SHORT COMMUNICATIONS

THE CONTRIBUTION OF PHONONS TO THE THOMSON COEFFICIENT*

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An electric current of density **j** flowing in a temperature gradient ∇T gives up heat in a reversible way ; the amount of heat thus liberated per unit volume and unit time is given by

$$-\mu j \nabla T, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

μ being the Thomson coefficient, which can be shown to be

$$\mu=\frac{T}{e}\frac{\mathrm{d}}{\mathrm{d}T}\left\{\frac{1}{T}\left(\frac{K_1}{K_0}-\zeta\right)\right\}, \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

where ζ is the Fermi energy, and the K's are the usual transport coefficients as defined by Mott and Jones (1936, p. 306, equation (**99**)), or more generally by Wilson (1953, p. 305).

In addition to this purely electronic Thomson coefficient, there is a component due to the lattice waves, arising as follows.

If a current **j** is set up, the phonons, interacting with the electrons, have their distribution altered from equilibrium with a tendency to acquire excess quasi-momentum in the direction of the current. There is a resulting heat flow **Q**, proportional to **j**, defining a contribution to the Peltier coefficient $\pi_p=Q/j$. Since the Thomson and Peltier coefficients are related by

$$\mu=-\frac{\pi}{T}+\frac{\mathrm{d}\pi}{\mathrm{d}T}, \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

the additional contribution to the Thomson coefficient is

$$\mu_p=\frac{1}{j}\frac{\mathrm{d}Q}{\mathrm{d}T}-\frac{1}{T}\frac{Q}{j}. \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

The electron distribution function can be written in the form

$$f=f^\circ+\frac{\boldsymbol{\lambda}\cdot\mathbf{k}}{KT}\frac{\mathrm{d}f^\circ}{\mathrm{d}\varepsilon}, \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

$\boldsymbol{\lambda}$ being a vector characterizing the deviation from equilibrium. Similarly the phonon distribution can be expressed as

$$n=\mathrm{N}+\frac{\boldsymbol{\lambda}'\cdot\mathbf{q}}{KT}\frac{\mathrm{dN}}{\mathrm{d}x}, \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

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f° and N being the respective equilibrium distributions, **k** and **q** the wave-vectors, $\varepsilon=(E-\zeta)/KT$ and $x=h\omega/2\pi KT$, E and $h\omega/2\pi$ being the energies of the electrons and phonons respectively. The electrons and phonons interact so as to conserve energy and total wave-vector. If there are no other interactions, the electrons and phonons are in quasi-equilibrium if $\lambda=\lambda'$, as pointed out elsewhere (Peierls 1930*a*, 1930*b*, 1932; Klemens 1951*b*). True equilibrium, stationary for any interaction, requires $\lambda=\lambda'=0$, but in the absence of processes capable of obliterating excess momentum ($\Sigma\mathbf{k}+\Sigma\mathbf{q}$), the electron-phonon interactions will merely distribute this excess momentum in such a way that λ and λ' are equal and constant for all electron and phonon energies.

The current density corresponding to a given value of λ is easily found from (**5**) to be

$$\mathbf{j}=\frac{2\pi eN}{h}\lambda, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

where N is the number of free electrons per unit volume. Similarly the heat current **Q** carried by phonons is found from (**6**) to be

$$\mathbf{Q}=\lambda' ST\frac{2\pi}{3h}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

where S is the lattice specific heat per unit volume. If the electron-phonon interaction is much stronger than the phonon-phonon interaction, which is due to anharmonicities or the elastic scattering of phonons by lattice imperfections, λ and λ' become equal, and μ_p is obtained from (**4**), (**7**), and (**8**). It is thus found that

$$\mu_p=\frac{1}{3Ne}T\frac{\mathrm{d}S}{\mathrm{d}T}. \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

More generally, if τ_p is the effective relaxation time for phonon-phonon interactions in the sense used in the theory of the lattice thermal conductivity (Klemens 1951*a*), and if τ_e is the relaxation time for phonons interacting with electrons, it is easily seen that

$$\lambda'=\lambda\frac{\tau_p}{\tau_e+\tau_p}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

and (**9**) has to be multiplied by the additional factor $\tau_p/(\tau_e+\tau_p)$. If the τ's do not have the same frequency dependence, the expression becomes

$$\mu_p=\frac{1}{3Ne}T\frac{\mathrm{d}}{\mathrm{d}T}\left\{\int S(\omega)\frac{\tau_p}{\tau_e+\tau_p}\mathrm{d}\omega\right\}, \qquad \ldots\ldots\ldots \quad (11)$$

where $S(\omega)\mathrm{d}\omega$ is the contribution towards the specific heat from frequencies ω, $\mathrm{d}\omega$.

The specific heat of a solid of N' atoms per unit volume is $233N'K(T/\theta)^3$ at very low temperatures, so that from (**9**)

$$\mu_p=\frac{233N'}{9Ne}\left(\frac{T}{\theta}\right)^3 K. \qquad \ldots\ldots\ldots\ldots\ldots \quad (12)$$

For a free-electron metal the electronic Thomson coefficient is $-\pi^2K^2T/e\zeta$. Thus $\mu_e \propto T$ and $\mu_p \propto T^3$. As an example of orders of magnitude, if $\zeta/K \sim 10^4$ °K, $\theta \sim 2\times10^2$ °K, and $N' \sim N$, then $|\mu_p| \sim |\mu_e|$ at about 20 °K, provided of course that $\tau_p > \tau_e$ at this temperature. Whether μ_p is of appreciable magnitude at any temperature depends upon the relative magnitudes of τ_p and τ_e at those temperatures where (**12**) is comparable with μ_e.

For a pure metal μ_e is not strictly proportional to T, since the constant of proportionality varies with the dominant scattering mechanism (static imperfections at lowest temperatures, lattice waves at higher temperatures). In such cases it may not be possible to identify the electronic component μ_e. However, in an alloy this difficulty is avoided. The alloy must be such that $\tau_e < \tau_p$; this is fulfilled below about 10 °K for well-annealed silver-palladium alloys (Kemp *et al.* 1954). Thus it seems that μ_p may be observable in this and similar cases.

In the case of semi-conductors $\tau_p \ll \tau_e$; hence

$$\mu_p \sim \frac{1}{3Ne} T \frac{\mathrm{d}}{\mathrm{d}T}\left(S\frac{\tau_p}{\tau_e}\right). \quad \ldots\ldots\ldots\ldots\ldots \quad (13)$$

While the factor τ_p/τ_e is small, so is N; hence μ_p may be appreciable, and will in general be proportional to the lattice thermal conductivity.

References

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