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Translated by J. G. Adashko

## Distribution of "hot" electrons in a metal at low temperatures

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(Submitted April 7, 1976)

Zh. Eksp. Teor. Fiz. 71, 1514-1519 (October 1976)

The electron distribution function at  $T=0$  is found for a thin metal plate in a "heating" stationary and uniform electric field ( $T$  is the lattice temperature) in the case in which the "temperature" approximations (Kaganov et al., 1956, 1967) are not satisfied.

PACS numbers: 72.15.Jf

1. Attention was called in the work of one of the authors<sup>[1]</sup> to the importance of the study of the effects of heating of an electron gas as applied to the analysis of the resistive behavior of thin superconducting films, in which such a heating is first revealed by the hysteresis of the critical current. The temperature dependence of this hysteresis was calculated in Ref. 1 in the approximation of two different temperatures for the electrons and the lattice<sup>[2]</sup> and it turned out to be in good agreement (for films of In and Sn) with experiment.<sup>[3]</sup>

As is well known, the electron-temperature approximation allows us to "bypass" the investigation of the kinetic equation for the electron distribution function in a strong electric field, and is correct when the criterion of thermalization of the electron gas is satisfied:  $\nu_{ep}^e \ll \nu_{ee}$ . Here  $\nu_{ep}^e$  is the frequency of the energy relaxation of the electrons from phonons and  $\nu_{ee}$  is the frequency of interelectron collisions. Taking into account the well-known estimates

$$\nu_{ec} \sim \frac{e_F}{\hbar} \left( \frac{T_e}{e_F} \right)^2, \quad \nu_{ep}^e \sim \frac{\Theta_D}{\hbar} \left( \frac{T_e}{\Theta_D} \right)^3$$

(here  $T_e$  is the characteristic energy of the electrons,  $e_F$  is the Fermi energy,  $\Theta_D$  is the Debye temperature,  $T_e \ll \Theta_D$ ), it is easy to see that a rough estimate for the electron temperature  $T_e$ , below which thermalization is guaranteed as a result of the interelectron collisions, is given by the inequality  $T_e \ll \Theta_D^2 / e_F$ . For such metals as Sn, In, Pb, Nb, the right side of this inequality is smaller than or of the order of 1 °K. At the same time, the electron temperature for these superconductors, as follows from the results given in Ref. 1, even with a

current  $j_{c2}$ , is only slightly below critical (apart from the dependence on the lattice temperature), i. e.,  $T_e \gtrsim 3$  °K and the thermalization criterion given above is obviously not satisfied. Moreover, what has been pointed out above means that precisely the opposite situation is of practical interest for the metals mentioned above. In such a case, the role of interelectron collisions in the formation of the distribution function of hot electrons is of little importance.

In this connection, the problem arises as to the finding of the electron distribution function in "heating" electric field in the absence of interelectron collisions generally. In the case of nondegenerate semiconductors, the answer to a similar question has already been obtained by Davydov.<sup>[4]</sup> By a significant simplifying circumstance, used in Ref. 4, account was taken of the known<sup>[5]</sup> ineffectiveness of the energy relaxation of the electrons from acoustic phonons in semiconductors. Therefore, expanding the desired distribution function in the collision integral of electrons with phonons in a series in the small ratio of the energies of the phonon and electron, we can replace the corresponding integral operator by a differential one. In metals, however, at  $T_e \ll \Theta_D$ , the energy relaxation is effective and a similar simplification is impossible.<sup>[1]</sup> Moreover, in contrast with the nondegenerate semiconductors, the collision integral of electrons with phonons in a metal contains a nonlinearity in the distribution function, associated with the necessity of taking into account the Pauli principle. The difficulties mentioned (absence of a small parameter and the essential nonlinearity of the problem, see Eq. (6) below) provide, in our opinion, the reason for the

absence of even qualitative discussions on the character of the distribution function of "hot" electrons for the case of metals (for example, whether or not it is monotonic, what are its asymptotes).

In the present work, we study the qualitative behavior of the solution of the corresponding nonlinear integro-differential equation for the electron distribution function for the case of the experimental situation of interest to us (thin film with dominant elastic scattering of the electrons<sup>2</sup>) in a constant, uniform electric field) in the limit  $T \rightarrow 0$  ( $T$  is the lattice temperature). In addition, an algorithm is proposed for the construction of a suitably accurate approximation to the desired function, and data of numerical computer calculations are given. It turns out that, in spite of the specific asymptote at infinity (see Eq. (15)), the discovered distribution function actually differs little, in the characteristic region of change of the energy, from the equilibrium Fermi distribution with some effective (dependent on the value of the field) temperature  $T_e$ . This latter circumstance, in our opinion, helps to explain the excellent applicability of the temperature distribution, used in Ref. 1, for the analysis of the experimental dependences of Ref. 3.

Further, the statement of the problem is discussed in Sec. 2, and the corresponding kinetic equation is introduced. The monotonic character of the desired distribution function is proven in Sec. 3, its asymptote is found and the procedure for finding the solution of Eq. (6) is described.

2. If the thickness of the metallic film  $d$  satisfies the inequality  $d \ll l_{pe}$ , where  $l_{pe} \approx a\varepsilon_F/T_e$  is the free path length of the phonon relative to scattering by electrons ( $a$  is the lattice constant), then almost all the phonons radiated by the electron are immediately thermalized in collisions with the film boundary (i.e., they leave the metal). Therefore, for films of thickness  $d \lesssim 10^3 \text{ \AA}$  ( $l_{pe} \sim 10^4 \text{ \AA}$  at  $T_e \sim 1^\circ$ ), we do not have to take into account the effects of dragging and heating of the phonon gas, i.e., we can assume the distribution function of the phonons to be an equilibrium one with the temperature of the thermostat. Account of this circumstance allows us to restrict ourselves to the investigation of the kinetic equation only for the distribution function of the electrons  $n_p$ , which in a uniform and constant electric field with intensity  $E$  can be written down in the form

$$\hat{v}_p n_p + \hat{v}_i n_p = eE \frac{\partial n_p}{\partial p},$$

where  $\hat{v}_i n_p$  is the "impurity" collision integral<sup>3)</sup> and

$$\hat{v}_p n_p = \sum_q W_q \{ [n_{p+q}(1-n_p)(N_q^0+1) - n_p(1-n_{p+q})N_q^0] \delta(\varepsilon_{p+q} - \varepsilon_p - \hbar\omega_q) + [n_p(1-n_p)N_q^0 - n_p(1-n_{p+q})(N_q^0+1)] \delta(\varepsilon_{p-q} - \varepsilon_p + \hbar\omega_q) \}$$

is the collision integral of electrons with phonons.<sup>7)</sup> Here  $\varepsilon_p$  is the energy of the electron with momentum  $p$ ,  $\hbar\omega_q$  is the energy of the phonon with momentum  $q$  and  $N_q^0 = [\exp(\hbar\omega_q/T) - 1]^{-1}$  is the equilibrium phonon distribution function at temperature  $T$ . In the following, we shall for simplicity limit ourselves to the consideration of an isotropic and quadratic dispersion law for the elec-

trons and a Debye phonon spectrum. Then, in accord with Ref. 8,  $W_q \approx \pi\alpha^2\omega/\rho s^2$ , where  $\alpha$  is the constant of electron-phonon interaction,  $\rho$  is the material density,  $\hbar\omega_q = sq$  ( $s$  is the velocity of the longitudinal phonons). For the "impurity" collision integral, we use the relaxation time approximation.

In what follows, as already noted in Sec. 1, we shall be interested in such a characteristic energy of the electron gas  $T_e \ll \Theta_D$  that the elastic relaxation of the electrons is dominant, i.e.,  $\nu_{ep}^e \ll \tau^{-1}$ , where  $\tau$  is the momentum relaxation time. On the one hand, this allows us to assume the conductivity of the film<sup>4)</sup>  $\sigma$  to be independent of the value of the field (the region of "residual" resistance). On the other hand, this also allows us to represent the distribution function  $n_p$  as a sum, dependent only on the energy of the isotropic part  $n(\varepsilon)$  and a small anisotropic addition  $n_p^{(1)}$ , where  $n_p^{(1)} \ll n(\varepsilon)$  in the measure of the smallness of the parameter  $\kappa \equiv eEl/T_e \ll 1$  (the estimate for  $T_e$  as a function of the value of the field  $E$  can be seen in formula (5) below). We shall now make use of the fact that  $\hat{v}_i n(\varepsilon) = 0$ . Then, assuming that  $\hat{v}_p n(\varepsilon) \ll \hat{v}_i n_p^{(1)} = -n_p^{(1)}/\tau$ , in first approximation in the parameter  $\kappa$ , we have

$$n_p^{(1)} = -\frac{e\tau}{m}(\rho E) \frac{dn(\varepsilon)}{d\varepsilon}.$$

In the second approximation in this same parameter, with account of the relation  $(\hat{v}_i n_p^{(2)})_\varepsilon = 0$ , (the symbol  $\langle \dots \rangle_\varepsilon$  means the average over the constant energy surface) we get the following equation for  $n(\varepsilon)$ :

$$\frac{\sigma E^2}{N(0)} \frac{d^2 n(\varepsilon)}{d\varepsilon^2} = -\hat{v}_p n(\varepsilon). \quad (1)$$

Here  $N(0)$  is the density of states at the Fermi level. In Eq. (1), it is convenient to transform to the dimensionless variable  $\xi = (\varepsilon - \varepsilon_F)/T_e$ , where  $T_e$  is some characteristic energy of the electron gas, after which Eq. (1) can be represented in the form

$$\frac{\sigma E^2}{N(0)} \frac{1}{T_e^2} \frac{d^2 n(\xi)}{d\xi^2} = -\nu \{ I^0(\xi) + I^T(\xi, \gamma) \}, \quad (2)$$

where  $\nu = \alpha T_e^3 / 4\pi v_F \rho \hbar^4 s^4$  has the order of the frequency of the energy relaxation of electrons with mean energy  $T_e$  from phonons ( $\nu \approx \nu_{ep}^e(T_e)$ ), and  $\gamma \equiv T_e/T$ . In Eq. (2) the electron-phonon collision integral is represented for convenience in the form of a sum of two terms. One of them ( $I^0(\xi)$ ) corresponds to processes connected only with the radiation of phonons by electrons, and does not depend on the thermostat temperature  $T$ :

$$I^0(\xi) = [1 - n(\xi)] \int_0^\infty dx x^2 n(\xi+x) - n(\xi) \int_0^\infty dx x^2 [1 - n(\xi-x)]. \quad (3)$$

The other term ( $I^T(\xi, \gamma)$ ) describes processes with participation of the thermostat and vanishes at  $T=0$ :

$$I^T(\xi, \gamma) = \int_0^\infty dx x^2 N^0(\gamma x) [n(\xi+x) + n(\xi-x) - 2n(\xi)]. \quad (4)$$

In the subsequent analysis of Eq. (2), we neglect the term<sup>5)</sup>  $I^T(\xi, \gamma)$ , which is physically equivalent to the in-

equality  $T_e \gg T(\gamma \gg 1)$ , which corresponds to the situation of "strong heating" (but such that the inequality  $\kappa \ll 1$  is nevertheless always satisfied). Finally, it is convenient to choose  $T_e$  from the condition

$$\sigma E^2 = N(0) T_e \nu, \quad (5)$$

so that Eq. (2) is greatly simplified and takes the form

$$-\frac{d^2 n(\xi)}{d\xi^2} = [1 - n(\xi)] \int_0^\infty dx x^2 n(\xi + x) - n(\xi) \int_0^\infty dx x^2 [1 - n(\xi - x)], \quad (6)$$

which clearly demonstrates the absence of the small parameter. We note that the condition (5) has a simple physical meaning: the power absorbed by the electrons from the electric field ( $\sigma E^2$ ), can be represented in the form of the product of the average number of phonons free to be radiated by the electrons  $N(0) T_e$ , the mean energy of the irradiated phonon  $T_e$  and the frequency of the energy relaxation  $\nu$ .

3. For the study of the solution of Eq. (6), it is convenient to introduce the function  $\varphi(\xi)$ :

$$n(\xi) = 1/2 [1 + \varphi(\xi)].$$

We note that  $\varphi(-\xi) = -\varphi(\xi)$  and  $\varphi(-\infty) = +1$ ,  $\varphi(+\infty) = -1$ . Then (6) can be rewritten in a more symmetric form:

$$-\frac{d^2 \varphi}{d\xi^2} = \frac{1}{2} \left\{ [1 - \varphi(\xi)] \int_0^\infty dx x^2 [1 + \varphi(x + \xi)] - [1 + \varphi(\xi)] \int_0^\infty dx x^2 [1 + \varphi(x - \xi)] \right\}, \quad (7)$$

and it follows from the oddness of  $\varphi(\xi)$  that the problem reduces to the solution of Eq. (7) on the semiaxis  $0 < \xi < \infty$  with the conditions  $\varphi(0) = 0$ ,  $\varphi(\infty) = -1$ . In this case, we shall seek a solution in a class of functions such that  $1 + \varphi(\xi)$  has an exponential asymptote at infinity. For further analysis, we introduce the additional notation:

$$y(\xi) = 1/2 \int_0^\infty dx x^2 [1 + \varphi(x + \xi)], \quad z(\xi) = 1/2 \int_0^\infty dx x^2 [1 - \varphi(\xi - x)].$$

It is obvious that

$$y'' = 1 + \varphi(\xi) = 2n(\xi), \quad z'' = 1 - \varphi(\xi) = 2[1 - n(\xi)].$$

It then follows that

$$y''' + z''' = 2, \quad (8)$$

$$y + z = \xi^3/3 + \alpha \xi, \quad (9)$$

where

$$\alpha = 2y'(0). \quad (10)$$

Equation (7) can be rewritten in the form

$$\varphi'' = yz'' + zy'''. \quad (11)$$

In turn, by integrating (11), with account of the exponential decay of  $y(\xi)$  at  $+\infty$ , we get

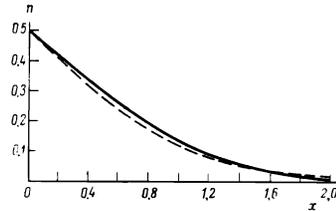


FIG. 1. Solid curve—plot of  $n(x)$  obtained by a computed solution of Eq. (13). For comparison, the plot of  $f(x) = [e^{2x} + 1]^{-1}$  is shown dashed. The dimensionless variable  $x = \gamma \xi$  is the abscissa.

$$\varphi' = yz'' + zy'' - z'y'. \quad (12)$$

Now setting  $\xi = \gamma x (\gamma^5 = 3)$  on the basis of (9), we can rewrite the final equation for  $y(x)$ :

$$\begin{aligned} y^{(1V)} - P(x)y'' + P'(x)y' \\ - P''(x)y + \gamma^2(2yy'' \\ - (y')^2) = 0, \\ P(x) = x^3 + \gamma x, \\ \gamma = \alpha \gamma^2. \end{aligned} \quad (13)$$

We note that the statement of the problem for Eq. (13) is now the following: it is required to find the number  $\alpha$  and the solution of Eq. (13) such that  $y(x)$  falls off exponentially at infinity and

$$y'(0) = \alpha/2, \quad y'''(0) = 1. \quad (14)$$

Thus, although we have obtained a differential equation, the stated problem has remained as a whole non-local. Here, in place of the nonlinear integro-differential equation (7), however, we have the nonlinear differential equation (13) and the problem for it, of the type of a boundary problem on the semiaxis. We note here that it follows easily from (12) that the desired function  $\varphi(\xi)$  falls off monotonically. Actually, it is seen from the positiveness of  $n(\xi)$  and the definitions of the functions  $y(\xi)$  and  $z(\xi)$  that for all  $\xi$  we have  $(-1)^n y^{(n)} < 0$  and  $z^{(n)} > 0$  ( $n = 0, 1, 2$ ). Then the right side in (12) is negative.

To find the solution of the problem posed for (13), we begin with an estimate of the asymptotic behavior of  $y(x)$ . The nonlinear terms in the equation here can be discarded and we get the following asymptote for the linear equation as  $x \rightarrow \infty$ :

$$y \approx x^{-n/4} \exp \{-2/3 x^{3/4} - \gamma x^{5/4}\} [1 + O(x^{-5/4})]. \quad (15)$$

Further analysis has been carried out on a computer. The general scheme is the following. We express  $y$  in the form

$$y = \beta x^{-n/4} \exp \{-2/3 x^{3/4} - \gamma x^{5/4}\}$$

and find  $y^{(n)}$  ( $n = 1, 2, 3$ ) at the point  $x = x_0$ , where  $x_0$  is sufficiently large. Fixing  $\alpha$  and  $\beta$ , we find  $y(x)$ . The final choice of  $\alpha$  and  $\beta$  is obtained from the two conditions (14), which are the equations for these parameters. Without pausing on the details of the numerical analysis (the accuracy of which is of the order of 0.1%),

we write out the final results in the form of a drawing (the continuous curve). For comparison we have drawing the equilibrium Fermi function  $f(x) = [e^{2x} + 1]^{-1}$  as a dashed curve; it is sufficiently close to the one found by us in the characteristic range  $0 < x < 2$ .

The authors are grateful to R. N. Gurzhi and the participants in the seminar organized by him for discussion of the work.

<sup>1</sup>In this connection, one should recall the work of Shabanskiĭ,<sup>[6]</sup> where an incorrect attempt was made to establish the possibility of such a simplification. This has already been pointed out in Ref. 3.

<sup>2</sup>This could actually be either a "dirty" film with  $l < d$  ( $l$  is the free path length,  $d$  the film thickness) or a "clean" film ( $l > d$ ) with diffuse scattering by the boundary.

<sup>3</sup>The word "impurity" is put in quotation marks since in the case of a "clean" film, we are speaking of scattering by the boundaries with a characteristic momentum relaxation time  $\tau \sim d/v_F$ , and the corresponding kinetic equation does not contain the term  $v \cdot \nabla n_p$ , which is necessary for calculation of the conductivity  $\sigma$ .

<sup>4</sup>For a "clean" film, it is given by the well known relation

$\sigma = (3/4)\sigma_0(d/l) \ln(l/d)$ , where  $\sigma_0$  is the conductivity of the bulk specimen.

<sup>5</sup>The analysis of the effect of the thermostat on the behavior of the distribution function in the case of an arbitrary relation between  $T_e$  and  $T$  ( $0 < \gamma < \infty$ ) is connected with the account of the term  $I^T(\xi, g)$ , will be the purpose of a separate publication.

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Translated by R. T. Beyer

## Optical polarization of nuclei in molecular crystals at 4.2°K

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(Submitted April 8, 1976)

*Zh. Eksp. Teor. Fiz.* **71**, 1520–1528 (October 1976)

Polarization of hydrogen nuclei induced by unpolarized, near-ultraviolet light in molecular fluorene crystals with impurities is investigated at 4.2°K. Two characteristic peaks separated by a narrow gap, which have not been observed previously, are found in the dependence of the polarization on the external magnetic field intensity. The positions of the peaks are found to coincide with the regions of minimal distance between the magnetic sublevels of the triplet state of localized fluorene molecules. The effect is explained on the basis of the model of selective population and mixing of electron-nuclear triplet states. The calculations are in satisfactory agreement with the experiments and this uniquely defines the mechanism of optical polarization of nuclei at low temperatures.

PACS numbers: 35.20.My, 32.20.Ft

### 1. INTRODUCTION

About ten years ago, the phenomenon of optical polarization of nuclei (OPN) was discovered in molecular crystals by a group of German investigators.<sup>[1]</sup> At room temperature (and all the experiments on OPN to date have been carried out under these conditions), an enhancement of nuclear polarization was obtained that was record-breaking in comparison with other methods, and the effect arose under the action of unpolarized light. This feature drew serious attention to OPN in molecular crystals and stimulated a whole series of researches devoted to the elucidation of its physical mechanism.<sup>[2–8]</sup> At the present time, it is clear that OPN in molecular crystals is due to the nonequilibrium population of the electron spin sublevels that arises upon excitation of

phosphorescent triplet states of the molecules. Two specific mechanisms of transfer of polarization from the electron spins to the nuclear spins were proposed in Refs. 4, 5: a modification of the Overhauser effect in the migration of the excitation in the triplet exciton band of the matrix<sup>[4]</sup> and selective population and depletion of the electron-nuclear magnetic sublevels of triplet molecules with account of the mixing of states by hyperfine interaction (HFI).<sup>[5]</sup> In crystals with impurities, about which we shall speak below, the first mechanism is of little effect<sup>[4]</sup>; so far as the second is concerned, although general considerations and calculated estimates indicate its usefulness,<sup>[5,8]</sup> the most characteristic feature of this mechanism has not been observed experimentally up to the present. This feature is the sharp increase in nuclear polarization (predicted by the theory)