Two-dimensional treatment of nonlinear thermoelectricity in homogeneous metals

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Electron transport due to large temperature gradients in a homogeneous monovalent metal is studied. In contrast to linear theory, a nonlinear thermoelectric current depends on temperature variations not only in one direction but in other directions as well. When a temperature distribution is essentially two dimensional, the calculated current has circular components. Thus, contrary to linear theory, it is impossible to use a zero-current steady-state condition to calculate the voltage induced by this effect. A new steady-state condition is proposed which allows currents to complete a circuit. A thermoelectric voltage is evaluated for the case which closely approximates recent experimental results creating large temperature gradients in metals.

I. INTRODUCTION

It has been generally accepted that large temperature gradients cannot be produced in metals because of their high thermal diffusivity, and thus electron-transport phenomena of thermal origin have always been considered within the framework of a linear theory.[1-3] For semiconductors, on the other hand, nonlinear transport phenomena are well known and widely explored.[4] New experimental data indicate that a nonlinear theory is now appropriate for metals as well, and this is the purpose of this paper.

Modern achievements in short-pulse-laser generation and thin-film technology allow us to produce very large temperature gradients in metals without sample destruction. In recent experiments,[5] a pulsed laser was used to heat a thin metal film deposited on a grating. The edges of the film were far from the laser spot and thus at a constant, ambient temperature. Typical pulse-duration times were 0.1–1 μs, and the grating wavelength was $\Lambda \approx 10$ μm. A small potential was developed by each ripple of the grating, and the voltage was summed across the $N \approx 10^3$ periods producing a measured voltage of up to 1 V. The large temperature gradients in this experiment (in metal films) were estimated to be on the order of 10^6 K/cm.[5] This technology may permit the development of small, inexpensive, convenient sensors.

Linear thermoelectric effects cannot account for the measured voltage.[5] Nonlinear contributions to the thermopower may be a possible explanation of these experiments. Thus new experimental possibilities to create large temperature gradients force us to reexamine a branch of physics very popular in the first half of this century: thermoelectricity in metals.

We have already studied nonlinear thermopower coefficients in metals in the case of monovalent homogeneous metals obeying a parabolic dispersion law where temperature distribution was one dimensional.[6] In the present paper, we will enlarge that derivation to include monovalent homogeneous metals generally, and to develop a two-dimensional theory. The latter is of great importance, because in laser-irradiated thin films deposited on a grating there are not only large gradients in the x direction, parallel to the film surface, but also in the z direction, perpendicular to the surface. Indeed, our estimate of the z gradient is about 10^8 K/cm. This makes the usual open-circuit approximation invalid for calculating the thermoelectric field, since the cold portion of the film serves to complete the circuit. Similarly, a multidimensional analysis implies that x and z gradients will be coupled in the nonlinear regime. Developing this idea is the primary focus of the present work.

In Sec. II we briefly describe the derivation of Ref. 6, with a particular idea toward generalization to all monovalent metals. In Sec. III we consider the two-dimensional calculation using parameters consistent with experiment.[5] Finally, Sec. IV contains concluding remarks, and we discuss new possibilities opened up by this research. Throughout the paper we assume local thermal equilibrium, without which temperature would be undefined.

II. THEORY OF NONLINEAR THERMOPOWER IN HOMOGENEOUS MONOVALENT METALS

We now briefly reproduce the results from Ref. 6, with an eye toward generalization to all monovalent metals and greater physical insight. We being with an electron current j arising from large temperature gradients ∇T as

$$\mathbf{j}=\sigma[\mathbf{E}-\nabla(\zeta/e)-\alpha\nabla T-\alpha_1\nabla(\Delta T)-\alpha_2\nabla T(\Delta T) -\alpha_3\nabla(\nabla T)^2-\alpha_4(\nabla T)^3\cdots] , \quad (1)$$

where σ is the conductivity, ζ is the chemical potential, and α_i are the thermopower coefficients. Using the Boltzmann equation to describe electron transport in the conventional τ approximation,[7] and assuming a spherically symmetric Fermi surface, we find that nonlinear contributions to the electric current due to ∇T can be written as

$$\mathbf{j}^i=e\int dS\frac{1}{4\pi^3\hbar v_k}d\varepsilon_k v_k^i(\tau v_k^j\nabla_j)(\tau v_k^l\nabla_l)(\tau v_k^m\nabla_m)n_k^0 . \quad (2)$$

Here k refers to electron state space, v_k and ε_k refer to the electron velocity and energy, respectively, n_k^0 is the electron density at local thermal equilibrium, and dS denotes integration in k space, as per Ref. 6.

At this point we generalize the result obtained in Ref. 6, given by Eq. (2) above, by introducing the relaxation time $\tau(k)$, instead of $\tau(\varepsilon_k)$. This removes the condition of a spherical symmetry in k space, and then Eq. (2) is valid for all metals with a single conduction band. In the simplest case (Bloch model), where $\varepsilon_k=(\hbar k)^2/2m$, m is the electron mass, and $\tau(\varepsilon_k)\approx\varepsilon_k^{3/2}$, we obtain for $\mathbf{j}^i$

$$\mathbf{j}^i=\sigma\frac{7\pi^2k_B^2\tau^2(\mu)}{15me}[\nabla(\Delta T^2)+\tfrac{4}{3}T\nabla(\Delta T)] , \quad (3)$$

where $\tau(\mu)$ is the relaxation time averaged over the Fermi surface, and k_B is the Boltzmann constant. It follows from Eq. (3) that

$$\alpha_1=C_1T\frac{\pi^2k_B^2\tau(\mu)^2}{me},\quad \alpha_i=C_i\frac{\pi^2k_B^2\tau(\mu)^2}{me},\quad i=1,3, , \quad (4)$$

where $C_1=\frac{14}{5}$, $C_2=C_3=\frac{14}{15}$. This is the major result of Ref. 6.

Fortunately, Eq. (4) is very general. We note that a precise knowledge of the shape of the Fermi surface and of the exact $\tau(k)$ dependence only changes the numerical value of the coefficients C_i. For free electrons when τ is independent of energy,[8] for example, $C_i=1$.

At the high-temperatures relevant here, $\tau(\mu)\approx 1/T$ due to electron phonon interaction. Separating out temperature-dependent terms, and combining everything else into constants β and γ, we can rewrite Eq. (3) more generally as

$$\mathbf{j}^i=\frac{\sigma}{T^2}[\beta\nabla(\Delta T^2)+\gamma T\nabla(\Delta T)] . \quad (5)$$

Setting $\mathbf{j}=\mathbf{0}$ in Eq. (1), we obtain a general expression for the thermopower coefficients valid for all monovalent metals at high temperatures,

$$E=\alpha\nabla T+\frac{\beta}{T^2}\nabla(\Delta T^2)+\frac{\gamma}{T}\nabla(\Delta T) . \quad (6)$$

We can provide a physical interpretation of Eq. (6) as follows. The net electron flux is from high- to low-temperature regions, because the electron velocities are greater at high temperatures. The electric field required to counter this flux is the first-order effect, but it is produced by small deviations of the total electron density from its average value. This, in turn, changes the total electron flux, which depends not only on relative velocities, but also upon the variation in total electron concentration. The electric field required to neutralize this concentration effect is precisely the nonlinear effect discussed above.

It should be noted that nonlinear contributions to the thermoelectric field in a given direction depend not only on variations in this direction, but also on other directions. For example, in the two-dimensional case the nonlinear thermoelectric field in the x direction may be written as

$$E_x=\frac{\beta}{T^2}\frac{\partial^3}{\partial x^3}T^2+\frac{\gamma}{T}\frac{\partial^3}{\partial x^3}T+\frac{\beta}{T^2}\frac{\partial^3}{\partial x\partial z^2}T^2 +\frac{\gamma}{T}\frac{\partial^3}{\partial x\partial z^2}T . \quad (7)$$

The first two terms stem from derivatives in the x direction, while others depend on z gradients also. The consequence of this equation will be considered in the next section.

III. TWO-DIMENSIONAL NONLINEAR THERMOPOWER

We now apply the general theory of nonlinear thermopower reviewed in the preceding section. We are only interested in the nonlinear contributions, and so we restrict ourselves to the situation where linear effects cancel out. Thus we insist that points A and B between which the thermoelectric potential is developed be at the same temperature. Further, we are interested in two-dimensional effects, the two dimensions being along the x axis, and the z axis perpendicular to the surface. We assume that no temperature gradients exist in the y direction. This geometry closely matches the experimental circumstances described above.

In the previous paper, we assumed a stringently stationary state in which $\mathbf{j}=\mathbf{0}$.[1-3,7,8] But in the two-dimensional case, $\mathrm{curl}\mathbf{E}=\mathbf{0}$ contradicting Eq. (6), and we should use the continuity equation,

$$\frac{\partial\rho}{\partial t}+\mathrm{div}\mathbf{j}=0 . \quad (8)$$

The stationary condition now becomes

$$\mathrm{div}\mathbf{j}=0 , \quad (9)$$

which is a much less stringent constraint. In effect, it allows for the circuit to be completed in the cold part of the film. We now separate the electric field into linear and nonlinear terms, so that $\mathbf{E}=-\nabla(\phi+\phi_0)$, where ϕ is the nonlinear term. By assumption, all linear contributions are zero, and thus combining Eqs. (9) and (5), we get

$$\nabla\left[\sigma\left[\nabla\phi+\frac{\beta}{T^2}\nabla(\Delta T^2)+\frac{\gamma}{T}\nabla(\Delta T)\right]\right]=0 . \quad (10)$$

A general solution to Eq. (10) is readily found to be

$$\mathbf{E}(\mathbf{r})=-\nabla\phi$$
$$=\frac{1}{\sigma}\int\frac{\nabla\left[\frac{\beta}{T^2}\nabla(\Delta T^2)+\frac{\gamma}{T}\nabla(\Delta T)\right]}{|\mathbf{r}-\mathbf{r}'|^2}(\mathbf{r}-\mathbf{r}')d\mathbf{r}' . \tag{11}$$

There is another way to find the electric field in Eq. (11). Taking the curl of Eq. (5), we get

$$0=2\frac{\beta}{T^3}[\nabla T\times\nabla(\Delta T^2)]+\frac{\gamma}{T^2}[\nabla T\times\nabla(\Delta T)]+\nabla x\frac{\mathbf{j}}{\sigma} . \tag{12}$$

Solving this equation yields both j and E. Integrating E between points A and B gives us the measured voltage.

These results are quite general, but for the sake of specificity we now model the temperature distribution in a manner that closely approximates the experimental evidence described in the Introduction. In Ref. 6 we have considered a sawtooth geometry, but in the paper we use another analytical form adequate to describe the experiments. This is (Fig. 1)

$$T(x,z)=T_0+(T_1\sin gx+T_2\sin 2gx)\exp(-\kappa z) , \tag{13}$$

where $g=2\pi/\Lambda$ is the wave number of the grating, and κ is a parameter associated with laser irradiation which, in the case of sufficiently thick films, is roughly proportional to the reciprocal of the skin depth. This model is actually very general since any continuous temperature distribution can be written as a Fourier series.

We can find j by expanding Eq. (12) in a Fourier series. Only terms of zeroth order will contribute to the voltage V_{AB}, and for $T_1, T_2 \ll T_0$ this yields

$$j_x=g\sigma_0\frac{T_1^2T_2}{T_0^3}\exp(-3\kappa z)[\beta(17g^2-4\kappa^2)+\tfrac{9}{2}\gamma T_0g^2]-j_0 . \tag{14}$$

Here j_0 is the constant of integration which we can find from the condition of zero net current as

$$\int_0^h j_x dz=0 , \tag{15}$$

where h is the thickness of the film.

From Eq. (14), we can calculate the potential induced over N ripples as

$$V=V_0\frac{1-\exp(-3\kappa h)}{3\kappa h} , \tag{16}$$

where

$$V_0=2\pi N\frac{T_1^2T_2}{T_0^3}[\beta(17g^2-4\kappa^2)+\tfrac{9}{2}\gamma T_0g^2] . \tag{17}$$

It is now important to mention that the induced voltage consists of two components: the first term in Eq. (17) stemming from gradients in the x direction, and the second term originating from gradients in the z direction, as per Eq. (7). The thermal relaxation times for these gradients are very different. In the absence of a substrate, the thermal relaxation time may be evaluated as $\tau\approx\ell^2/\chi$, where ℓ is the distance between points with different temperatures, and χ is the thermal diffusivity.[9] For the discussed temperature distribution we find that $\tau_x\approx\Lambda^2/\chi\approx10^{-6}$ s and $\tau_z\approx h^2/\chi\approx10^{-10}$ s. Thus the potential associated with the z gradients should follow a laser pulse rate of about 0.1–1 μs, whereas those associated with x gradients will decay more slowly. While the presence of a substrate can significantly change this qualitative result, it is nevertheless noted[5] that two, time-differentiated signals are experimentally observed.

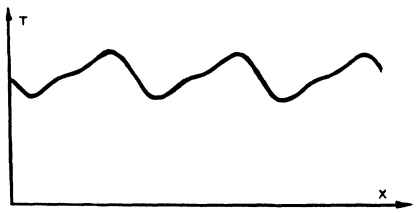

FIG. 1. Temperature distribution along the surface of the film resulting in a nonlinear thermoelectric voltage.

In order to evaluate V in Eq. (16), we must extract the temperature distribution from the experimental data. This is easy to do in the case of $h>\delta$, where δ is the skin depth, about 0.05 μm. In this event, $\kappa\approx1/\delta\approx2\times10^5$ cm^{-1}. Assuming $T_1=150$ K, $T_2=50$ K, $g=2\pi\times10^3$ cm^{-1}, and $N=10^3$, all consistent with experiment, then for monovalent metals with linear thermopower of $\alpha_0\approx10^{-6}$ V/K, we calculate $V_0=0.05$ V. Assuming that no parameters change as a function of h, we obtain for V

$$V=\frac{V_0}{3\kappa h}\approx\frac{V_0}{h\sqrt{\sigma}} \quad \text{for } h>\delta$$
$$V\approx V_0 \quad \text{for } h<\delta . \tag{18}$$

It would appear from Eq. (18) that the thinner the film, the greater the potential, but this is misleading. For very thin films, thermal diffusivity will tend to equilibrate temperature gradients, especially in the z direction, and thus reduce the value of V_0. Thus there is an optimal thickness at which nonlinear effects will be maximized, at about $h\approx\delta$. For thinner films, a detailed calculation would require a knowledge of the thermal diffusivity.

It should also be mentioned, however, that the voltage measured in the experiment is larger than that calculated by Eq. (17). One possible reason for this is the fact that transition metals and semimetals were used in the experiment. These systems have overlapping conduction bands, and even linear thermopower measurements yield results 1–2 orders of magnitude larger than the monovalent materials assumed in the previous calculation. For transition metals, the nonlinear terms increase significantly because of the greater length required for the interband transition of electrons, particularly because of the longer transmission time between d and s zones. Detailed calculations of this will be given elsewhere.

IV. CONCLUSION

In this paper we have considered the electron transport phenomena arising in monovalent metals under large

temperature gradients. We have found nonlinear contributions to the thermopower and carefully studied the case when voltage is generated between two points at the same temperature in a homogeneous material. This voltage equals zero in linear theory, and the experimental measurement of such a potential constitutes experimental support for this theory.

In our previous paper, we considered the effect of gradients only in one dimension. In this paper, we have discussed the dependence of this effect on film thickness. For very thick films, we find that the potential goes to zero since the cold bulk serves to complete the circuit. For thin films, the potential goes to V_0. However, for very thin films, V_0 becomes smaller because temperature gradients in the z direction are reduced due to thermal diffusivity.

The theory may be extended to include thermomagnetic phenomena as well. This case is most interesting when linear effects cancel, leaving only nonlinear terms. Another interesting issue will arise when the film thickness and/or grating wavelength is on the order of the electron free path. Finally, at low temperatures but with large temperature gradients, phonon drag must be considered.

Nonlinear thermoelectric phenomena have many technical applications. For example, very small, cheap and convenient sensors may be produced.[10] Analogous use could be made from similar thermomagnetic devices.

We have assumed local thermal equilibrium throughout. There is some experimental evidence to indicate that this may not be a valid assumption in all circumstances, in which case a new theory must be developed.

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