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A. N. Grigorenko, P. I. Nikitin, Daniel A. Jelski and Thomas F. George

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THERMOELECTRIC PHENOMENA IN METALS UNDER LARGE TEMPERATURE GRADIENTS

A. N. Grigorenko and P. I. Nikitin
General Physics Institute, USSR Academy of Sciences
38 Vavilov Street, 117942 Moscow, USSR

Daniel A. Jelski*
Department of Chemistry
State University of New York, College at Fredonia
Fredonia, New York 14063

Thomas F. George
Departments of Chemistry and Physics & Astronomy
239 Fronczak Hall
State University of New York at Buffalo
Buffalo, New York 14260

ABSTRACT

Nonlinear contributions to thermoelectricity are studied when large temperature gradients are present in metals. A theory is presented to account for these phenomena in the case of monovalent metals obeying a parabolic dispersion law. Simple experiments are proposed in which nonlinear terms are relevant and produce measurable effects.

* Author to whom correspondence should be addressed.

The conventional theory of thermoelectric phenomena is based on the concept of local equilibrium and small deviations from global thermal equilibrium. In this case, only linear relations between flows and thermodynamic forces should be considered, and linear nonequilibrium thermodynamics is valid. Such considerations account for the well-known Thomson and Seebeck effects, described in many textbooks.[1,2]

However, the conventional theory of thermoelectricity excludes the so-called Benedicks' effect in metals.[3] This effect is a thermoelectric phenomenon in which a potential is developed between two points at the same temperature, but separated by nonzero temperature gradients as described below. It is much smaller than the Thomson effect, in which a potential is developed between two points at different temperatures, and initial experiments demonstrating Benedicks' effect were therefore inconclusive.[4] Similar observations for semiconductors are less ambiguous.[5]

It has been hitherto assumed that large temperature gradients cannot be produced in metals because of the high thermal diffusivity. But modern acheivements in short-pulse laser generation and thin-film technology force a change in this perspective. In recent experiments[6] high voltages were measured when a pulsed laser is used to heat a thin metal film deposited on a grating, creating temperature gradients as high as 10^6 K/cm. The complexities of the these experiments are beyond the scope of this paper, but suffice it to say that Benedicks' effect is one possible explanation of the observed phenomenon. In this view, the potential is produced by nonlinear thermoelectric effects caused by differential laser heating. This possibility prompts the present work, which is the first theoretical account of nonlinear thermoelectric effects in metals.

Throughout, we assume local thermal equilibrium, without which temperature would be undefined. If we define a dimensionless parameter ω as a measure of the deviation from local equilibrium, then for the experiment just described, ω can be estimated as $\omega = \frac{\ell_0 \nabla T}{T} \approx 0.1$, where ℓ_0 is the electron free path. For simplicity, we consider metals with one parabolic conduction band, e.g., for Ag, $\ell_0 \approx 10^{-5}$ cm (see Ref. 7, p. 268), and for the value of $\nabla T \approx 3 \times 10^6$ K/cm, we get $\omega \approx 0.1$. Thus ω is not necessarily small, and it is no longer sufficient to consider only first-order

terms. On this scale, nonlinear terms are essential and can produce measurable experimental effects. For simplicity, we consider metals with one parabolic conduction band.

It is well known[7] that for a bulk metal with a conductivity σ, linear non-equilibrium thermodynamics yields an electric current j as

$$j = \sigma(E_{eff} - \alpha\nabla T) \quad , \tag{1}$$

where E_{eff} is the effective electric field and α is the absolute thermoelectric coefficient. The E_{eff} can be written as

$$E_{eff} = E + \nabla(\zeta/e) \quad , \tag{2}$$

where E is the external electric field and ζ is the chemical potential. When temperature gradients are sufficiently large, then Eq. (1) is insufficient, and nonlinear terms must be taken into account:

$$j = \sigma(E_{eff} - \alpha\nabla T - \alpha_1\nabla(\Delta T) - \alpha_2\nabla T(\Delta T) - \alpha_3\nabla(\nabla T)^2 - \alpha_4(\nabla T)^3 \ldots) \tag{3}$$

It should be noted that the concept of local equilibrium is still valid because otherwise a local temperature T(x) is undefined. This implies that $\omega < 1$, as described in above.

Our task is to evaluate the thermoelectric coefficients α_i, for i = 1, 2, ... For this purpose, we use the conventional theory of electron transport in metals,[8] keeping terms up to third order. Let n_k be the electron density in k-state. For a stationary state in the absence of external fields, the Boltzmann equation reduces to

$$(v_k\nabla)n_k = \frac{\partial n_k}{\partial t}\Big|_{coll} \quad . \tag{4}$$

To simply evaluate the collision term on the rhs, we use the conventional τ-approximation[8] and neglect the effect of phonon drag, assuming that the temperature is sufficiently high. By expanding n_k in a series of temperature gradients, we obtain

$$n_k = n_k^0 + g_k^1 + g_k^2 + g_k^3 + \ldots \quad , \tag{5}$$

where

$$n_k^0 = \frac{1}{\exp(\frac{\varepsilon_k - \zeta}{\tau}) + 1} \quad , \tag{6}$$

and where ε_k is the electron energy in the k-state. Substituting Eq. (5) into Eq. (4) and comparing the terms of same order in both parts of the expression, we get

$$g_k^1 = -\tau(\varepsilon_k)(v_k \nabla) n_k^0 \quad , \tag{7}$$

$$g_k^2 = -\tau(\varepsilon_k)(v_k \nabla) g_k^1 \quad , \tag{8}$$

$$g_k^3 = -\tau(\varepsilon_k)(v_k \nabla) g_k^2 \quad . \tag{9}$$

We then derive an expression for j, valid for large ω, as

$$j = e \sum_k (g_k^1 v_k + g_k^2 v_k + g_k^3 v_k) \quad . \tag{10}$$

The first term in Eq. (10) is familiar from linear thermoelectric theory,[7,8] and yields $j = -\sigma\alpha\nabla T$. The second term vanishes because of symmetry after integrating over k-space. The third term is of interest here.

In the simplest case of a spherically-symmetric Fermi surface, the integration over k-space yields[8]

$$j^i = -e\int \frac{dSd\varepsilon_k}{4\pi^3\hbar v_k} v_k^i(\tau v_k^j\nabla_j)(\tau v_k^l\nabla_l)(\tau v_k^m\nabla_m)n_k^0 \quad . \tag{11}$$

At high temperatures, the electron free path is limited by electron-phonon scattering,[7] and τ is inversely proportional to T. Then performing simple, but somewhat cumbersome, calculations, we obtain

$$\alpha_1/T = \alpha_2/3 = \alpha_3/3 = \frac{14\pi^2 k_b^2 \tau(\mu)^2}{5me} \quad , \quad \alpha_4 = 0 \quad , \tag{12}$$

where $\tau(\mu)$ refers to the scattering time at the Fermi energy μ, k_b is the Boltzmann constant, and where terms to order $(k_bT/\mu)^2$ are retained.

We now evaluate Benedicks' effect in metals for the following sawtooth geometry. Suppose two points, A and B, are at a temperature T_0, and are separated by a point C at temperature T_1. Let the temperature gradient on the segment (AC) be twice the gradient along the segment (CB). This system may be approximated by a triangle-like temperature function, in which case the problem is analytically solvable.

As usually assumed in the stationary state, there is no current, and therefore $j = 0$. From Eq. (3) the electric field can be written as

$$E = -\nabla(\zeta/e) + \alpha\nabla T + \alpha_1\nabla(\Delta T) + \alpha_2\nabla T(\Delta T) + \alpha_3\nabla(\nabla T)^2 \quad . \tag{13}$$

Then the voltage arising between points A and B is

$$V_{AB} = \int_A^B E\, dx = \int_A^B \left(\frac{d^2\alpha_1}{2dT^2} - \frac{d}{2dT}(\alpha_2 + 2\alpha_3)\right)T_x'^3\, dx \quad , \tag{14}$$

where A and B are assumed to lie along the x-axis separated by distance Λ, and $T' = dT/dx$.

From (12) it follows that $\alpha_1 \sim 1/T$ and $\alpha_2 \sim 1/T^2$. Then

$$V_{AB} = \frac{28(\pi k_b \tau_0 T_0)^2}{5me} \int_A^B \frac{T'^3}{T^3}\, dx \approx 40\, \alpha_0 \frac{(T_1-T_0)^3(T_0+T_1)}{T_1^2 T_0} \frac{\ell_0^2}{\Lambda^2} \quad . \tag{15}$$

where the 0 subscript refers to values at T_0, and where the evaluation of the integral depends explicitly on the geometry described above. If the gradients along (AC) and (CB) are equal, then the integral vanishes and the effect disappears. If $T_0 = 300$ K, $T_1 = 600$K, $\Lambda = 10\ \mu$m, $\ell_0 = 10^{-5}$ cm and $\alpha_0 = 10^{-6}$V/K, then $V_{AB} \approx 2\ \mu$V. This very small potential can be measured as follows. A thin, flat metal film is irradiated by short-pulsed light with spatially modulated intensity, the modulation stretching over $N = 10^4$ periods, and each period assuming the sawtooth geometry. The modulation must be accomplished by masking, since interfering laser beams will always produce symmetric gradients, and hence no effect. Summing the voltage over 10^4 periods yields $V = NV_{AB} \approx 20$ mV, which can be easily measured by conventional stroboscopic methods.

Experiments with laser irradiation of metal gratings[6,9] provides another interesting example where large temperature gradients arise. In these experiments, thin transition or semi-metal films are evaporated onto gratings and are illuminated by pulsed laser light. Unexpectedly high voltages of about 1 V are measured along the gratings. One possible reason for this phenomenon may be Benedicks' effect caused by a laser-induced, periodic but asymmetric temperature distribution similar to that just described and evaluated for monovalent metals.

Calculations show that for transition and semi-metals, nonlinear contributions to thermoelectricity are considerably larger because of overlapping conduction bands. In this case, an inverted conduction band may be regarded as a trap,[7] and even linear thermoelectric coefficients are one or two orders of magnitude greater than for monovalent metals. The nonlinear terms increase because of the greater length required for inter-band transmission of electrons, in particular, because of longer transmission times from d- to s-zones for transition metals. Detailed calculations of this will be given elsewhere.

We further remark that as a consequence of Eq. (3), we can see that j_x depends not only on $\partial T/\partial x$ but also on the Laplacian. Under laser irradiation of metal gratings, in addition to the periodic gradients in the x-direction, 10^6 K/cm along

the film, high-temperature gradients arise in the z-direction. The value of such gradients can easily be estimated by $\partial T/\partial z \approx (T_1 - T_0)/\delta \approx 10^8$ K/cm, where the skin depth δ is about 0.05 μm in the present case. For such gradients, the dimensionless parameter ω assumes a value greater than 1, and we are clearly in the domain of nonequilibrium thermodynamics. Any description of electron transport in this regime will require a new physical approach. Further, in the 2-dimensional case $\nabla \times \mathbf{E}$ is not necessarily zero in Eq. (13), and for this reason, the $j = 0$ condition cannot be assumed. The cold bulk substrate will serve to complete the circuit. Thus a 2-dimensional treatment of thermoelectric phenomena is significantly more complex, and this very interesting problem will be the subject of further discussion.

In conclusion, we have calculated the nonlinear contributions to thermoelectricity arising from large temperature gradients in a monovalent metal. Such contributions play an important role in various transport processes, of which one example is Benedicks' effect. We have evaluated Benedicks' effect, forbidden in the linear theory, but which may explain interesting experimental phenomena. Practical applications could include very small and convenient sensors of laser radiation parameters.[10] This theory can also be extended to double-band metals such as Ni, Ti, and Bi, where the effects could be significantly greater, and also to situations where a magnetic field is present.

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