Thermoelectric convection in liquid semiconductors

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(Submitted 19 January 1993)
Zh. Eksp. Teor. Fiz. **103**, 1633–1643 (May 1993)

A new thermoelectric mechanism, which, like the well-known buoyancy and thermocapillary mechanisms, can lead to instability of a heated liquid and to cellular convective motion, is analyzed for liquid semiconductors (semimetals). It is shown that electric-field structures arise together with convection cells. Possible mechanisms for thermal convection are compared and it is shown that the thermoelectric mechanism is more important in thin layers. A hierarchy of scales is established. The thermoelectric mechanism makes possible convection with heating from above or from the free-surface side, which is impossible with the other excitation mechanisms. The amplitudes of the velocity and electric field which arise in the process are calculated. The effect of different types of boundary conditions as well as rotation on the excitation conditions is taken into account. Comparison is made with existing experiments and new experiments are suggested.

1. Thermal convection in a liquid semiconductor (semimetal) differs from the case of an ordinary liquid in that in the semiconductor case the difference of the temperatures T_h and T_c of the hot and cold surfaces, respectively, results in the appearance of an electric field **E**. More precisely, the temperature gradient

$$A=|\nabla T_0|=(T_h-T_c)/d,$$

where d is the distance between the experimental surfaces, generates a stationary thermoelectric field $\mathbf{E}_0=\gamma\nabla T_0$ determined by the thermoelectric power γ, which is significant for semiconductors (semimetals).

A fluctuation-induced deviation of the temperature by T_1 from the equilibrium value T_0 results in the appearance of an electric field $\mathbf{E}_1=\gamma\Delta T_1$ and an associated space charge with density $en_1=\varepsilon\gamma\Delta T_1$ (n is the density of carriers with charge e), determined by the dielectric permittivity ε of the semiconductor. The presence of this charge in the "external" field γA results in the appearance of heat-induced electric-force density $\varepsilon\gamma^2 A\nabla T_1$.

It is this latter force that competes with the conventional buoyancy force, which is generated by thermal expansion (coefficient β) and under such conditions can be written as $\rho_0\beta g T_1$ (ρ is the density of the liquid and **g** is the acceleration of gravity),[1,2] and with the thermocapillary force $\sigma\Delta T_1$,[3] arising due to the temperature dependence of the surface tension σ.

The structures arising due to thermoelectric instability are a variety of electric convection structures.[4] For this reason, the thermoelectric mechanism, in contrast to nonelectric mechanisms of excitation of thermal convection, also operates with heating from above or from a free surface, when the buoyancy (Rayleigh) or thermocapillary (Pearson) forces do not operate. In the case of excitation from a free surface, surface waves can appear in addition to the motion excited by the thermoelectric effect.[1,5]

The excitation conditions, i.e., the conditions under which the thermoelectric force predominates over the viscosity and heat-conduction dissipation forces (ν and $\varkappa$ are the coefficient of kinematic viscosity and the thermal diffusivity, respectively), make it necessary to introduce the new dimensionless number

$$\mathscr{E}=\frac{\gamma^2\varepsilon A^2 d^2}{\rho\varkappa\nu}, \qquad (1)$$

which has the value $\mathscr{E}_*\simeq 40$ at the moment cellular convective motion appears with longitudinal and transverse cell dimension ratio $\simeq 3$.

The number $\mathscr{E}$ has the same meaning as the Rayleigh and Marangoni numbers:

$$R=\frac{\beta g A d^4}{\varkappa\nu}, \quad M=\frac{\sigma A d^2}{\rho\varkappa\nu}, \qquad (2)$$

which must reach values of approximately 1000 and 80 with cell dimension ratios of about 4 and 4.5 in order for instability to be induced by the buoyancy force[2] or thermocapillary force,[3] respectively.

According to Eqs. (1) and (2) the numbers R and M are directly proportional to A, so that they depend on the direction of heating. Excitation by the mechanisms determining these numbers is impossible in the case of heating from above or from a free surface. The number $\mathscr{E}$ does not depend on the direction of heating. Thus in order for thermoelectric excitation of cellular convective motion in experiments to be distinct from excitation by buoyancy or thermocapillary forces the heating must be done from above.[6–10] It is found that for long pulses ($\simeq 1$ msec) and irradiation energy not much greater than the energy required for melting, the ratio of the dimensions of the alloying zone, i.e., the zone where motion occurred, is of the order of 3. Surface waves, which compete with this mechanism with respect to energy absorption, in principle cannot give such a ratio.

This paper is organized as follows. In Sec. 2 the problem of excitation of thermal convection in an infinite flat layer is formulated, taking into account the thermoelectric effect. In Sec. 3 this problem is solved and the excitation

 1063-7761/93/050802-06$10.00

conditions and the coordinate dependence of the velocity and electric field which are excited in the process are found for free and isothermal boundaries. In this case exact analytical solutions can be obtained and the qualitative effects can be analyzed. It is also shown how thermoelectric convection interacts with Rayleigh convection. In Sec. 4 it is shown that the same results are obtained with more realistic boundary conditions—a solid lower boundary. It is also shown how the thermocapillary effect affects thermoelectric convection. In Sec. 5 the amplitudes of the motion and electric field arising with the instability are calculated and the nonlinear problem is solved. In Sec. 6 the effect of rotation of the liquid on the excitation effect is examined. Finally, in Sec. 7 experimental data are analyzed and it is proved that thermoelectric convection must be taken into account in order to explain the phenomena observed in thin films and in the case of heating from above.

2. The linearized system of equations describing the effect of the instability consists of the equation of motion[1]

$$\nu\Delta\mathbf{v}-\frac{\nabla p_1}{\rho_0}-\beta g T_1=-\frac{en_1\mathbf{E}_0}{\rho_0}, \tag{3}$$

where $\mathbf{v}$ and p are, as usual, the velocity and pressure, respectively, and $en_1\mathbf{E}_0/\rho_0$ is the Coulomb force, and the usual equations—the equation of continuity for an incompressible liquid div $\mathbf{v}=0$, the equation of continuity for the current $\operatorname{div}(\mathbf{E}_1-\gamma\nabla T_1)=0$ in the presence of only a thermoelectric field, the equation of electrostatics $\operatorname{div}\mathbf{E}_1=en_1/\varepsilon$, and the heat-conduction equation (assuming Joule heating is small) $\varkappa\Delta T_1-(\mathbf{v}\cdot\nabla)T_0=0$.

Stationary excitation of convection is studied in the Boussinesq approximation.[2]

Oscillatory convection is not excited for the same reasons as in an ordinary liquid (see also Sec. 6).

In the flat-layer model we orient the z-axis perpendicular to the surface of the layer, so that the acceleration of gravity g will be directed in the opposite direction.

The variables p_1, T_1, n_1, and $\mathbf{E}_1$ are eliminated by the standard method.[2,3] The result, obtained from Eq. (3), is an equation for v_z, where the following units are introduced in order to make the variables dimensionless (retaining the notation): length—layer thickness d; velocity—ν/d; time—d^2/ν; pressure—$\nu^2\rho/d$; temperature—$Ad\nu/\varkappa=AdP$; intensity—γAP; and, electric charge density—$\varepsilon\gamma A/d$. This gives the equation

$$(\Delta^3\pm R\Delta_\perp+\mathscr{E}\Delta\Delta_\perp)v_z=0;\quad \Delta_\perp=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}, \tag{4}$$

which is of the same degree (sixth) as the equation for conventional Rayleigh convection. The upper and lower signs corresponds to heating from below and above, respectively.

In the model of an infinite flat layer, the translational symmetry along the layer makes it possible to seek a solution in the form

$$v_z=v(z)\cos(k_x x+k_y y), \tag{5}$$

where $k_{x,y}=2\pi d/\lambda_{x,y}$. This definition of the wave vector $k_\perp^2=k_x^2+k_y^2$ corresponds to an arrangement of the coordinate system such that the cell boundaries are $x,y=\pm\lambda_{x,y}/2$, where $\lambda_{x,y}$ are the cell dimensions in the longitudinal directions. The equations then become ordinary differential equations with constant coefficients, and the solution of these equations has the form $\exp(ik_z z)$, where k_z is, generally speaking, a complex variable.

In order to solve the problem completely it is also necessary to have six boundary conditions in order to determine v_z, T_1, E_{1z}, and n_1, and two additional conditions at the boundary in order to determine v_x, v_y, E_{1x}, and E_{1y}. We now formulate these conditions.

Besides the natural "nonefflux" boundary condition $v_z=0$, there can be two types of boundary conditions:[2,3] 1) isothermal conditions on a solid surface $T_1=0$ and attachment conditions $v_x=v_y=0$, whence follows $\partial v_z/\partial z=0$, and 2) conditions on a free boundary, when the components of the stress tensor are determined by the thermocapillary effect $\partial v_{x,y}/\partial z=-M\partial T_1/\partial x,y$. Estimates show (see Sec. 7) that the effect of thermoelectricity can be neglected in the boundary conditions. Hence there follows the condition

$$\partial^2 v_z/\partial z^2=M\Delta_\perp T_1.$$

The thermocapillary effect does not operate at an isothermal boundary. Without analyzing the conditions of heat transfer at a free boundary,[3] we assume that in the presence of the thermocapillary effect the boundaries are thermally insulated, $\partial T_1/\partial z=0$. The boundary conditions for the electric field do not depend on the type of boundary and consist of the fact[4] that the tangential components of the electric field vanish at the boundary $E_{1x}=E_{1y}=0$.

Thus the problem of excitation of thermoelectric convection is a dual eigenvalue problem. Homogeneous boundary conditions correspond, however, to a homogeneous system of equations. The condition for the existence of a nontrivial solution is the excitation condition. This condition can be written as an equation relating $\mathscr{E}$ and $\mathbf{k}(k_x, k_y, k_z)$. The temperature difference T_h-T_c required in order for an instability to be excited with some ratio $w=k_\perp^2/k_z^2$, showing the ratio of the dimensions of the convection cell at the start of the motion, is determined by minimizing this relation.

3. In order to determine the qualitative effects, we give the solution of the above-formulated problem in the case of free and isothermal boundaries. In this case, just as in Ref. 2, systematic analysis of the equations at the boundaries gives the condition $\partial^{2n}v_z/\partial z^{2n}=0$ for any integer n. The only function that satisfies this condition is $v(z)=V\sin(\pi z)$, so that there is no need to solve an eigenvalue problem.

The equation (4) then becomes the excitation condition

$$-k^6\pm Rk_\perp^2+\mathscr{E}k^2k_\perp^2=0, \tag{6}$$

whence follow all the well-known[1] conditions for excitation of Rayleigh convection: $R=R_*=27\pi^4/4\simeq 658$ with $\lambda=\lambda_x\simeq\lambda_y\simeq 4d$ only in the case of heating from below.

When only the thermoelectric mechanism operates $\mathscr{E}=\mathscr{E}_*=4\pi^2\simeq 40$ with $\lambda=\lambda_x\simeq\lambda_y\simeq 2\sqrt{2d}$, irrespective of the direction of heating. Under these conditions the thermocapillary effect does not influence excitation. It is easy to find the range of values of the parameters where the new effect predominates:

$$d \lesssim d_{R\mathscr{E}} = 2\pi(\varepsilon\gamma^2\varkappa\nu/4\beta^2 g^2\rho)^{1/6}.$$

The indices show that the force characterized by the second index predominates in the thinner layer and the force characterized by the first index predominates in the thicker layer. In this region $A_{\mathscr{E}} = A_R d^3/d^3{}_{R\mathscr{E}} \lesssim A_R$ (the indices correspond to the excitation mechanisms), i.e., convection arises under conditions when Rayleigh convection is still impossible. The cell appearing in this case is somewhat smaller (by a factor $\sqrt{2}$) in the longitudinal direction.[11]

The formula (6) makes it possible to analyze the effect of the interplay of Rayleigh and thermoelectric convection on the excitation condition.

The effect of Rayleigh convection on the excitation of thermoelectric convection in the case of heating from above can be significant for analysis of experimental data. Using the fact that $\mathscr{E} = 4R^2(d^6_{R\mathscr{E}}/(2\pi d)^6)$ we find that the number $\sqrt{\mathscr{E}}$ is given by

$$\sqrt{\mathscr{E}} = \pi\frac{1+w}{\sqrt{w}}\left[\left(1+\frac{4w}{(1+w)^4}\frac{d^6}{d^6_{R\mathscr{E}}}\right)^{1/2} - \frac{1}{1+w}\frac{d^3}{d^3_{R\mathscr{E}}}\right],$$

which must be minimized. Analysis of this formula shows that in the case of heating from above Rayleigh convection decreases the ratio of the longitudinal and transverse cell dimensions, namely, $w_* \geqslant 1$ (as opposed to $w_* = 1$ when only the thermoelectric effect operates). The ratio $\mathscr{E}/\mathscr{E}_* = \mathscr{E}/(2\pi)^2 > 1$ at the point of excitation, i.e., as expected, the buoyancy force has a stabilizing effect.

In the case of heating from below, when both effects augment one another, R can be easily found as a function of $\mathscr{E}$ with the help of Eq. (6). From this function it is possible to determine the values of $R(<700)$ and $\sqrt{\mathscr{E}}$ (<6.5) at the moment of excitation with a given thickness of the layer. In reality, however, in the case of heating from below the thermoelectric effect is weak and the thermocapillary effect appears first. The thermoelectric effect is important only in layers of thickness such that the thermocapillary effect is stronger than the buoyancy effect (see Sec. 4 below).

Using Eq. (5) it is easy to find the convective quantities as a functions of the coordinates (in dimensionless form) in the case when the Rayleigh and thermoelectric mechanisms operate simultaneously:

$$\begin{aligned} &v_z = V\sin(k_z z)\cos(k_x x + k_y y); \quad n_1 = \mp v_z; \quad T_1 = \pm\frac{v_z}{k^2}; \\ &v_{x,y} = -V\frac{k_z k_{x,y}}{k_\perp^2}\cos(k_z z)\sin(k_x x + k_y y); \\ &E_{1z} = \pm V\frac{k_z}{k^2}\cos(k_z z)\cos(k_x x + k_y y); \\ &E_{1x,y} = \mp V\frac{k_{x,y}}{k^2}\sin(k_z z)\sin(k_x x + k_y y). \end{aligned} \qquad (7)$$

Thus electric structures arise together with the usual values of the velocity and temperature.[2]

It is evident that the boundaries of the electric-field structures are also the boundaries of the convection cells (velocity structures) and the electric charge depends on the coordinates as v_z.

The thermoelectric field generates on the surface of the liquid an electric charge with surface density (in dimensional form)

$$\sigma_e = \frac{\varepsilon\gamma A V d}{\pi\varkappa}\left(\frac{4d^2}{\lambda_x^2} + \frac{4d^2}{\lambda_y^2} + 1\right)^{-1}\cos(k_x x + k_y y),$$

which depends only on the amplitude and cell shape at the moment of excitation.

4. For other boundary conditions the excitation problem must be solved numerically. The solution in the case when the lower boundary is solid and the upper boundary is free and isothermal and in the case when both boundaries are solid shows that the critical value of the number $\mathscr{E}$ with excitation of purely thermoelectric convection increases insignificantly ($\simeq 42$ and $\simeq 45$, respectively). The ratio of the cell dimensions at the moment of excitation, however, remains virtually unchanged and, as before, $\lambda \simeq 3d$.

This result is very similar to the well-known fact[2,3] that when the boundary conditions change, the critical values of R and M change only slightly and the cell-dimension ratio at the moment of excitation does not change at all.

As already mentioned above, the thermocapillary effect can be manifested at a free nonisothermal boundary. The thermocapillary effect predominates in thin layers, i.e., layers thinner than $d_{RM} = (\sigma/(\beta\rho g))^{1/2}$, heated from below.

In even thinner layers, whose thickness is less than

$$d_{M\mathscr{E}} = \left(\frac{\rho\varkappa\nu\varepsilon\gamma^2}{\sigma^2}\right)^{1/2},$$

the thermoelectric excitation mechanism predominates over the thermocapillay mechanism.

We note, however, that when the thermoelectric is taken into account, structure formation in an ordinary liquid with $\sigma > 0$ by the thermocapillary mechanism is, of course, possible for any orientation of the layer with respect to the force of gravity, but it is impossible in the case of external heating at a free surface. For this reason, in the case of heating through a free surface it is more important to take into account the influence of the thermocapillary effect on thermoelectric convection.

Dropping in Eq. (4) the term with R and using boundary conditions such that the lower boundary is solid and the upper boundary is free and thermally insulated we obtain the excitation condition

$$\frac{\mathscr{E}}{M} = 1 + \frac{\sqrt{\mathscr{E}}\,\mathrm{sh}k_\perp\ \mathrm{sh}\varkappa_+\mathrm{sh}\varkappa_- + \varkappa_+\mathrm{sh}\varkappa_- - \varkappa_-\mathrm{sh}\varkappa_+}{\mathrm{ch}k_\perp\ (\varkappa_-\mathrm{sh}\varkappa_+\mathrm{ch}\varkappa_- - \varkappa_+\mathrm{sh}\varkappa_-\mathrm{ch}\varkappa_+)}, \qquad (8)$$

where $\varkappa_\pm^2 = k_\perp^2 \pm k_\perp\sqrt{\mathscr{E}}$.

The problem under the same types of boundary conditions but different heat-transfer conditions at a free boundary was solved numerically. As in the case when only the thermocapillary effect operates, deviation from "thermal-insulation" conditions only increases the heat required for excitation and does not change the qualitative picture.

In the case of heating from a free surface $M<0$ and $\mathscr{E}$ can be found as a function of M and $k_\perp$ from Eq. (8). As expected, the thermocapillary effect, similarly to Rayleigh convection, suppresses somewhat the thermoelectric effect, i.e., it increases the value of $\mathscr{E}$ required for excitation, but thermocapillary has the reverse effect on the cell dimensions, i.e., it increases the ratio of the longitudinal and transverse dimensions $w_*\leqslant 1$.

In the case of heating from below, in the region $d_{RM}>d>d_{M\mathscr{E}}$, Eq. (8), represented in the form of M as a function $\sqrt{\mathscr{E}}$, is once again the stability function. The critical values $M<80$ and $\sqrt{\mathscr{E}}<11$, corresponding to a definite layer thickness, can be determined from this function with the help of the relation $M=\sigma d/\gamma(\rho\varkappa\nu\varepsilon)^{-1/2}\sqrt{\mathscr{E}}$.

The ratio of the cell dimensions changes from 4.5 to 3. Of course, the quantity $d_{M\mathscr{E}}$ is small, but the region $d<d_{RM}$ is of some interest. Thus the excitation conditions for thermoelectric convection remain qualitatively the same for boundary conditions different from free and isothermal conditions. For this reason, in Secs. 5 and 6 we shall once again investigate this physically most pellucid case.

5. In order to calculate the amplitude of the convective velocities and fields that arise it is necessary to calculate V in accordance with Eqs. (7). This can be done using the same equations from Sec. 2 but including the nonlinear terms $(\mathbf{v}\cdot\nabla)\mathbf{v}$ and $en_1\mathbf{E}_1/\rho_0$ in the pressure equation and $(\mathbf{v}\cdot\nabla)T_1$ in the heat-conduction equation. The other equations do not change. All quantities acquire additional terms, proportional to the second, third, and so on powers of V. Next, carrying out the calculations described in Secs. 2 and 3 we find that T_1 does and v_z does not have second-order corrections.

The excitation condition to second-order is

$$\mp(R-R_*)-(\mathscr{E}-\mathscr{E}_*)k^2=\mp\frac{P^2V^2}{8k^2}(R_*\pm\mathscr{E}_*k^2) \quad (9)$$

and makes it possible to find the required amplitude of the quantities characterizing the state of the liquid immediately after excitation, if R and $\mathscr{E}$ are somewhat higher than their values required for instability to arise. This result corresponds to the general assertion[1] that the amplitudes V of the deviations arising are proportional to the square root of the "supercriticality." This is true in both thick layers $(d>d_{R\mathscr{E}})$ heated from below, when Rayleigh convection predominates, and thin layers $(d<d_{R\mathscr{E}})$ or with heating from above. Then $V\sim(\mathscr{E}-\mathscr{E}_*)^{1/2}$, and convection cells and field structures arise due to the thermoelectric effect.

The motion and field which arise influence cell shape only in the next order of smallness. These corrections, just as the correction terms for the convective quantities, can be easily calculated by continuing the iterative solution of the equations of Sec. 2 taking into account nonlinear terms, but the formulas so obtained are complicated and are not required in order to analyze the experimental data.

Thus in the case when the thermoelectric effect predominates (the temperature of the cold surface remaining constant) and the temperature T_h of the hot surface is somewhat higher than the value T_h^* required for excitation, the amplitude is given in the dimensional form by

$$V_{\mathscr{E}}=4\pi\frac{\varkappa}{d}\sqrt{\frac{T_h-T_h^*}{T_h^*-T_c}},\quad V_{\mathscr{E}}=\frac{2\sqrt{2}}{\sqrt{3}}V_R\simeq 1.63V_R,$$

where the amplitude index indicates which mechanism predominates when motion with this amplitude is excited. Thus for the same parameters of the liquid the amplitude of thermoelectric excitation is 1.63 times higher than in the case for ordinary convection.

Under the same conditions the ratio of convective quantities and the quantity before excitation of instability is

$$\frac{|\nabla T_1|}{A}=\frac{E_1}{\gamma A}$$
$$=4\sqrt{\frac{T_h-T_h^*}{T_h^*-T_c}}[2\sin^2(k_zz)\sin^2(k_xx+k_yy)$$
$$+\cos^2(k_zz)\cos^2(k_xx+k_yy)]^{1/2}.$$

Using Eq. (9) it is easy to analyze how the thermoelectric effect influences ordinary convection in the case of heating from below, but it is more important to indicate how Rayleigh convection influences thermoelectric convection in the case of heating from above. We have

$$V=4\pi\frac{\varkappa}{d}\sqrt{\frac{T_h-T_h^*}{T_h^*-T_c}}\left[1-\frac{\mathscr{E}}{R-\mathscr{E}}\right]^{1/2}.$$

The amplitude arising in the case of such stabilizing action of ordinary convection decreases somewhat.

6. For experiments designed to observe and investigate the thermoelectric convection conditions when the liquid rotates with angular velocity Ω, parallel to the z axis, may be more convenient.

Under such conditions (when the problem contains a quantity defined by a polar vector) convection has, besides a stationary branch, a branch of growth oscillating with frequency ω.[2]

The effect of the new factor itself is manifested[2,3] in that the dimensionless Taylor number $\mathrm{Ta}=4\Omega^2d^4/\nu^2$ appears in the excitation condition.

The analysis in the case of thermoelectric convection is identical to the case of Rayleigh convection in the presence of rotation.[2,3] Only the results are presented here. The condition (6) is replaced by the formula

$$(-i\omega P+k^2)[(-i\omega+k^2)^2k^2+k_z^2\mathrm{Ta}]$$
$$+(-i\omega+k^2)k_\perp^2(\mp R-\mathscr{E}k^2)=0.$$

Hence we obtain for the branch with aperiodic growth $\omega=0$ the same formula (6) but with the additional term $(-k_z^2\mathrm{Ta})$. The excitation condition for the branch with oscillatory growth will be

$$-k^6+(\pm R+\mathscr{E}k^2)\frac{k_\perp^2}{2(1+P)}-\frac{k_z^2P^2}{(1+P)^2}\mathrm{Ta}=0,$$

with oscillation frequency

$$\omega^2=-k^4+\frac{(1-P)k_z^2}{(1+P)k^2}\mathrm{Ta}.$$

These formulas must still be minimized. Minimization will show how the cell dimension ratio depends on Ω.

Without dwelling on the case of heating from below, we indicate that in the case of heating from above the asymptotic values are

$$\mathscr{E}_*^{\mathrm{rot}}\simeq(2/\pi)(2\mathrm{Ta}/\pi^4)^{2/3} \quad\text{and}\quad w_*=(2\mathrm{Ta}/\pi^4)^{1/3}-1$$

for the aperiodic branch. Since under laboratory conditions $P\simeq1$ (under astrophysical conditions the case $\nu\ll\varkappa$ is possible), the differences between the aperiodic and oscillatory branches are small.

Thermoelectric convection in a magnetic field can be studied similarly.

7. The existing experimental data whose interpretation may require the concept of thermoelectric convection can be divided into two groups. These are Bénard's experiments on the observation of convection in comparatively thin layers of spermaceti heated from below (see the description and analysis in Ref. 2). For spermaceti (spermaceti wax) the following values can be used for the parameters of the liquid:[12,13] $\beta=(9\text{–}6)\cdot10^{-4}\ \mathrm{K}^{-1}$; $\rho\simeq0.9\text{–}1$ g/cm^3; $\nu\simeq1\text{–}5$ mm^2/sec; $\varkappa\simeq5\cdot10^{-2}\text{–}1$ mm^2/sec; and, $\sigma=(3\text{–}7)\cdot10^{-5}$ N/(m·K).

Then the thickness is found to be $d_{RM}\simeq1\text{–}10$ mm. It is under these conditions that Bénard performed his experiments. Quantitative agreement between the experimental results and theory was achieved only after Pearson's discovery of thermocapillary excitation of cellular convective motion.[12]

The thermoelectric power γ for spermaceti is unknown (I was not able to find a value in the literature). Setting $\gamma=ak_B/e$, where k_B is Boltzmann's constant and e is the electron charge, the value of a can range from 10^{-2} up to 10^2. The $d_{M\mathscr{E}}\simeq2\text{–}20\ \mu$m, i.e., in experiments with even the thinnest layers ($d\simeq0.1$ mm) thermoelectric convection in the case of heating from below should be weak.

The problem of excitation conditions in the case when the thermocapillary and thermoelectric effects operate simultaneously with a solid isothermal lower boundary and a free thermally insulated upper boundary is solved using the relations (8). For $d\simeq10d_{M\mathscr{E}}$ we obtain $M=M_*(1-0.42\mathscr{E})$. Since the quantity $\mathscr{E}$ itself is small ($\mathscr{E}=0.1$) in this case, the correction to the critical Marangoni number is only several percent. It is important, however, that M_* decreases; this agrees with calculations based on experiments in the thinnest layers. The cell dimension ratio also decreases to 4.1–4.3 (as compared with 4.5 in the case of "pure" thermocapillarity). This also falls within the purview of thermoelectricity. We note that ordinary convection is completely negligible in layers of this thickness.

Numerous other experiments[2,4] on layers of mercury, liquid sodium, oils, and so on heated from below have been performed in layers of this thickness, for which the thermoelectric effect is insignificant.

The main types of experiments which can be interpreted on the basis of a theoretical analysis of the excitation conditions for thermoelectric convection are the experiments already mentioned in Sec. 1 on laser heating from above.[6–10] Unfortunately, the experiments described in Refs. 6–10 were designed for technological purposes and the conditions of these experiments are very different from those of the model studied in this work. Although fused steels transform into semimetal and have high thermoelectric power ($a\simeq100$), in order to check the theory developed here it is still desirable to obtain data on laser melting in a much wider range.

The phenomena observed in Refs. 6–8 are explained in Ref. 5 by excitation of surface waves. Of course, surface waves are observed, but the depth to which the alloying material penetrates into the steel cannot be explained with the help of surface waves. For the radiation flux densities assumed in Ref. 5, there appears a temperature gradient sufficient[14] for not only excitation of surface waves on the melt but also the appearance of thermoelectric instability.

Indeed, the intensity of heating from above for which the stabilizing effect of the Rayleigh and thermocapillary mechanisms is overcome can be found by comparing the presented dimensionless numbers R and M with the number $\mathscr{E}$.

The necessary conditions are $A>a_1\rho\beta gd^2/(\gamma^2\varepsilon)$ and $A>a_2\sigma/(\gamma^2\mathscr{E})$, where a_1 and a_2 are numerical factors of the order of 1–10. Both conditions are satisfied in the experiments of Refs. 6–10.

Comparing to the degree of heating A_W, found in Ref. 5, required for excitation of surface waves the degree of heating $A_{\mathscr{E}}$ required for excitation of thermoelectric convection shows that

$$A_W/A_{\mathscr{E}}=a_3(\varepsilon\rho\varkappa\nu)^{1/2}(\sigma d/\gamma)^{-1}\simeq1$$

with $d\simeq0.01$ mm, while for thicker layers, as observed in Refs. 7 and 8, thermoelectric convection predominates.

In experiments on thermoelectric convection in rotating samples or samples in an external magnetic field, information can be obtained by recording the electromagnetic radiation emission during the oscillations.

I thank I. V. Ioffe, who directed this work, for calling my attention to this problem.

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Translated by M. E. Alferieff