SURFACE MAGNETIZATION OF METALS

S. S. NEDOREZOV

Physico-technical Low Temperature Institute, Ukrainian Academy of Sciences

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The contribution of magnetic surface levels to the thermodynamic properties of metals is investigated. Formulas are obtained for the magnetic surface levels in the case of an arbitrary dispersion law. It is shown that the strong surface magnetization of metals in weak magnetic fields, assumed in a number of papers, is nonexistent.

1. The effect of the surface of a metal on its magnetic properties in a parallel magnetic field is due to magnetic surface levels and has been investigated in[1-5]. At present it is known that magnetic surface levels exist. They were first detected by Khaĭkin[6] in an investigation of oscillations of the surface impedance (see[7]). The present paper is devoted to investigation of the contribution of magnetic surface levels to the thermodynamic properties of metals.

If one takes account of the bounding surface of a metal, the thermodynamic quantities can be expressed as the sum of two terms, one of which is proportional to the volume V and the second to the area of the bounding surface S. Thus for the magnetic moment M, we have

$$\mathrm{M} = V\mathrm{M}^{(v)} + S\mathrm{M}^{(s)}. \tag{1}$$

Here $\mathrm{M}^{(V)}$ is related to the magnetic Landau levels and has been quite thoroughly investigated. The value of $\mathrm{M}^{(S)}$ is basically determined by the magnetic surface levels.

In[1] only an order-of-magnitude estimate of $\mathrm{M}^{(S)}$ was obtained. Later Steel[2] and Dingle[5] calculated $\mathrm{M}^{(S)}$ by using a quasiclassical approximation for the magnetic surface levels. As a result, the following dependence on the magnetic field H was obtained for the surface part of the magnetic moment:

$$M^{(s)}_{\text{quas}} \sim H^{-1/3}, \tag{2}$$

which leads to a strong surface magnetization of metals in weak magnetic fields[1)].

Another approach to the problem was indicated by E. Lifshitz and Kosevich[3,4]. They showed that in the calculation of $\mathrm{M}^{(S)}$, it is necessary to take account of the exact values of the magnetic surface levels, since $\mathrm{M}^{(S)}$ differs significantly from $\mathrm{M}^{(S)}_{\text{quas}}$. According to an estimate obtained in[4], $\mathrm{M}^{(S)}/\mathrm{M}^{(S)}_{\text{quas}} < 0.1$. In[3,4] the assertion was also implied, though in general unproved, that in the dependence of the magnetic moment on H, the singularity described by formula (2) is nonexistent.

In one of the later papers[9], the effect of the magnetic field on the spectrum was taken into account by perturbation theory, within whose framework, of course, it was impossible to allow for any singularities that might be present in the dependence of the magnetic surface levels on H. In[10], the metallic surface was modeled by a parabolic potential with a certain frequency ω_0; here the usual Landau expression for the susceptibility was obtained.

2. The magnetic surface levels $\epsilon_n(p_x, p_z)$ in the quasiclassical range ($n \gg 1$) are determined by the quantization condition[11]

$$S(p_x, p_z, \varepsilon) = \frac{2\pi\hbar eH}{c}(n + {}^3/_4), \quad n = 0, 1, 2, 3, \ldots, \tag{3}$$

where $S(p_x, p_z, \epsilon)$ is the area of a cross-section of the isoenergetic surface $\mathscr{E}(p) = \epsilon$ in the plane p_z = const. The section is bounded by the straight line p_z = const (see Fig. 1).

In the range of small quantum numbers, $n \sim 1$, the magnetic surface levels can be found by solution of Schrödinger's equation

$$\hat{\mathscr{H}}\Psi(x, y, z) = \varepsilon\Psi(x, y, z), \quad \Psi(x, 0, z) = 0, \tag{4}$$

with the effective Hamiltonian

$$\hat{\mathscr{H}} = \mathscr{E}(\hat{p}_x, p_{y_0}, \hat{p}_z) - \frac{\partial\mathscr{E}}{\partial\hat{p}_x}\frac{eHy}{c} - \frac{\hbar^2}{2}\frac{\partial^2\mathscr{E}}{\partial p_{y0}^2}\frac{\partial^2}{\partial y^2} \tag{5}$$

where $\mathbf{p} = -i\hbar\partial/\partial\mathbf{r}$, and the quasimomentum p_{y0} satisfies the condition

$$\partial\mathscr{E} / \partial p_{y_0} = 0. \tag{5'}$$

Hence we get for the magnetic surface levels

$$\varepsilon_n(p_x, p_z) = \mathscr{E}(p_x, p_{y0}, p_z) + s_n\left(\frac{v_x\hbar eH}{c\sqrt{2m^*}}\right)^{2/3}, \tag{6}$$

where $-s_n$ are the roots of the Airy function

$$\mathrm{Ai}(-s_n) = 0. \tag{6'}$$

Here

$$v_x = \partial\mathscr{E} / \partial p_x|_{p_y = p_{y_0}}, \quad m^* = (\partial^2\mathscr{E} / \partial p_{y_0}{}^2)^{-1}.$$

The asymptote ($n \gg 1$) of the roots of the Airy

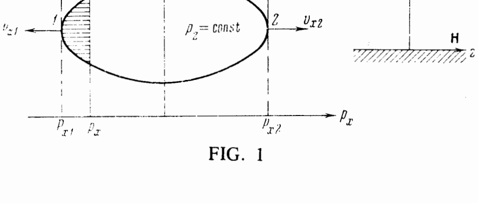

FIG. 1

[1)]In a recently published paper [8], the quasiclassical approximation for the magnetic surface levels was also used in the calculation of $\mathrm{M}^{(s)}$ If one corrects an apparent error in sign (see formula (6) in [8]), the result obtained agrees with Dingle's result [5] and also with the quasiclassical part of the magnetic moment $\mathrm{M}^{(s)}_{\text{quas}}$ calculated in [3].

function is determined by the expression

$$s_n \sim \left[\frac{3\pi}{2}\left(n+\frac{3}{4}\right)\right]^{2/3} + \frac{5}{48}\left[\frac{3\pi}{2}\left(n+\frac{3}{4}\right)\right]^{-4/3} - \dots \tag{7}$$

Solution of equation (3) on the supposition that $|p_x - p_{x1}|/R \ll 1$ (R = radius of curvature of the section S at the point where $v_y = 0$) agrees with (6) in the case of large quantum numbers, $n \gg 1$. For magnetic fields such that $\hbar eH/cp_F^2 \ll 1$ (p_F = Fermi momentum), the condition $|p_x - p_{x1}|/R \ll 1$ is satisfied for sufficiently large quantum numbers n, so that the solutions ϵ_n obtained from (3) and from (6) match well and completely describe the magnetic surface levels in the case of an arbitrary dispersion law.

3. The information thus obtained about the energy spectrum is sufficient for investigation of the contribution of the magnetic surface levels to thermodynamic quantities. In the calculation, it is convenient to express the thermodynamic potential

$$\Omega = -\frac{2VT}{L(2\pi\hbar)^2}\sum_{n=0}^{\infty}\iint dp_x\,dp_z \ln\left[1+\exp\frac{\zeta-\varepsilon_n(p_x,p_z)}{T}\right] \tag{8}$$

in the form

$$\Omega = \Omega^{\text{quas}} + \delta\Omega, \tag{9}$$

where Ω^{quas} is described by formula (8) with energy levels $\epsilon_n^{\text{quas}}(p_x, p_z)$ determined by the condition (3), and

$$\delta\Omega = -\frac{2VT}{L(2\pi\hbar)^2}\iint dp_x\,dp_z\sum_{n=0}^{n_0}\left\{\ln\left[1+\exp\frac{\zeta-\varepsilon_n(p_x,p_z)}{T}\right] - \ln\left[1+\exp\frac{\zeta-\varepsilon_n^{\text{quas}}(p_x,p_z)}{T}\right]\right\}. \tag{10}$$

Here the energy levels ϵ_n and ϵ_n^{quas} are determined by formula (6) with, respectively, the exact values s_n and the quasiclassical values $s_n^{\text{quas}} = [\tfrac{3}{2}\pi(n+\tfrac{3}{4})]^{2/3}$; n_0 satisfies the condition for applicability of formula (6).

We calculate the thermodynamic potential Ω^{quas} in the well-known manner[12], summing by Poisson's formula. In the calculation of $\delta\Omega$, it is necessary to make use of the smallness of the second term in (6) in comparison with the first. As a result, we get for the surface part of the thermodynamic potential, $\Omega^{(S)}$,

$$\Omega^{(s)} = \frac{\alpha}{2^{1/3}(2\pi\hbar)^2}\left(\frac{\hbar eH}{c}\right)^{2/3}\int_0^{\epsilon_F} d\varepsilon\int dp_z\left[R_1^{-1/3}(\varepsilon,p_z)+R_2^{-1/3}(\varepsilon,p_z)\right] \tag{11}$$

where $R_i(\epsilon, p_z)$ are the radii of curvature of the section of the isoenergetic surface $\mathscr{E}(p) = \epsilon$ by the plane p_z = const at the points i = 1 and 2 (see Fig. 1), and

$$\alpha = \sum_{n=0}^{\infty}\left(s_n - \left[\frac{3\pi}{2}\left(n+\frac{3}{4}\right)\right]^{2/3}\right) - \frac{\Gamma(2/3)}{6^{1/3}\pi}\sum_{k=1}^{\infty}\frac{1}{k^{5/3}}\cos\left(\frac{\pi k}{2}-\frac{\pi}{6}\right). \tag{12}$$

In the first sum in this formula, we have gone to the limit, letting $n_0 \to \infty$; this may be done, since the series converges (see formula (7) for the asymptote of s_n). The remaining term is negligibly small by virtue of the small parameter

$$(\mu H/\varepsilon_F)^{1/3} \ll 1, \tag{13}$$

where μ is the Bohr magneton and ϵ_F is the Fermi level. On differentiating $\Omega^{(S)}$, we get the corresponding expression for the surface part of the magnetic moment, $M^{(S)} = -\partial\Omega^{(S)}/\partial H$.

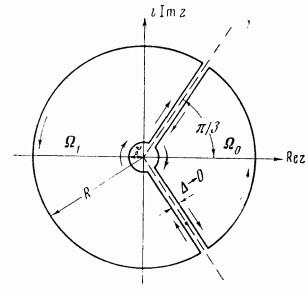

FIG. 2

In formula (11) we have retained only the principal terms of the expansion in H, those proportional to $H^{2/3}$. Higher terms of the series, of order $H^{4/3}$, are not considered in this paper.

4. The further calculations are concerned with finding the number α. The first sum in formula (12) can be calculated by a method explained in[13] 2). The desired result is obtained immediately from a calculation of the integral

$$J = \frac{1}{2\pi i}\int_{C_R} z\left[\frac{d}{dz}\mathrm{Ai}(-z)/\mathrm{Ai}(-z) - \varphi(z)\right]dz \tag{14}$$

along the contour C_R (see Fig. 2), where

$$\varphi(z) = z^{1/2}\operatorname{ctg}\left(\frac{2}{3}z^{3/2}+\frac{\pi}{4}\right)+\frac{5}{48}\frac{1}{z}\left[\operatorname{ctg}^2\left(\frac{2}{3}z^{3/2}+\frac{\pi}{4}\right)-\frac{7}{5}\right],\quad z\in\Omega_0$$
$$\varphi(z) = (-z)^{1/2} - \frac{1}{4}\frac{1}{z},\qquad z\in\Omega_1. \tag{15}$$

The integral on the circles of radius R and of radius γ vanishes when $R \to \infty$ and $\gamma \to 0$. On applying the theory of residues and calculating the integral J on the boundary of the regions Ω_0 and Ω_1, we get as a result

$$\sum_{n=0}^{\infty}\left(s_n - \left[\frac{3\pi}{2}\left(n+\frac{3}{4}\right)\right]^{2/3}\right) = \frac{\Gamma(2/3)}{6^{1/3}\pi}\sum_{k=1}^{\infty}\frac{1}{k^{5/3}}\cos\left(\frac{\pi k}{2}-\frac{\pi}{6}\right). \tag{16}$$

Hence it follows that $\alpha = 0$.

Thus the strong surface magnetization of metals in weak magnetic fields, obtained in[1,2,5,8], is actually nonexistent in the model considered (mirror reflection of the electrons is assumed at the surface of the metal).

Singularities in the dependence of the magnetic surface levels on the magnetic field can occur only in higher terms of the expansion of the thermodynamic potential Ω in the magnetic field H, which can lead to the following dependence of the magnetic susceptibility $\chi^{(S)}$ on H:

$$\chi^{(s)} \sim H^{-2/3}. \tag{17}$$

This question will be treated in more detail elsewhere.

In closing, I express my sincere thanks to Academician I. M. Lifshitz and to Professor M. I. Kaganov for their interest in the research and for valuable discussions.

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2) I take this opportunity to thank F. S. Rofe-Beketov for acquainting me with reference [13].

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