SOVIET PHYSICS JETP VOLUME 24, NUMBER 3 MARCH, 1967

SURFACE EFFECTS IN THE THERMODYNAMICS OF CONDUCTION ELECTRONS

S. S. NEDOREZOV[1]

Physico-technical Institute, Academy of Sciences, Ukrainian S.S.R.

Submitted to JETP editor March 31, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) **51**, 868–877 (September, 1966)

We consider the semi-classical energy quantization of a conduction electron with an arbitrary dispersion law in a metal film. We obtain formulae for the surface part of the electronic density of states; this is used to discuss thermodynamic surface quantities: Fermi level shift, surface tension of metals, and surface specific heat. We have studied the most characteristic anomalies of the thermodynamic surface characteristics of a metal in the vicinity of an electronic transition point which is caused by a change in the topology of the Fermi surface when it is deformed continuously at high pressures.

INTRODUCTION

SOMETIMES it is necessary to take into account the influence of the surface of a metal on the thermodynamics of conduction electrons (for instance, in the theory of the surface tension of metals when the thermodynamic properties of metallic particles and films are studied). Considering the conduction electrons in a metal to be a perfect gas of quasi-particles with some dispersion law $\mathscr{E}(p)$ in a volume with an impenetrable boundary surface,[1] we obtain in the present paper formulae for the surface part of the electronic density of states, and we discuss then thermodynamic surface quantities using that result.

The surface part of the density of states can be found if we know the energy levels of a conduction electron. The problem is solved for a layer. The formulae obtained for the density of states is then generalized in the limit of short wavelengths to the case of an arbitrary surface bounding a given volume.

It is necessary to note that if the energy spectrum is anisotropic the well-known quantization rule

$$p_z = \pi\hbar n / L, \quad n = 1, 2, 3, \ldots, \tag{1}$$

where L is the layer thickness, $2\pi\hbar$ Planck's constant, and where the z axis is perpendicular to the layer, for the quasi-momentum of a conduction electron in a layer is not applicable. When the quasi-particle is reflected from the boundary of the layer the absolute magnitude of the normal component of the quasi-momentum p_z changes if the dispersion law $\mathscr{E}(\mathbf{p})$ is asymmetric with respect to p_z and this leads to the quantization rule (4) which is different from (1) (see Sec. 1).[2] This fact influences very substantially the surface part of the density of states—while leaving its volume part unchanged—and hence the thermodynamic surface quantities.

We have shown, using the formulae for the surface part of the density of states which we obtain taking into account the anisotropy of the electronic energy spectrum of metals, that at the point of the electronic transition predicted by I. Lifshitz[2] and confirmed experimentally[3] the change in the topology of the Fermi surface leads to a peculiar anomaly of the thermodynamic surface quantities. The anomalies differ essentially depending on how the topology changes, either through the appearance of a new gap in the Fermi surface or by a diminishing of its connectivity. The peculiarities of the surface characteristics of a metal are much stronger than the volume ones, as in a relatively narrow range near the transition point the singularity of the thermodynamic quantities is determined by its surface part.

We have calculated the shift in the Fermi level caused by the surface of the metal. This may turn out to be important for oscillating effects[4] as it has been shown[5] that a relatively small shift in the chemical potential when a metal is deformed strongly influences the de Haas–van Alphen oscillations in metals with abnormally small groups of electrons.

It is well known[6] that the conduction electrons contribute appreciably to the surface tension of

---

[1] Permanent address: S. M. Kirov Polytechnical Institute, Tomsk.

[2] I. M. Lifshitz pointed out the necessity to replace the quantization condition (1) by the more general condition (4).

metals. Using the Sommerfeld model of metals (a quadratic dispersion law) Breger and Zhukhovitskiĭ[7] have considered the theory of the surface tension. In the present paper we obtain formulae for the surface tension of metals in the framework of a model of a gas of quasi-particles with an arbitrary dispersion law.

1. SEMI-CLASSICAL QUANTIZATION OF THE ENERGY OF A CONDUCTION ELECTRON IN A LAYER

We can find the energy levels of a quasi-particle with an arbitrary dispersion law $\mathscr{E}(\mathbf{p})$ in the semi-classical approximation if we know how the energy $\mathscr{E}$ can be expressed in terms of the action variables I_m.[8] The action variable I, corresponding to the finite motion along the z axis which is perpendicular to the layer is for the case of a quasi-particle in a layer with infinitely high potential walls equal to

$$I = \oint p_z\,dz = |p_z^{(1)} - p_z^{(2)}|L, \tag{2}$$

where the $p_z^{(i)}$ are the roots of the equation

$$\mathscr{E}(\mathbf{p}_\perp, p_z^{(i)}) = \varepsilon \tag{3}$$

for fixed values of $\mathbf{p}_\perp = \mathbf{i}p_x + \mathbf{j}p_y$ and of the energy ϵ.

The quantization

$$|p_z^{(1)} - p_z^{(2)}| = 2\pi\hbar n/L, \quad n = 1, 2, \ldots \tag{4}$$

leads to the following quantum energy levels $\epsilon(\mathbf{p}_\perp, n)$:

$$\varepsilon(\mathbf{p}_\perp, n) = \mathscr{E}[\mathbf{p}_\perp, p_z(\mathbf{p}_\perp, n)], \tag{5}$$

where $p_z(\mathbf{p}_\perp, n)$ is determined by the equation

$$\mathscr{E}(\mathbf{p}_\perp, p_z) = \mathscr{E}(\mathbf{p}_\perp, p_z - 2\pi\hbar n / L). \tag{5$'$}$$

The left-hand side of Eq. (4) is equal to the length of the section which is cut by the energy surface $\mathscr{E}(\mathbf{p}) = \epsilon(\mathbf{p}_\perp, n)$ from the line which goes through the point $(\mathbf{p}_\perp, n)$ parallel to the p_z axis.

The roots $p_z^{(i)}$ of Eq. (3) which are the appropriate pairs of roots which are quantized according to Eq. (4) are uniquely determined by the condition that the quasi-particles are reflected by the potential walls. Indeed, on reflection the kinetic energy of the quasi-particles is decreased and later again increased to its initial value so that the roots of the appropriate pair are separated by a region in which the kinetic energy is less than the fixed value (see Appendix I in [9]).

In the case of several pairs of roots, there occur just as many levels, each of which is determined by Eqs. (5) and (5′). A similar situation occurs for the semi-classical quantization in a magnetic field when the energy surface has bulges (see Appendix in [1]).

When $p_z^{(2)} = p_z^{(1)}$ the quantization condition (4) leads to the condition (1), which thus holds for isotropic dispersion and for the particular case of anisotropic dispersion with one pair of roots if $p_z = 0$ is a symmetry plane.

2. SURFACE PART OF THE ELECTRONIC DENSITY OF STATES

The number $\mathscr{N}(\epsilon)$ of electronic states with an energy less than ϵ is for the case of a layer determined by the formula

$$\mathscr{N}(\varepsilon) = \frac{gV}{(2\pi\hbar)^2 L} \sum_{n=1}^{\infty} \int \theta[\varepsilon - \varepsilon(\mathbf{p}_\perp, n)]\,d^2\mathbf{p}_\perp, \tag{6}$$

where

$$\theta(x) = \begin{cases} 0, & x < 0 \\ 1, & x > 0 \end{cases}, \tag{7}$$

g = 2s + 1, s is the quasi-particle spin and V the volume of the layer.

Using Poisson's formula to sum Eq. (6) and neglecting the oscillating terms of higher order than λ/L where λ is the wavelength of an electron with the given energy ϵ, we find

$$\mathscr{N}(\varepsilon) = \frac{gV}{(2\pi\hbar)^2 L} \Big\{ \int_0 dn \int d^2\mathbf{p}_\perp \theta[\varepsilon - \varepsilon(\mathbf{p}_\perp, n)] - \frac{1}{2} \int d^2\mathbf{p}_\perp \theta[\varepsilon - \varepsilon(\mathbf{p}_\perp 0)] \Big\} \tag{6$'$}$$

Here $\epsilon(\mathbf{p}_\perp, 0)$ is the energy for which the roots of the appropriate pair coincide. In other words, the straight line going through the point $(\mathbf{p}_\perp, 0)$ parallel to the p_z axis is tangent to the given energy surface $\mathscr{E}(\mathbf{p}) = \epsilon(\mathbf{p}_\perp, 0)$.

The first term in (6′) determines the well-known[1] volume part of the number of states $\mathscr{N}_0$, and the second one the required surface part $\mathscr{N}_\sigma(\epsilon)$:

$$\mathscr{N}_\sigma(\varepsilon) = -\frac{g\sigma}{(4\pi\hbar)^2} S(\varepsilon, \mathbf{e}_z), \tag{8}$$

where σ is the area of the surface bounding the given layer,

$$S(\varepsilon, \mathbf{e}_z) = \int \theta[\varepsilon - \varepsilon(\mathbf{p}_\perp, 0)]\,d^2\mathbf{p}_\perp. \tag{8$'$}$$

In the case of one pair of roots the quantity $S(\epsilon, \mathbf{e}_z)$ is equal to the area of the projection of the energy surface $\mathscr{E}(\mathbf{p}) = \epsilon$ onto the plane with normal $\mathbf{e}_z$.

The surface part of the electronic density of states per unit energy range $\nu_\sigma(\epsilon) = \mathscr{N}'_\sigma(\epsilon)$ is determined by the equation

$$\nu_\sigma(\varepsilon) = -\frac{g\sigma}{(4\pi\hbar)^2} \int_{C(\varepsilon, e_z)} \frac{dl}{v}, \tag{9}$$

where the integration contour $C(\epsilon, \mathbf{e}_z)$ is the projection onto the plane with normal $\mathbf{e}_z$ of the curve on the energy surface $\mathcal{E}(\mathbf{p}) = \epsilon$ along which $v_z = 0$; $v = |\nabla_p \mathcal{E}|$ is the absolute magnitude of the electron velocity along this curve.

In the short wavelength limit the formulae obtained here for the surface part of the number and density of states can be generalized for the case of an arbitrary surface σ bounding a given volume V. Provided

$$\lambda \ll R, \tag{10}$$

where R is the radius of curvature of the boundary surface σ,

$$\mathcal{N}_\sigma(\varepsilon) = -\frac{g}{(4\pi\hbar)^2}\int_\sigma S(\varepsilon, \mathbf{n})\,d\sigma, \tag{11}$$

$$\nu_\sigma(\varepsilon) = -\frac{g}{(4\pi\hbar)^2}\int_\sigma \left\{ \int_{C(\varepsilon,\,\mathbf{n})} \frac{dl}{v} \right\} d\sigma. \tag{12}$$

Here $\mathbf{n}$ is the normal to the surface σ.

This generalization has been proved exactly in the case of a quadratic dispersion law (see, e.g., [10]).

Just like the volume density of states, $\nu_\sigma(\epsilon)$ is a complicated function of its argument. Its explicit form can be obtained only when we make special assumptions about the dispersion law. We give here expressions for $\nu_\sigma(\epsilon)$ in some of the most typical cases.

A. Isotropic dispersion law

$$\mathcal{E}(\mathbf{p}) = \varepsilon, \tag{13}$$

$$\nu_\sigma(\varepsilon) = -\frac{g\sigma}{8\pi\hbar^2}\frac{p(\varepsilon)}{v(\varepsilon)}, \tag{14}$$

where the momentum $p(\epsilon)$ and the velocity $v(\epsilon)$ are determined from (13).

B. Ellipsoidal dispersion law

$$\mathcal{E}(\mathbf{p}) = \varepsilon_k + \frac{(p_1 - p_{10})^2}{2m_1} + \frac{(p_2 - p_{20})^2}{2m_2} + \frac{(p_3 - p_{30})^2}{2m_3}, \tag{15}$$

$$\nu_\sigma(\varepsilon) = -\frac{g\sqrt{m_1 m_2 m_3}}{8\pi\hbar^2}\int_\sigma \left(\frac{n_1^2}{m_1} + \frac{n_2^2}{m_2} + \frac{n_3^2}{m_3}\right)^{1/2} \times d\sigma\,\theta(\varepsilon - \varepsilon_k), \tag{16}$$

where the n_i are the components of the normal $\mathbf{n}$ to the bounding surface σ along the principal axes of the ellipsoid, $\theta(x)$ is the function defined by (7).

C. In the neighborhood of a conic point

$$\mathcal{E}(\mathbf{p}) = \varepsilon_k + \frac{(p_1 - p_{10})^2}{2m_1} + \frac{(p_2 - p_{20})^2}{2m_2} - \frac{(p_3 - p_{30})^2}{2m_3}, \tag{17}$$

$$\nu_\sigma(\varepsilon) = \frac{g\sqrt{m_1 m_2 m_3}}{8\pi^2\hbar^2}\int_\sigma \left(\frac{n_1^2}{m_1} + \frac{n_2^2}{m_2} - \frac{n_3^2}{m_3}\right)^{1/2} d\sigma \ln|\varepsilon - \varepsilon_k| + \tilde{\nu}_\sigma(\varepsilon), \tag{18}$$

where $\tilde{\nu}_\sigma(\epsilon)$ is a smooth function.

From the formulae given here it is clear that in contradistinction to the volume part of the density of states[1] the surface part $\nu_\sigma(\epsilon)$ possesses essentially different singularities when the topology of the energy surface is changed, depending on whether a new region of the surface is split off or whether its connectivity is decreased because a connection is severed.

3. THERMODYNAMIC SURFACE QUANTITIES

1. Shift of Fermi level. The Fermi level ϵ_F is determined from

$$\mathcal{N}_0(\varepsilon_F) + \mathcal{N}_\sigma(\varepsilon_F) = N, \tag{19}$$

where N is the number of electrons and $\mathcal{N}_0(\epsilon)$ the volume part of the number of states with a density $\nu_0(\epsilon)$.

From (19) and (11) we get for the shift in the Fermi level $\Delta\epsilon_F = \epsilon_F - \epsilon_F^0$ caused by the boundary of the metal

$$\Delta\varepsilon_F = \frac{1}{8\pi^2\hbar^2}\frac{1}{\nu_0}\int_\sigma S(\varepsilon_{F^0}, \mathbf{n})\,d\sigma, \tag{20}$$

where ϵ_F^0 is the Fermi level for a bulk specimen, $S(\epsilon_F^0, \mathbf{n})$ is the area of the projection of the Fermi surface on the plane with normal $\mathbf{n}$.[3)]

The Fermi level shift (20) can be observed through the de Haas–van Alphen effect.[5] It is well known[1] that the periods of the oscillations $(\delta H^{-1})_i$ are determined by the areas of the extremal cross sections $S_m^i(\epsilon_F)$ of the Fermi surface with the plane perpendicular to the magnetic field **H**. The changes in the extremal cross sections

$$\Delta S_m{}^i = S_m{}^i(\varepsilon_{F^{0i}} + \Delta\varepsilon_F) - S_m{}^i(\varepsilon_{F^{0i}}), \tag{21}$$

when the Fermi level is shifted, where ϵ_F^{0i} is the Fermi level reckoned from the bottom of the i-th energy band, lead to corresponding changes in the periods of oscillation. For films with $L \sim 10^4$ cm we have as far as order of magnitude is concerned $\Delta\epsilon_F/\epsilon_F \sim 10^{-3}$ so that for abnormally small electron groups $\Delta\epsilon_F/\epsilon_F^{0i} \sim 10\%$. From this it follows that the changes in the periods of oscillations can be appreciable.

For films at right angles to the magnetic field H, the change in the periods of oscillation $(\delta H^{-1})_i$ is determined by the equation

---

[3)] The shift in the Fermi level for electrons with a quadratic dispersion law in a potential well with a finite depth U_0 was calculated in[4]. As $U_0 \to \infty$ the expression obtained differed from (20) and from the corresponding formulae in[10]. This can be explained by the fact that in [4] the absence of electrons from levels with zero quantum numbers[7] was not taken into account.

$$\Delta\left[\left(\delta\frac{1}{H}\right)_i^{-1}\right]=\frac{1}{L}\frac{cm_i{}^*}{4\pi^2e\hbar^3}\frac{V}{v_0}S(\varepsilon_{F^0},\mathbf{n}),\tag{22}$$

where $m_i^* = (2\pi)_m^{-1}\, dS_m^i/d\epsilon_F^0$ is the effective mass for the given cross section for the case of a bulk specimen.

It is clear from (22) that the period of oscillation $(\delta H^{-1})_i$ in a film (for the case where $m_i^* > 0$) is less than the corresponding period in a bulk specimen and decreases with decreasing film thickness L. If the film is oriented in a different way the changes in the periods of oscillation may be different; this is connected with the anisotropy of $S(\epsilon_F^0, \mathbf{n})$, i.e., with the anisotropy of the Fermi surface.

2. Surface tension and surface specific heat of metals. In the low temperature region

$$T\,/\,|\varepsilon_F-\varepsilon_k|\ll 1,\tag{23}$$

where ϵ_k are singular (critical, extremal) energy values, the free energy F is determined from the well-known expression[1]

$$F=N\varepsilon_F-\int_0^{\varepsilon_F}\mathcal{N}(\varepsilon)\,d\varepsilon-\frac{\pi^2}{6}T^2\nu(\varepsilon_F).\tag{24}$$

Taking into account the Fermi level shift (20) we get from (24) for the surface part of the free energy, F_σ,

$$F_\sigma(T)=F_\sigma(0)+\frac{\pi^2}{6}T^2\nu_0\frac{d(\Delta\varepsilon_F)}{d\varepsilon_{F^0}},\tag{25}$$

$$F_\sigma(0)=\frac{1}{8\pi^2\hbar^2}\int_\sigma\left\{\int_0^{\varepsilon_{F^0}}S(\varepsilon,\mathbf{n})\,d\varepsilon\right\}d\sigma.\tag{25$'$}$$

Hence we have for the surface tension κ of metals

$$\varkappa(T,\mathbf{n})=\varkappa(0,\mathbf{n})+\frac{1}{48}T^2\frac{v_0}{\hbar^2}\frac{d}{d\varepsilon_{F^0}}\left(\frac{1}{v_0}S(\varepsilon_{F^0},\mathbf{n})\right),\tag{26}$$

$$\varkappa(0,\mathbf{n})=\frac{1}{8\pi^2\hbar^2}\int_0^{\varepsilon_{F^0}}S(\varepsilon,\mathbf{n})\,d\varepsilon.\tag{27}$$

It is clear from these formulae that if the Fermi surface is anisotropic the surface tension κ (T, **n**) depends on the orientation of the corresponding crystal boundary.4)

We get from (25) for the surface part C_σ of the electronic specific heat

$$C_\sigma=-\frac{\pi^2}{3}T\nu_0\frac{d(\Delta\varepsilon_F)}{d\varepsilon_{F^0}},\tag{28}$$

where the function $\Delta\epsilon_F$ is determined by Eq. (20). For the total specific heat C we have

$$C=C_0(1-d(\Delta\varepsilon_F)\,/\,d\varepsilon_{F^0}),\tag{29}$$

where C_0 is the specific heat of a bulk specimen.

4. ANOMALIES IN THE THERMODYNAMIC SURFACE CHARACTERISTICS OF METALS AT HIGH PRESSURES

In the vicinity of an electronic transition point[2] the thermodynamic surface quantities have peculiar anomalies which are clearly manifested at low temperatures,

$$T\ll|z|,\tag{30}$$

where $z = \zeta - \epsilon_k$, ζ is the chemical potential and ϵ_k an energy where the Fermi surface topology changes. Anomalies are caused by the fact that near a transition point the density of states has a singularity which shows up strongly in the derivatives of the thermodynamic potentials.

When calculating derivatives we can neglect the oscillating part of the thermodynamic potentials,[8] if

$$T>\Delta\varepsilon,\tag{31}$$

where $\Delta\epsilon$ is the distance between the quantum energy levels. Condition (31) is practically always satisfied. An exception are thin films at relatively low temperatures. In that case characteristic oscillations occur which will be considered separately.

The anomalies of the surface quantities differ appreciably depending on how the topology of the Fermi surface changes.

1. Anomalies in the case when there appear new gaps at the Fermi surface. If new gaps appear at the Fermi surface, for instance, due to uniform compression of the metal, in the vicinity of a transition point at temperatures determined by (30) the singularity of the surface free energy F_σ will be described by the formula

$$F_\sigma=\tilde{F}_\sigma+\delta F_\sigma,\quad \delta F_\sigma=\begin{cases}\beta_1T^2\exp\left(-|z|/T\right) & \text{(I)}\\ {}^1/_2\beta_1z^2+\pi^2\beta_1T^2/6 & \text{(II)}\end{cases}\tag{32}$$

where $\tilde{F}_\sigma$ is a smooth function, and

$$\beta_1=\frac{\sqrt{m_1m_2m_3}}{4\pi\hbar^2}\int_\sigma\left(\frac{n_1{}^2}{m_1}+\frac{n_2{}^2}{m_2}+\frac{n_3{}^2}{m_3}\right)^{1/2}d\sigma.\tag{33}$$

---

4) In the case of a quadratic dispersion law Eq. (27) agrees with the corresponding expression for the surface tension of metals at T = 0 found in[7]. The difference between the temperature dependence κ(T) determined from (26) when we go over to a quadratic dispersion law and the formulae found in[11] is explained by the fact that in[11] the temperature dependence of the chemical potential was not taken into account in the calculations.

When deriving Eq. (32) we used the density of states (16).

The dependence of z on the volume V and on the applied pressure p is determined by the well-known expression:[2]

$$z=\gamma(V-V_k)=\frac{\gamma}{\varkappa_0}(p_k-p), \qquad (34)$$

$$\gamma=-\frac{1}{\nu_0}\left(\frac{\partial\mathcal{N}_0}{\partial V_k}+\nu_0\frac{d\varepsilon_k}{dV_k}\right),\quad \varkappa_0=-\left(\frac{\partial p}{\partial V_k}\right)_{T=0}, \qquad (34')$$

where V_k and p_k are respectively the critical values of the volume and the pressure at which the Fermi surface topology changes.

The transition from region (I) to region (II) corresponds to the appearance of a new gap at the Fermi surface.

From (32) we get at once the anomalies in the following thermodynamic surface quantities: for the surface specific heat C_σ

$$\delta\frac{C_\sigma}{T}=-\delta\frac{\partial^2 F_\sigma}{\partial T^2}=\begin{cases}0\ , & \text{(I)}\ .\\ -\dfrac{\pi^2}{3}\beta_1, & \text{(II)}\end{cases} \qquad (35)$$

for the surface part of the electronic compressibility $\partial p_\sigma/\partial V$

$$\delta\frac{\partial p_\sigma}{\partial V}=-\delta\frac{\partial^2 F_\sigma}{\partial V^2}=\begin{cases}0\ , & \text{(I)}\\ -\beta_1\gamma^2, & \text{(II)}\end{cases} \qquad (36)$$

The anomaly in the surface part of the paramagnetic susceptibility χ_σ is determined by the equation

$$\delta\chi_\sigma=-{}^1\!/_2\beta_1\mu^2\{\theta[\pm(z+\mu H)]+\theta[\pm(z-\mu H)]\}, \qquad (37)$$

where there is a plus sign in the first term, if in the region (II) $z+\mu H>0$, and a minus sign if $z+\mu H<0$; and analogously in the second term. The function $\theta(x)$ is defined by Eq. (7).

The second derivatives of the thermodynamic surface potentials have thus in a point of an electronic transition a discontinuity (Fig. 1).

We now write down the equations for the anomalies in the thermodynamic quantities taking also the volume singularity[2] into account:

$$C=C_0\left\{1+\left[\frac{\alpha}{\nu_0}|z|^{1/2}-\frac{\beta_1}{\nu_0}\right]\theta(\pm z)\right\}, \qquad (35')$$

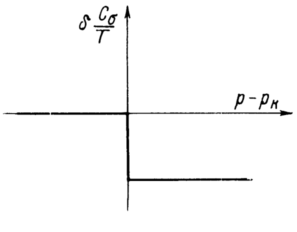

FIG. 1. The anomaly in the surface heat C_σ in the case of the appearance of a new gap at the Fermi surface when the pressure increases at the point p_k.

$$\frac{\partial p}{\partial V}=\left(\frac{\partial p}{\partial V}\right)_0+[\alpha\gamma^2|z|^{1/2}-\beta_1\gamma^2]\,\theta(\pm z), \qquad (36')$$

$$\chi=\chi_0+{}^1\!/_2\mu^2\{[\alpha|z+\mu H|^{1/2}-\beta_1]\theta[\pm(z+\mu H)]$$
$$+[\alpha|z-\mu H|^{1/2}-\beta_1]\theta[\pm(z-\mu H)]\}, \qquad (37')$$

where

$$\alpha=\frac{\sqrt{2}}{\pi^2}\frac{V}{\hbar^3}\sqrt{m_1m_2m_3.} \qquad (38)$$

The smooth part of the various quantities is indicated by the index zero.

The contribution of the surface of the metal to the pressure temperature coefficient $\partial p/\partial T$ and to the thermal expansion coefficient $\partial V/\partial T$ is unimportant in the case considered.

2. Anomalies in the case where the connectivity of the Fermi surface decreases. The thermodynamic surface quantities have much stronger singularities if at the transition point the connectivity of the Fermi surface diminishes because connections are broken. In the range of temperatures determined by (30) we get by using (18) for δF_σ

$$\delta F_\sigma=-\frac{1}{2}\beta_2 z^2\left(\ln|z|-\frac{3}{2}\right)-\frac{\pi^2}{6}\beta_2 T^2\ln|z|, \qquad (39)$$

where

$$\beta_2=\frac{\sqrt{m_1m_2m_3}}{(2\pi\hbar)^2}\int_\sigma\left(\frac{n_1^2}{m_1}+\frac{n_2^2}{m_2}-\frac{n_3^2}{m_3}\right)^{1/2}d\sigma. \qquad (40)$$

We get from (39) the anomalies of the surface part of the following thermodynamic quantities: specific heat

$$\delta\frac{C_\sigma}{T}=\frac{\pi^2}{3}\beta_2\ln|z|, \qquad (41)$$

electronic compressibility

$$\delta\partial p_\sigma/\partial V=\beta_2\gamma^2\ln|z|, \qquad (42)$$

pressure temperature coefficient

$$\delta\frac{1}{T}\frac{\partial p_\sigma}{\partial T}=-\delta\frac{\partial^2 F_\sigma}{\partial T\partial V}=\frac{\pi^2}{3}\beta_2\gamma\frac{1}{z}. \qquad (43)$$

The anomaly in the surface part of the paramagnetic susceptibility is determined by the equation

$$\delta\chi_\sigma={}^1\!/_2\mu^2\beta_2(\ln|z+\mu H|+\ln|z-\mu H|). \qquad (44)$$

When the volume and surface singularities are both taken into account the anomalies of the thermodynamic quantities have the following form:

$$C=C_0\left\{1-\frac{\alpha}{\nu_0}|z|^{1/2}\theta(\mp z)+\frac{\beta_2}{\nu_0}\ln|z|\right\}, \qquad (41')$$

$$\frac{\partial p}{\partial V}=\left(\frac{\partial p}{\partial V}\right)_0-\alpha\gamma^2|z|^{1/2}\theta(\mp z)+\beta_2\gamma^2\ln|z|, \qquad (42')$$

$$\frac{\partial p}{\partial T}=\frac{\pi^2}{3}T\left\{\frac{\partial v_0}{\partial V}\pm\frac{1}{2}\cdot\alpha\gamma|z|^{-1/2}\theta(\mp z)+\beta_2\gamma\frac{1}{z}\right\}, \quad (43')$$

$$\chi=\chi_0+{}^1/_2\mu^2\{-\alpha|z+\mu H|^{1/2}\theta[\mp(z+\mu H)]$$
$$+\beta_2\ln|z+\mu H|-\alpha|z-\mu H|^{1/2}\theta[\mp(z-\mu H)]$$
$$+\beta_2\ln|z-\mu H|\}. \quad (44')$$

The transition from region (I) to region (II) corresponds to a decrease in the connectivity of the Fermi surface. In the equations the upper sign corresponds to the case where in region (II) $z < 0$, and the lower sign to $z > 0$.

The thermal expansion coefficient $\partial V/\partial T$ has the same singularity as the pressure temperature coefficient

$$\frac{\partial V}{\partial T}=\frac{\pi^2 T}{3\varkappa_0}\left\{\frac{\partial v_0}{\partial V}\pm\frac{1}{2}\alpha\gamma|z|^{-1/2}\theta(\mp z)+\beta_2\gamma\frac{1}{z}\right\}. \quad (45)$$

From the equations obtained here it is clear that in a rather small neighborhood of the transition point the contribution from the surface to the singular dependence of the thermodynamic quantities is very important. When $|z| < z_k$ the singularity of the thermodynamic characteristics of a metal is determined by its surface part, where z_k as to order of magnitude can be found from the equation

$$\left(\frac{z_k}{\varepsilon_F}\right)^{1/2}\sim\frac{\hbar}{\sqrt{m\varepsilon_F}}\frac{\sigma}{V}\left|\ln\frac{z_k}{\varepsilon_F}\right|.$$

For films of thickness $L \sim 10^{-4}$ cm, and assuming, to get some estimates, that $\epsilon_F \sim 1$ eV we have $z_k \approx 10^{-4}$ eV.

In contradistinction to the anomalies in the bulk thermodynamic quantities which differ only in sign in their dependence on how the Fermi surface topology changes, the anomalies in the surface quantities have a qualitatively different character (see Figs. 1, 2, 3).

We note that in the neighborhood $|z| \ll \Delta\epsilon$ it is necessary to take into account the oscillating terms which we have dropped. For those values of z the formulae given here lose their meaning as by virtue of the condition (31) this range of values is unimportant since in it the singularities of the thermodynamic quantities are completely smeared out.

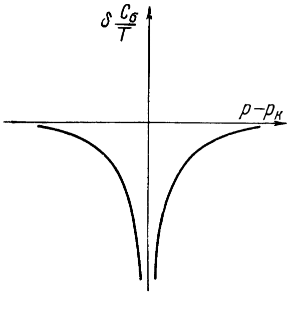

FIG. 2. The anomaly in the surface specific heat C_σ for the case when the Fermi surface connectivity decreases in the point p_k.

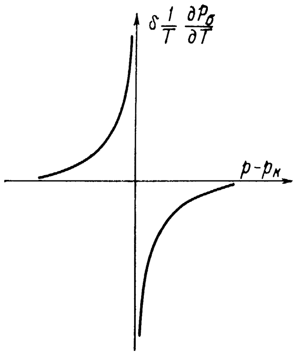

FIG. 3. The anomaly in the surface part of the pressure temperature coefficient $\partial p_\sigma \partial T$ for the case when the Fermi surface connectivity diminishes at the point p_k.

In conclusion I express my deepest gratitude to Professor I. M. Lifshitz for his careful guidance during this work.

---

[1] I. M. Lifshitz and M. I. Kaganov, UFN **78**, 411 (1962), Soviet Phys. Uspekhi **5**, 878 (1963).

[2] I. M. Lifshitz, JETP **38**, 1569 (1960), Soviet Phys. JETP **11**, 1130 (1960).

[3] V. I. Makarov and V. G. Bar'yakhtar, JETP **48**, 1717 (1965), Soviet Phys. JETP **21**, 1151 (1965); V. I. Makarov, Thesis, Physico-technical Inst., Acad. Sc., Ukr. SSR, Khar'kov, 1965.

[4] B. G. Smith, Physics Letters **18**, 210 (1965).

[5] A. M. Kosevich, JETP **35**, 249 (1958), Soviet Phys. JETP **8**, 171 (1959); Dmitrenko Verkin, and Lazarev, JETP **35**, 328 (1958), Soviet Phys. JETP **8**, 229 (1959).

[6] S. N. Zadumkin, in Collection: ''Poverkhnostnye yavleniya v rasplavakh i protsessakh poroshkovoĭ metallurgii'' (Surface Phenomena in Melts and Powder-Metallurgy Processes) Kiev, Acad. Sc. Ukr. SSR, 1963, p. 7.

[7] A. Kh. Breger and A. A. Zhukhovitskiĭ, J. Chem. Phys. (USSR) **20**, 355 (1946).

[8] I. M. Lifshitz and A. M. Kosevich, Izv. AN SSSR ser. fiz. **19**, 395 (1955), transl., Bull. Acad. Sci. Phys. Ser. **19**, 353 (1955).

[9] I. M. Lifshitz and M. I. Kaganov, UFN **87**, 389 (1965), Soviet Phys. Uspekhi **8**, 805 (1966).

[10] S. S. Nedorezov, Izv. Vuzov, Fizika, No. 3, 11 (1965).

[11] A. Kh. Breger, J. Chem. Phys. (USSR) **22**, 920 (1948).

Translated by D. ter Haar
102