Anomalies in the thermoelectric power of semimetals in the intervalley scattering of the carriers at the surface

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(Submitted 15 June 1987; resubmitted 21 August 1987)
Pis'ma Zh. Eksp. Teor. Fiz. **46**, No. 7, 267–270 (10 October 1987)

The intervalley scattering of carriers from the surface of a crystal plays an important role in the production of thermoelectric power of pure bulk semimetals at liquid-helium temperatures. A method is suggested to verify this effect experimentally.

At liquid-helium temperatures the thermoelectric properties of semimetals are customarily assumed to be determined by the phonon drag of the current carriers. This assertion is based on two experimental observations. First, the measured values of the thermoelectromotive force α are much higher than those of the diffusion thermal emf of the degenerate electron gas and, secondly, evidence in favor of this experimental observation comes from the temperature dependence of the thermal-emf coefficient, which is characteristic for the corresponding dependence of the phonon mean free paths, and also the size-effect maximum which correlates with the maximum of the phonon thermal conductivity.[1–3]

Pure bulk semimetal single crystals of the bismuth type have, however, some specific properties in this respect, since there is no phonon drag when the electron density n^- is exactly equal to the hole density n^+. The momentum imparted to the phonons by the electric field (the Herring π-method) in this case is proportional to $(n^+ - n^-)$, and the phonon-drag thermoelectric power vanishes. This behavior is valid only when the scattering occurs inside an electron-phonon system and when it does not depend on the degree of anisotropy of either the electron-hole spectrum or the phonon spectrum. To decompensate the system and to generate an average phonon drift, an additional carrier-scattering mechanism, in which the momentum loss of electrons differs from the momentum loss of hole, must be introduced. In the samples currently studied the sample surface may be such a mechanism. Since the carrier range $l^\pm$ in bismuth ($T = 4.2$ K) is only several tenths of a millimeter, the phonon-drag contribution to the thermoelectric power of a bulk crystal should contain a small parameter l/d, where d is the transverse dimension of the sample. From this standpoint, the results of Refs. 2 and 3 seem to be slightly paradoxical in comparison with the data of the previous authors.[1] Despite the fact that single crystals with a much larger ratio $\gamma = \rho_{300\ \mathrm{K}}/\rho_{4.2\ \mathrm{K}}$ and a larger cross section were studied by those investigators,[2,3] the thermoelectric power which they obtained, $\alpha \simeq 100$ mV/K, was an order of magnitude higher than that obtained in Ref. 1 ($\gamma \simeq 150$). An explanation of this effect in terms of the classical size effect runs into some basic difficulties. Although the maximum value obtained by those investigators[4] was on the order $\alpha \approx 20 + 30$ mV/K, the calculations carried out in Ref. 5 on the basis of a more realistic carrier-spectrum model, in which the anisotropy for the scattering of the carriers by phonons is taken

0021-3640/87/190337-04$01.00

into account, yield a maximum phonon drag at the level 5–7 mV/K; i.e., these results are in better agreement with the data of Ref. 1.

We suggest that there is another explanation for the anomalously high thermoelectric power. As was shown in Ref. 6, in multivalley materials the region of the crystal near the surface has nonequilibrium-concentration gradients which decay to the bulk values at a distance on the order of the diffusion length L. From the standpoint of the phonon drag, this behavior can be interpreted as concentration decompensation. The maximum effect, of course, arises when $d/L<1$, and there is no mechanism for balancing the carrier concentration from various valleys. In this limit, however, intervalley scattering must necessarily occur. From the physics standpoint, it is clear that the maximum drag-induced thermoelectric power is seen in the case of weak intervalley scattering, since the concentration decompensation is otherwise negligible. It should also be noted that at $T<5$ K the scattering of electrons and holes by phonons is not elastic, so that calculation of the kinetic coefficients should be based on a variational procedure for solving the kinetic equation, with allowance for the surface.

The equations for the distribution of carriers φ in valley β and of phonons, ignoring the intervalley bulk scattering, are

$$v_z \frac{\partial \varphi^\beta}{\partial z} - e^\beta (\mathbf{E}\mathbf{v}) = \hat{I}\{\varphi^\beta, \psi_q\} \tag{1}$$

$$\frac{\partial \omega}{\partial q} \vec{\nabla}_{\mathbf{T}} \frac{\partial F^0}{\partial T} = \hat{I}\{\psi_q, \psi_q\}. \tag{2}$$

Here the $\hat{I}$ are the collision integrals of the collision between the carriers and the phonons and of the phonons with each other. The boundary conditions at the surfaces of the plate, $z=\pm d$, are

$$\varphi^{\gtrless \beta}(v^*, \pm d) = \chi^\pm , \tag{3}$$

where v^* is the velocity of the reflected carriers. The coefficients $\chi^\pm$ can then be determined from the condition for the integral flux balance at the surface. With allowance for the intervalley scattering at the surface, we can write the relevant equation in the form

$$\langle v_z \varphi^{\gtrless\beta} \rangle = - \sum_{\beta'} d_{\beta\beta'} \langle v_z \varphi^{\lessgtr \beta'} \rangle, \tag{4}$$

where $d_{\beta\beta}$ and $d_{\beta\beta'}$ are the probabilities for the intravalley and intervalley scattering at the surface, and the angle brackets denote $\langle x\rangle = (2/\hbar^3)\int x(\partial f^0/\partial\epsilon)d^3k$. Omitting laborious calculations, we write the results for the distribution function

$$\begin{aligned}\varphi^{\gtrless\beta} &= \overline{\varphi}^\beta(z) + \left[\chi^\pm - \overline{\varphi}(\pm d)\right]\exp\left(-\frac{\pm z + d}{l}\right)\\ &+ \frac{s^2\tau_{ph}}{T}\nabla_x T \lambda^\beta_{xi} k_i \left[1 - \exp\left(-\frac{\pm z + d}{l}\right)\right]\\ &\pm \frac{1}{l}\int_{\mp d}^{z} e^\beta(\epsilon_i l_i)\exp\left(\pm\frac{z'-z}{l}\right)dz',\end{aligned} \tag{5}$$

where we introduce the notation $\bar{\varphi} = \langle \varphi \rangle / \langle 1 \rangle$,

$$\epsilon = \left[E_x, E_y, E_z - \frac{1}{e}\left(\frac{d}{dz}\bar{\varphi}\right)\right], \quad l = \left(\frac{\tau}{m}\right)_{zz} \frac{1}{\sqrt{\epsilon_{zz}}}, \quad l_i = \tau_{ij} v_j,$$

ϵ_{ik} is the tensor of the inverse effective masses, τ_{ph} is the relaxation time of the phonon subsystem, τ_{ik} is the "relaxation-time" tensor of the carriers arising from their scattering by equilibrium phonons, $\lambda_{ik} = (\hat{A}R\hat{A}^{-1})$ describes the phonon spectrum R in a transformed coordinate system, and s is the speed of sound. The components τ_{ik} do not correspond to the elastic-scattering relaxation times but rather to the conductivity formally recorded in standard form. The numerical values of the corresponding components are given in Ref. 5. The self-consistency condition[7] gives rise to the integral equation for $\bar{\varphi}$:

$$\bar{\varphi} - \frac{1}{2l}\int_{-d}^{d} \bar{\varphi} \exp\left(-\frac{|z' - z|}{l}\right) dz'$$

$$= (E_x l_x + \chi^+) \exp\left(\frac{z-d}{l}\right) - (E_x l_x - \chi^-) \exp\left(-\frac{z+d}{e}\right). \tag{6}$$

To simplify the problem, we consider the cases in which the orientation of the valleys with respect to the surface of the sample has the highest symmetry, where $\vec{\nabla} \| \vec{C}_2$ and the C_3 axis runs in the same direction as the normal to the surface and where $\nabla \mathbf{T} \| C_3$ and the C_2 axis is parallel to the normal. The field E_z may be assumed zero in these cases. Equation (6) has an exact solution and the distribution function is defined completely. The expression for the drag-induced thermoelectric power, α^{Σ}, can be derived in the usual way from the equation for the mean current density in the plate. For the relevant cases we find

$$\alpha^{\Sigma}_{xx} = \frac{n_0 s^2 \tau_{ph}}{T\sigma^{\Sigma}} \sum_{\beta} e^{\beta} \left\{ \left(\lambda^{\beta}_{xx} - \frac{\lambda^{\beta}_{xz}\sigma^{\beta}_{xz}}{\sigma^{\beta}_{zz}}\right) \left[\left(1 - \frac{l}{2d}\left(1 - \exp\left(-\frac{2d}{l}\right)\right)\right)\right] \right.$$
$$\left. + \frac{\lambda^{\beta}_{xz}\sigma^{\beta}_{xz}}{\sigma^{\beta}_{zz}} d_{ee} d / [l(1 - d_{ee}) + d_{ee} d] \right\}, \tag{7}$$

where d_{ee} describes the intervalley umklapp processes proceeding from one electron valley to another. As was to be expected, α^{Σ} reaches a maximum at $d_{ee} \approx 0$.

The case corresponding to thick plates in the sense of the classical size effect (but $d < L$) is worth analyzing further. In the opposite limit, the intervalley scattering affects the thermoelectric power negligibly, since the current carriers do not have time to link up with another valley after being reflected from the surface. If the inequality $(l/d) < d_{ee}$ holds, then α^{Σ}_{xx} is given by

$$\alpha^{\Sigma}_{xx} = \frac{n_0 s^2 e \tau_{ph}}{T\sigma^{\Sigma}} \left\{ \left(\frac{l^- - l^+}{d}\right) + \frac{\lambda^-_{xz}\sigma^-_{xz}}{\sigma^-_{zz}} \frac{l}{d_{ee} d} \right\}. \tag{8}$$

The second term in (8) is the dominant term if the conditions indicated above are satisfied. If the probability for intervalley scattering is low, $d_{ee} = 0.03$, the drag-induced thermoelectric power could be greater than 100 mV/K for the given orientations. The fact that the result obtained by us makes it possible to estimate the magnitude of intervalley scattering in an independent experiment is of fundamental importance, since all the parameters in (8), with the exception of d_{ee}, can be calculated or measured with reasonable accuracy. Since the numerical values of d_{ee} can also be linked with the two-dimensional lattice symmetry at the surface, the nature of intervalley scattering can be understood more clearly by measuring the thermoelectric power of pure bulk bismuth single crystals, whose crystal axes have different orientations with respect to the planes which bound the crystal surface.

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Translated by S. J. Amoretty