)\Phi'(\mathbf{K}), \tag{A.1}$$

where we employ the prime to avoid possible confusion with $\Phi(\mathbf{K})$ in Sec. 2.

From Eqs. (2.1), (2.3b), and (A.1) we obtain by the usual statistical argument

$$[\partial f/\partial t]_{\text{def}}=(\partial f_0/\partial\epsilon)\mathfrak{L}_1\{\Phi'\}. \tag{A.2}$$

Using Eqs. (1.1), (A.1), and (A.2), we obtain the desired form of the equation of transport,

$$\frac{1}{\tau(\epsilon)}\Phi(\mathbf{K})+\mathfrak{L}_1\{\Phi'\}=\frac{1}{\hbar}\frac{d\epsilon}{dK}\xi\cdot\{\mathfrak{M}+\epsilon\mathfrak{N}\}. \tag{A.3}$$

Letting $\mathbf{X}'^{(n)}$ be a solution of

$$\frac{1}{\tau(\epsilon)}\mathbf{X}'^{(n)}(\mathbf{K})+\mathfrak{L}_1\{\mathbf{X}'^{(n)}(\mathbf{K})\}=\frac{1}{\hbar n}\frac{d}{dK}(\epsilon^n)\xi, \tag{A.4}$$

it is clear that

$$\Phi'=\mathfrak{M}\cdot\mathbf{X}'^{(1)}(\mathbf{K})+\mathfrak{N}\cdot\mathbf{X}'^{(2)}(\mathbf{K}), \tag{A.5}$$

is a solution of Eq. (A.3) because of the linearity of $\mathfrak{L}_1$.

Following the pattern of Sec. 3, we develop $\mathbf{X}'^{(n)}$ in a series of type (3.15), *viz.*,

$$\mathbf{X}'^{(n)}(\mathbf{K})=\sum_{r=0}^{\infty}\mathbf{X}'^{(n,r)}(\mathbf{K}), \tag{A.6}$$

where the vectors $\mathbf{X}'^{(n,r)}$ obey the set of equations,

$$\begin{aligned}&\mathbf{X}'^{(n,0)}(\mathbf{K})=\frac{1}{\hbar n}\frac{d}{dK}(\epsilon^n)\tau(\epsilon)\xi;\\ &\mathbf{X}'^{(n,r)}(\mathbf{K})=-\tau(\epsilon)\mathfrak{L}_1\{\mathbf{X}'^{(n,r-1)}(\mathbf{K})\}.\\ &\qquad(r\geq 1).\end{aligned} \tag{A.7}$$

Denoting by $\chi'_j{}^{(n,r)}$ the jth component of $\mathbf{X}'^{(n,r)}$, we can write, by a known property of complete orthonormal sets and the fact that ϵ depends on K only, by virtue of Eq. (2.1),

$$\chi'_j{}^{(n,r)}(\mathbf{K})=\sum_{i=1}^{3}\varphi'_{i,j}{}^{(n,r)}(\epsilon)\xi_i+\psi_j{}^{(n,r)}(\mathbf{K}), \tag{A.8}$$

where the coefficients $\varphi'_{i,j}{}^{(n,r)}(\epsilon)$ depend solely on ϵ, and where $(\psi_j{}^{(n,r)}(\mathbf{K}),\xi_l)=0$ for $l=1, 2, 3$.

From Eqs. (A.7) and (A.8) we obtain

$$\varphi'_{i,j}{}^{(n,1)}=-\frac{3}{4\pi}\frac{1}{\hbar n}\frac{d}{dK}(\epsilon^n)\tau^2(\epsilon)(\xi_i,\mathfrak{L}_1\{\xi_j\}), \tag{A.9}$$

where we have employed the orthogonality of the ξ_l's.

Comparing the first Eq. (A.7) with (3.22b) and (A.9) with (3.22c), we conclude for $T\gg\Theta$ that

$$\chi'_j{}^{(n,0)}(\mathbf{K})=\chi_j{}^{(n,0)}(\mathbf{K});\quad\varphi'_{j,i}{}^{(n,1)}(\epsilon)=\varphi_{j,i}{}^{(n,1)}(\epsilon). \tag{A.10}$$

Let us denote the changes in electrical resistivity, thermal conductivity, and absolute thermoelectric power computed by means of the transport equation (A.3) by $\delta\varrho'$, $\delta\kappa'$, and $\delta\mathbf{S}'$, respectively. Restricting ourselves to terms of order $r\leq 1$, we can prove by the methods of Sec. 4 that the tensors $\delta\varrho'$, $\delta\kappa'$, and $\delta\mathbf{S}'$ are functions of $\chi'_i{}^{(n,0)}$ and $\varphi'_{j,i}{}^{(n,1)}$ only, just as $\delta\varrho$, $\delta\kappa$, and $\delta\mathbf{S}$ are functions of $\chi_i{}^{(n,0)}$ and $\varphi_{j,i}{}^{(n,1)}$ only. Moreover, the corresponding functions in both sets are *identical*. Employing these facts in conjunction with (A.10), we conclude that

$$\delta\varrho'=\delta\varrho,\quad\delta\kappa'=\delta\kappa,\quad\delta\mathbf{S}'=\delta\mathbf{S}, \tag{A.11}$$

for $T\gg\Theta$, which was to be demonstrated.