Possibility of determining the surface band curvature in semimetals

V. A. Kozlov, E. E. Narimanov, and K. A. Sakkarov
Moscow Physicotechnical Institute, 141700, Dolgoprudnyĭ

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The band curvature near the surface in a semimetal determines the behavior of the sign of its thermoelectric power. An experiment for determining the magnitude and sign of the surface charge is proposed.

Determining the magnitude of the band curvature near the surface in semimetals is of fundamental importance for surface physics. In particular, this curvature gives rise to a space-charge region at the surface. This region substantially alters the way in which carriers are reflected at the surface. Under these conditions some of the carriers of one sign are reflected from the space-charge region in a specular fashion, while the rest of these carriers and also the carriers with the charge of the opposite sign are scattered by the actual surface. Simple energy considerations show that among the carriers whose sign is the same as that of the surface charge the only ones that reach the interface are those for which the angle between their velocity and the normal to the surface does not exceed $\theta_{\max} = \arccos(\sqrt{eU/E_F})$, where eU is the magnitude of the surface band curvature, and E_F is the Fermi energy.

Whether a surface band curvature is present in semimetals is usually decided by measuring the extent to which the reflection coefficients for electrons and holes are specular; in particular, this is done in experiments on the focusing of carriers by a magnetic field.[1] At temperatures near the boiling point of liquid helium, however, a description of the surface scattering by means of the specular parameter alone is not completely adequate.[2]

In this letter we wish to call attention to a fundamentally different possibility for determining the magnitude of the surface band curvature in semimetals. The idea is to measure the phonon-drag thermoelectric power at ultralow temperatures. Let us explain.

In compensated materials, the phonon-drag thermoelectric power vanishes since

the densities of the electrons and the holes are equal, if the scattering occurs only in the electron-phonon system. In high-quality pure single crystals, the surface scattering of carriers causes a decompensation of the system and gives rise to an average phonon drift. In the case $d/l \ll 1$, this drift is proportional to $d(1/l^+ - 1/l^-)$. Since the temperature dependence $l^+(T)$ is different from $l^-(T)$, there exists a certain T^0 at which the thermoelectric power again vanishes. In turn, the appearance of a space charge near the surface leads to the appearance of a group of carriers which do not reach the surface and which are indeed reflected in a specular fashion. This circumstance obviously changes the effective mean free path of (for example) the electrons (the charge is negative) and thus leads to a shift of T^0 in proportion to the number of electrons, i.e., $\propto \cos\theta_{\max} = \sqrt{eU/E_F}$.

Since bismuth is the substance which has been studied in most detail, and one for which a quantitative theory of kinetic effects can be derived rigorously, corresponding calculations were carried out for this semimetal. Since the kinetic coefficients are determined by the anisotropy and size effects in multivalley materials if the mean free path with respect to intravalley scattering (l), the diffusion length L, and the dimensions of the sample (d) satisfy the inequality $l < d < L$ (Ref. 3), the analysis below is restricted to temperatures in which the relations $L > l > d$ hold. Under these conditions, intervalley scattering, either in the interior or at the surface, has essentially no effect on the kinetic coefficients. The reasons is that the current carriers do not have time to demonstrate an association with the other valley before the next collision with the surface.

Under these conditions the corresponding system of kinetic equations for the nonequilibrium part of the distribution function of the carriers of species α, i.e., φ^α, and that of the phonons, χ, is

$$v_z \partial\varphi^\alpha/\partial z - e^\alpha(\vec{E}\vec{v}) = \hat{I}\{\varphi^\alpha, \chi\}, \tag{1}$$

$$\frac{\partial F^0}{\partial T}\frac{\partial \omega}{\partial \vec{q}}\vec{\nabla}T = \hat{I}\{\chi,\chi\} + \sum_\alpha \hat{I}\{\varphi^\alpha,\chi\}. \tag{2}$$

The corresponding boundary conditions can be written as follows, where we are taking account of the surface band curvature $e^\alpha U$ and assuming a purely diffuse scattering by the actual surface:

$$\begin{aligned} &\varphi^{\lessgtr\alpha}(\pm d) = \varphi^{\gtrless\alpha}(\pm d), \quad v_z^2/2\epsilon_{zz}^\alpha < e^\alpha U, \\ &\varphi^{\lessgtr\alpha}(\pm d) = B^\alpha, \quad v_z^2/2\epsilon_{zz}^\alpha > e^\alpha U, \end{aligned} \tag{3}$$

where ϵ_{ik}^α is the tensor of inverse effective carrier masses of valley α, and the quantities B^α are found from the condition for an overall flux balance:

$$< v_z \varphi^{>\alpha} > = - < v_z \varphi^{<\alpha} > .$$

Since the carrier scattering by the phonons is not elastic at the temperatures

under consideration here, a solution of Eqs. (1) and (2) was found by a variational method. For the phonon-drag thermoelectric power we found

$$\alpha_{xx}^{\Sigma} = \frac{s^2\tau^{ph}}{T\sigma_{xx}^{\Sigma}} \sum_{\alpha} e^{\alpha} n_0^{\alpha} R_{xx}^{2\alpha} \left(1 - \frac{R_{xz}^{2\alpha}\sigma_{xz}^{\alpha}}{R_{xx}^{2\alpha}\sigma_{zz}^{\alpha}}\right)$$

$$\times\left(1 - \left(1 - \frac{3}{2}\lambda^{\alpha} + \frac{1}{2}(\lambda^{\alpha})^3\right)\frac{l^{\alpha}}{2d}\left(1 - \exp(-2d/l^{\alpha})\right)\right), \tag{4}$$

where

$$\lambda^{\alpha} = \begin{cases} 1, & e^{\alpha}U \geq E_F^{\alpha}, \\ \sqrt{e^{\alpha}U/E_F^{\alpha}}, & 0 \leq e^{\alpha}U \leq E_F^{\alpha}, \\ 0, & e^{\alpha}U \leq 0, \end{cases}$$

τ^{ph} is the effective relaxation time in the phonon subsystem, and τ_{ik}^{α} is the "relaxation-time" tensor of the carriers. This tensor does not correspond to the relaxation times for elastic scattering. It corresponds instead to the τ in the standard formal expression for the conductivity, $\sigma = ne^2\tau/m$. In addition, σ_{xx}^{Σ} is the total conductivity of the system, $l^{\alpha} = \sqrt{E_F^{\alpha}/\epsilon_{xx}^{\alpha}}(\tau/m)_{xx}^{\alpha}$ is the mean free path, and $R_{ik}^{\alpha} = (A^{\alpha}RA^{\alpha-1})_{ik}$ is the transformed matrix R of the phonon dispersion law $\omega_{\vec{q}} = s|R_{\vec{q}}|$. The corresponding transformation A^{α} is chosen in such a way that the space $v_z > 0$ remains unchanged. Here n_0^{α} is the carrier density of valley α.

To pursue the analysis, we need to specify in detail the temperature dependence of the electron and hole mean free paths l^{α}. These paths can be calculated by the method of Ref. 4. A corresponding analysis of Eq. (4) is shown in Fig. 1. It follows from these results that the thermoelectric power crosses zero as a function of the temperature. The particular temperature T^0 at which α_{xx}^{Σ} vanishes is related in an unambiguous way to the surface band curvature:

$$\sqrt{-\frac{|e|U}{E_F^e}} = \frac{2}{3}\frac{\partial}{\partial T}\left[\sum_{\alpha}\frac{e^{\alpha}d}{|e^{\alpha}|l^{\alpha}}\right]\Big|_{T=T^*}(T^0 - T^*), \quad T^0 > T^*,$$

$$\sqrt{\frac{|e|U}{E_F^h}} = \frac{2}{3}\frac{\partial}{\partial T}\left[\sum_{\alpha}\frac{e^{\alpha}d}{|e^{\alpha}|l^{\alpha}}\right]\Big|_{T=T^*}(T^* - T^0), \quad T^0 < T^*. \tag{5}$$

The temperature T^* is found from the condition $\alpha_{xx}^{\Sigma} = 0$ in the absence of a surface charge. It depends on only the orientation of the test sample with respect to the crystallographic coordinate system. In particular, for bismuth, if the normal to the surface is parallel to the C_3 axis, we have $T^* = 0.66$ K and $\partial/\partial T\left[\Sigma_{\alpha}e^{\alpha}/|e^{\alpha}|l^{\alpha}\right]|_{T=T^*} = 0.8\ \text{cm}^{-1}$. If the C_2 axis is perpendicular to the surface, we have $T^* = 0.67$ K and $\partial/\partial T\left[\Sigma_{\alpha}e^{\alpha}/|e^{\alpha}|l^{\alpha}\right]|_{T=T^*} = 0.6\ \text{cm}^{-1}$. Note that the numerical values found here depend only weakly on the solution method. The reason is that even at $T/\Theta_D = 0.1$, where Θ_D is the Debye temperature, the error of the kinetic coefficients found by the variational method is less than 1%; it is even smaller at the temperatures under consideration here.[4] We wish to stress that there is no change in the actual functional dependence in (5) here.

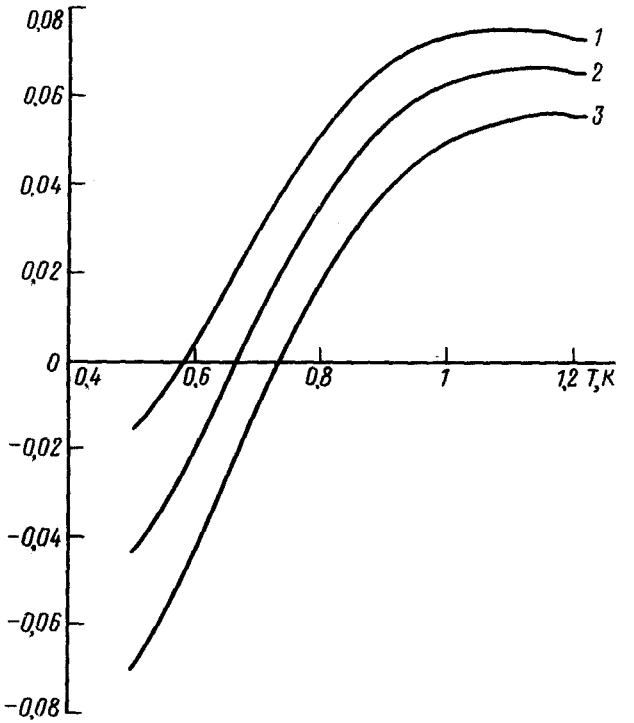

FIG. 1. Temperature dependence of the thermoelectric power (in units of $s^2\tau^{ph}|e|n_0T\sigma_{xx}^{\Sigma}$ for $\check{n}\|C_2$ and $d = 0.5$ cm, for three values of the surface charge density: 1—10^{-4} C/cm^2; 2—0; 3— – 10^{-4} C/cm^2.

We thus believe that the magnitude and sign of the surface band curvature can be found through a study of the temperature dependence of the phonon-drag thermoelectric power at ultralow temperatures. Calculations show (Fig. 1) that α_{xx}^{Σ} vanishes in the temperature interval $T = 0.5$–0.8 K. According to Ref. 5, the thermoelectric power of bismuth in this temperature region is substantially higher than the diffusion thermoelectric power; furthermore, it remains predominant down to 0.05 K.

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