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SURFACE ELECTRONIC FLUCTUATIONS IN METALS

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The effect of a surface on electronic fluctuations in anisotropic metals is theoretically studied. The Coulomb interaction of the electron-hole excitations is taken into account selfconsistently. A system of the Boltzmann equation for electronic fluctuations and the Maxwell equations for the interaction field is solved with required boundary conditions. The observed inelastic scattered light out metal is a result of the collective electron interaction with a radiation inside metal. The scattering cross section consists of the bulk contribution of electron - hole pairs and plasmons, which differs from the scattering by infinite metal only in the effect of the penetration of radiation in skin layer. The surface contribution to the cross section is attributed to the electromagnetic excitations of the nonradiative into vacuum surface plasmons (the sharp peak) and the radiative surface plasmons (the continuum).

1. Inelastic light scattering is the known method of the experimental study of the electronic fluctuations. Recently the electron Raman light scattering has been observed [1 – 4] in various high temperature superconductors in order to determine the energy superconducting gap Δ. It has been found out that there is a peculiarity appearing below the temperature of the superconducting transition at a low frequency transfer $\omega \simeq 2\Delta \simeq 200 \div 400$ cm^{-1}. At a larger frequency transfer, i.e. $\omega \simeq 10^2 \div 10^4$ cm $^{-1}$, the cross section depends neither on ω nor temperature; on this background there are phonon peaks which are not considered here. According to the theory the electronic contribution to the Raman light scattering must diminish with increasing of ω. In the pure superconductor or a normal metal [5,6] it takes place at $\omega > v/\delta \simeq 10 \div 100$ cm^{-1} if $\Delta << v/\delta$ and at $\omega > \Delta$ if $\Delta >> v/\delta$ [7], where δ is the skin depth and v is the Fermi velocity. In the dirty metal the cross section decreases [8,9] at $\omega >> \tau^{-1}$ if $\tau^{-1} > \Delta$. The estimation of τ according to various experimental data for HTSC (see, e.g., Ref.10,11) gives $\tau^{-1} \simeq (10^{13} \div 10^{14}) s^{-1} \simeq (10^2 \div 10^3)$ cm^{-1} for temperature $T \simeq 100$K. Thus we should like to find the collisionless mechanism of such non decreasing behavior in the range $\omega \simeq (10^3 \div 10^4)$ cm^{-1}.

The abnormal behavior of the cross section on large frequencies is explained also by the nesting on the Fermi surface [12] or by the strong electron-phonon interaction [13].

In this paper we focus on the effect of the surface, taking into account a metal anisotropy. Usually a theory of fluctuations in an electronic system is formulated for an infinite space [14]. However, the typical distances of fluctuations are of the order of the skin depth in the optical frequency range. For such distances the presence of a surface is especially significant, because specified surface excitations exist nearby. We include the electron-electron interaction. Usually it is treated as

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the Coulomb interaction and described in the theory of the plasma fluctuations by the Poisson equation [14]. Within this approach one loses the dispertion of the surface plasmons. Therefore the retardation of electromagnetic interaction should be considered.

2. We calculate here the density-density correlation function

$$K_{\gamma^*\gamma}(\mathbf{r},t;\mathbf{r}',t') = < \delta n_{\gamma^*}(\mathbf{r},t)\delta n_\gamma(\mathbf{r}',t') >, \tag{1}$$

where the density fluctuation

$$\delta n_\gamma(\mathbf{r},t) = \int \frac{d^3p}{(2\pi)^3}\gamma(\mathbf{p})\delta f_p(\mathbf{r},t) \tag{2}$$

is modified by the vertex factor

$$\gamma(\mathbf{p}) = e_\alpha^{(i)} e_\beta^{(s)} \left(\delta_{\alpha\beta} + \frac{1}{m}\sum_n \frac{p_{fn}^\beta p_{nf}^\alpha}{\epsilon_f(\mathbf{p}) - \epsilon_n(\mathbf{p}) + \omega^{(i)}} + \frac{p_{fn}^\beta p_{nf}^\alpha}{\epsilon_f(\mathbf{p}) - \epsilon_n(\mathbf{p}) - \omega^{(s)}} \right), \tag{3}$$

which in the framework of the band theory represents a sum of two Feynman diagrams describing the light scattering [15]. In the expression (3) we neglect the light momentum in comparison with the electron momentum. The subscript f denotes the index of the band in which the carriers exist, the transitions happen into any band n, $\mathbf{p}_{fn}$ is the electron momentum matrix element, m is the electron mass, $\omega^{(i)}$ and $\omega^{(s)}$ are frequencies of the incident and scattered light, respectively. For a free space, $\mathbf{e}^{(i)}$, $\mathbf{e}^{(s)}$ are the polarization vectors of the incident and scattered light. For the scattering in metal the parameters $\mathbf{e}^{(i)}$ and $\mathbf{e}^{(s)}$ are complex. The factor $\gamma(\mathbf{p})$ could be complex also because the damping for the intermediate states can be included in the denominator of Eq.(3). The concrete form $\gamma(\mathbf{p})$ does not play any important role because the dependence on the momentum transfer is essential for our calculations.

If metal occupies the half space, the electrodynamic problem should be solved to connect the incident (scattered) radiation in vacuum ($z < 0$) with the incident (scattered) radiation in metal ($z > 0$). One can find [16] the cross section is expressed by an integral over z and z' of two functions. One of them is the Fourier transform $K_{\gamma^*\gamma}(\mathbf{k}_S, z, z';\omega)$ of (1) with respect to spatial coordinates, parallel to the surface $\mathbf{s} - \mathbf{s}'$ and with respect to time $t - t'$. The other one $U^*(\mathbf{k}_S, z;\omega)U(\mathbf{k}_S, z';\omega)$ is determined by the distribution of the incident $A^{(i)}$ and scattered $A^{(s)}$ fields in metal:

$$A^{(i)}(\mathbf{r},t)A^{(s)}(\mathbf{r},t) = U(\mathbf{r},t) = U(\mathbf{k}_S, z;\omega)\exp[i(\mathbf{k}_S\mathbf{s} - \omega t)], \tag{4}$$

where the frequency and momentum transfers are $\omega = \omega^{(i)} - \omega^{(s)}$, $\mathbf{k}_S = \mathbf{k}_S^{(i)} - \mathbf{k}_S^{(s)}$. If the frequencies $\omega^{(s)}$ and $\omega^{(s)}$ are in the normal skin range, the field

$$U(\mathbf{k}_S, z;\omega) = \exp(i\zeta z), \quad \zeta = \zeta_1 + i\zeta_2 = \lambda^{(i)} + \lambda^{(s)}. \tag{5}$$

The constants λ depend on frequency and polarization. We consider the normal incidence ($\mathbf{k}_S^{(i)} = 0$), direct the x axis along $\mathbf{k}_S$ and assume, that our coordinate planes are the symmetry planes of a crystal. For the parallel polarization

$(\mathbf{E}^{(s)} = (E_x^{(s)}, 0, E_z^{(s)}))$ and for the perpendicular polarization $(\mathbf{E}^{(s)} = (0, E_y^{(s)}, 0))$ of the scattered field we get

$$\lambda_l^{(s)2} = \Big[\Big(\frac{\omega^{(s)}}{c}\Big)^2 \epsilon_{zz}(\omega^{(s)}) - k_x^{(s)2}\Big] \frac{\epsilon_{xx}(\omega^{(s)})}{\epsilon_{zz}(\omega^{(s)})}, \quad \lambda_t^{(s)2} = \Big(\frac{\omega^{(s)}}{c}\Big)^2 \epsilon_{yy}(\omega^{(s)}) - k_x^{(s)2} \tag{6}$$

respectively.

In order to calculate the Fourier transform of the correlation function (1) we apply the general fluctuation-dissipation theorem:

$$K_{\gamma^*\gamma}(\mathbf{k_S}, z, z'; \omega) = \frac{2}{1 - \exp(-\omega/T)} \operatorname{Im} \alpha(\mathbf{k_S}, z, z'; \omega), \tag{7}$$

where α is the generalized susceptibility in the field $U(\mathbf{k_S}, z; \omega)$ (4):

$$< \delta n_{\gamma^*}(\mathbf{k_S}, z; \omega) >= 2 \int \frac{d^3p}{(2\pi)^3} \gamma^*(\mathbf{p}) < \delta f_{\mathbf{p}}(k_x, z; \omega) >=$$

$$= - \int_0^\infty dz' \ \alpha(\mathbf{k_S}, z, z'; \omega) U(\mathbf{k_S}, z'; \omega). \tag{8}$$

We derive the generalized susceptibility by means of the Boltzmann equation

$$\mathbf{v} \frac{\partial \delta f_{\mathbf{p}}(\mathbf{r}, \omega)}{\partial \mathbf{r}} - i\omega \delta f_{\mathbf{p}}(\mathbf{r}, \omega) = - \big(\ \gamma(\mathbf{p}) \mathbf{v} \nabla U(\mathbf{r}, \omega) + e \mathbf{v} \mathbf{E}(\mathbf{r}, \omega) \ \big) \frac{df_o}{d\epsilon}, \tag{9}$$

where $\mathbf{v}$ is the electron velocity and f_o is the non fluctuating part of the distribution function which gives the Fermi distribution function for electrons in metal after taking the statistical average.

The electric field $\mathbf{E}(\mathbf{r}, \omega)$ represents the electron - electron interaction. For self-consistent determination of the field we apply the Maxwell equation. Conservation of tangential components of the electric and magnetic fields implies boundary conditions at the surface $z = 0$ for the Maxwell equations. Assuming the specular boundary condition for the kinetic equation (9) at $z = 0$ (a more realistic boundary condition for the distribution function [16] does not essentially affect the final results) we can use the even continuation in the $z < 0$ half space for the components $E_\alpha(\mathbf{r}, \omega)$ parallel to the surface and for the field $U(\mathbf{r}, \omega)$. For the perpendicular component $E_z(\mathbf{r}, \omega)$ we need to apply the odd continuation. Next we can take the Fourier transform with respect to the coordinates.

Using the solution of the Boltzmann equation we obtain the current density

$$j_\alpha(\mathbf{k}, \omega) = \frac{2e}{(2\pi)^3} \int d^3p \, v_\alpha < \delta f_{\mathbf{p}}(\mathbf{k}, \omega) >= \sigma_{\alpha\beta}(\mathbf{k}, \omega) E_\beta(\mathbf{k}, \omega) + \Gamma_\alpha(\mathbf{k}, \omega) U(\mathbf{k}, \omega), \tag{10}$$

where

$$\sigma_{\alpha\beta}(\mathbf{k}, \omega) = \frac{2ie^2}{(2\pi)^3} \int \frac{dS}{v} \frac{v_\alpha v_\beta}{\omega - \mathbf{k}\mathbf{v}}, \tag{11}$$

$$\Gamma_\alpha(\mathbf{k}, \omega) = \frac{2e}{(2\pi)^3} \int \frac{dS}{v} \frac{v_\alpha \mathbf{k}\mathbf{v}}{\omega - \mathbf{k}\mathbf{v}} \gamma(\mathbf{p}). \tag{12}$$

Here the integration is taken over the Fermi surface, since we assume $T << \epsilon_F$; $\alpha = x, y, z$.

3. Substituting (10) into the Maxwell equations, we arrive at the equations determining the electric field in a metal. One of the equations has the form:

$$(k_z^2 - \frac{\omega^2}{c^2}\epsilon_{xx}(\mathbf{k},\omega))E_x(\mathbf{k},\omega) - k_x k_z E_z(\mathbf{k},\omega) =$$

$$= \frac{4\pi i\omega}{c^2}U(\mathbf{k},\omega)\Gamma_x(\mathbf{k},\omega) - 2\frac{i\omega}{c}H_y(k_x, z=0;\omega). \tag{13}$$

where the contribution of the filled bands $\epsilon^o_{\alpha\beta}$ is included in the dielectric constant

$$\epsilon_{\alpha\beta}(\mathbf{k},\omega) = \epsilon^o_{\alpha\beta} + \frac{4\pi i}{\omega}\sigma_{\alpha\beta}(\mathbf{k},\omega). \tag{14}$$

The last term in (13) represents the surface effect.Before the Fourier transformation (with respect to z) it has the form

$$-\frac{d^2}{dz^2}E_x(k_x, z;\omega) + ik_x\frac{d}{dz}E_z(k_x, z;\omega)$$

After the even continuation this term reveals δ-like singularity at $z=0$ and the additional last term of the right side appears in the Fourier transform. By means of the Maxwell equations one can see that it gives the magnetic field in the right side of (13).

We find the solution of the Maxwell equations :

$$E_x = \frac{4\pi i\omega U(\mathbf{k},\omega)}{c^2\mathcal{D}(\mathbf{k},\omega)}\left[(k_x^2 - \frac{\omega^2}{c^2}\epsilon_{zz}(\mathbf{k},\omega))\Gamma_x(\mathbf{k},\omega) + k_x k_z\Gamma_z(\mathbf{k},\omega)\right] -$$

$$-\frac{2i\omega H_y(k_x, 0;\omega)}{c\mathcal{D}(\mathbf{k},\omega)}(k_x^2 - \frac{\omega^2}{c^2}\epsilon_{zz}(\mathbf{k},\omega)), \tag{15}$$

where

$$\mathcal{D}(\mathbf{k},\omega) = \frac{\omega^2}{c^2}(\frac{\omega^2}{c^2}\epsilon_{xx}(\mathbf{k},\omega)\epsilon_{zz}(\mathbf{k},\omega) - k_x^2\epsilon_{xx}(\mathbf{k},\omega) - k_z^2\epsilon_{zz}(\mathbf{k},\omega)). \tag{16}$$

In the vacuum the electric field is $E_x(k_x, z;\omega) = E_x(k_x, z=0;\omega)\exp(-iq_z z)$, where $q_z = ((\omega/c)^2 - k_x^2)^{1/2}$.
Conservation of the fields $E_x(k_x, z;\omega)$ and $H_y(k_x, z;\omega)$ at $z=0$ gives :

$$H_y(k_x, 0;\omega) = \frac{4\pi}{c}I_1(k_x,\omega)(iq_z\frac{c^2}{\omega^2} + 2I_2(k_x,\omega))^{-1}, \tag{17}$$

where

$$I_1(k_x,\omega) = \int\frac{dk_z}{2\pi}\frac{U(\mathbf{k},\omega)}{\mathcal{D}(\mathbf{k},\omega)}\left[(k_x^2 - \frac{\omega^2}{c^2}\epsilon_{zz}(\mathbf{k},\omega))\Gamma_x(\mathbf{k},\omega) + k_x k_z\Gamma_z(\mathbf{k},\omega)\right], \tag{18}$$

$$I_2(k_x,\omega) = \int\frac{dk_z}{2\pi}\frac{1}{\mathcal{D}(\mathbf{k},\omega)}(k_x^2 - \frac{\omega^2}{c^2}\epsilon_{zz}(\mathbf{k},\omega)) \tag{19}$$

As far as the field H_y (17) is known, we can find the field E_x (15) and calculate the generalized susceptibility (8):

$$< \delta n_{\gamma^*}(k_x, z;\omega) >=$$

$$= 2\int \frac{dk_z}{2\pi} e^{ik_z z} \int \frac{dS}{(2\pi)^3 v} \frac{\gamma^*(\mathbf{p})}{\omega - \mathbf{kv}} \left(\gamma(\mathbf{p})\mathbf{kv}U(\mathbf{k},\omega) + ie\mathbf{v}\mathbf{E}(\mathbf{k},\omega) \right). \tag{20}$$

We are interested in the integral

$$\int_0^\infty dzdz' \; U^*(k_x, z;\omega)U(k_x, z';\omega)K_{\gamma^*\gamma}(k_x, z, z';\omega). \tag{21}$$

According to (7),(8) and (20) this integral is proportional to

$$\Sigma(k_x,\omega) =$$

$$-2 \;\mathrm{Im} \int \frac{dk_z}{2\pi} U^*(\mathbf{k},\omega) \int \frac{dS}{(2\pi)^3 v} \frac{\gamma^*(\mathbf{p})}{\omega - \mathbf{kv}} \left(\gamma(\mathbf{p})\mathbf{kv}U(\mathbf{k},\omega) + ie\mathbf{v}\mathbf{E}(\mathbf{k},\omega) \right), \tag{22}$$

where symmetry of $\alpha(\mathbf{k}_S, z, z';\omega)$ with respect to z and z' was used.

4. The first term in the parentheses of the expression (22) represents the bulk unscreened electron-hole fluctuations. An similar expression has been obtained for superconductors by applying the Green function method [5] (see also [6]).

The second term in the parentheses in the expression (22), if in the field $\mathbf{E}(\mathbf{k},\omega)$ only the terms proportional to $U(\mathbf{k},\omega)$ are left in (15), represents also the volume effect. If $\omega << kv$, this term expresses the Coulomb screening of the electron-hole exitations. Therefore they contribute into the Raman scattering only if $\gamma(\mathbf{p})$ is anisotropic. A similar result was obtained by the Green function method in [18]. For the large frequency transfer $\omega >> kv$, this term describes the exitation of plasmons, if the transfer is larger than their frequency.

At last if we substitute the term proportional to H_y(16) in (22) for $\mathbf{E}(\mathbf{k},\omega)$ we obtain the surface contribution of the electronic fluctuations. The imaginary part of (22) arises in the parentheses of (17) at the condition $kv << \omega$. Putting $\mathbf{k} = 0$ in $\epsilon_{\alpha\beta}$ (14),(11) we integrate (19):

$$I_2(k_x,\omega) = \frac{c^2}{2\omega^2} \left(\frac{k_x^2 - \epsilon_{zz}(0,\omega)\omega^2/c^2}{\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)} \right)^{1/2}. \tag{23}$$

The expression in the parentheses (17) is proportional to

$$\mathcal{G}(k_x,\omega) = \left(i(\omega^2/c^2 - k_x^2)^{1/2} + \left(\frac{k_x^2 - \epsilon_{zz}(0,\omega)\omega^2/c^2}{\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)} \right)^{1/2} \right)^{-1}. \tag{24}$$

Under the condition $\omega^2/c^2 - k_x^2 < 0$, which means that the electric field of the electronic fluctuations is nonradiative into vacuum, $\mathcal{G}(k_x,\omega)$ has a pole which determines the dispersion law of the surface plasmons:

$$k_x^2(\omega) = \frac{\omega^2}{c^2} \frac{\epsilon_{zz}(0,\omega)(1 - \epsilon_{xx}(0,\omega))}{1 - \epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)}. \tag{25}$$

For the isotropic case the equation (25) gives the well known dispersion relation.

Separating the imaginary part at the pole we get

$$-\mathrm{Im}\mathcal{G}(k_x,\omega) = 2\frac{\omega}{c} \frac{\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)(1 - \epsilon_{zz}(0,\omega))^{1/2}}{(\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega) - 1)^{3/2}} \pi\delta(k_x^2 - k_x^2(\omega)),$$

where $k_x^2(\omega)$ is given by (25).

The imaginary part of $\mathcal{G}(k_x,\omega)$ (24) arises also at the condition $\omega^2/c^2 - k_x^2 > 0$, which means that the electric field of the electronic fluctuations is radiative into vacuum from the metal surface. Here the imaginary part is

$$-\mathrm{Im}\mathcal{G}(k_x,\omega) = (\omega^2/c^2 - k_x^2)^{1/2}\left(\frac{\omega^2}{c^2} - k_x^2 + \frac{k_x^2 - \epsilon_{zz}(0,\omega)\omega^2/c^2}{\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)}\right)^{-1} \mathrm{sign}\omega.$$

Using $\mathcal{D}(\mathbf{k},\omega)$ (16) with $\epsilon_{\alpha\beta}(0,\omega)$ and the Fourier transform $U(\mathbf{k},\omega)$ of (5) we integrate over k_z in (22) and get the Raman cross-section:

$$d\sigma = \left(\frac{8\pi e^2}{mc\hbar\omega^{(i)}}\right)^2 \frac{\Sigma(k_x,\omega)}{1-\exp(-\omega/T)} \frac{k_z^{(s)}\omega^{(s)}d\omega^{(s)}do^{(s)}}{c(2\pi)^3},$$

where $k_x^{(s)} = (\omega^{(s)}/c)\sin\theta^{(s)}$, $k_z^{(s)} = (\omega^{(s)}/c)\cos\theta^{(s)}, \theta^{(s)}$ is the scattering angle.

We note several qualitive results, remaining the details for further publications. The wide frequency interval $v|\zeta| < \omega < \omega_p$ (between electron-hole exitations and the volume plasmons) is filled by the surface plasmons. For an anysotropic metal the dieleçtric constants $\epsilon_{xx}(0,\omega)$ and $\epsilon_{zz}(0,\omega)$ vanish at the different ω. Therefore two types of the surface plasmons exist instead of single one in the interval $0 < \omega < \omega_p/\sqrt{2}$. At last the cross-section increases in the case of a large plasma dispertion parameter (usually of the order of the Fermi velocity) and for a small damping of the incident light.

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