Surface electronic fluctuations in metals

L. A. Falkovsky
L. D. Landau Institute for Theoretical Physics, Russian Academy of Sciences, 117334 Moscow, Russia

S. Klama
Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179 Poznan, Poland

(Submitted 22 December 1993)
Pis'ma Zh. Eksp. Teor. Fiz. **59**, No. 2, 127–132 (25 January 1994)

The effect of the surface on electronic fluctuations in anisotropic metals is studied theoretically. The Coulomb interaction of the electron–hole excitations is taken into account self-consistently. A system of Boltzmann's equations for electronic fluctuations and of Maxwell's equations for the interaction field is solved with the required boundary conditions. The observed inelastically scattered light outside the metal is the result of the collective electron interaction with the radiation inside the 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 to the skin layer. The surface contribution to the cross section is attributed to the electromagnetic excitations of the nonradiative surface plasmons to the vacuum surface plasmons (the sharp peak) and the radiative surface plasmons (the continuum).

1. Inelastic light scattering is a well-known method of experimental study of the electronic fluctuations. The electron Raman light scattering has recently been observed[1–4] in various high-temperature superconductors in order to determine the energy superconducting gap Δ. It was found that a peculiarity appears below the temperature of the superconducting transition at a low frequency transfer, $\omega \simeq 2\Delta \simeq 200$–$400\ \mathrm{cm}^{-1}$. At a higher frequency transfer, i.e., $\omega \simeq 10^2$–$10^4\ \mathrm{cm}^{-1}$, the cross section depends neither on ω nor on the temperature; against 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 an increase in ω. In a clean superconductor or a normal metal[5,6] it takes place at $\omega > v/\delta \simeq 10$–$100\ \mathrm{cm}^{-1}$ if $\Delta \ll v/\delta$ and at $\omega > \Delta$ if $\Delta \gg v/\delta$ (Ref. 7), where δ is the skin depth, and v is the Fermi velocity. In a dirty metal the cross section decreases[8,9] at $\omega \gg \tau^{-1}$ if $\tau^{-1} > \Delta$. An estimate of τ according to various experimental data for HTSC (see, e.g., Refs. 10 and 11) gives $\tau^{-1} \simeq 10^{13}$–$10^{14}\ \mathrm{s}^{-1} \simeq (10^2$–$10^3)\ \mathrm{cm}^{-1}$ for a temperature $T \simeq 100$ K. It would therefore be worthwhile to determine the collisionless mechanism of such a non-decreasing behavior in the range $\omega \simeq 10^3$–$10^4\ \mathrm{cm}^{-1}$.

The abnormal behavior of the cross section at high frequencies can also be explained by the nesting on the Fermi surface[12] or by the strong electron–phonon coupling.[13]

In this paper we focus on the effect of the surface, taking into account the metal

 © 1994 American Institute of Physics

anisotropy. Usually a theory of fluctuations in an electronic system is formulated for an infinite space.[14] However, the typical distances of fluctuations are on the order of the skin depth in the optical frequency range. For such distances the presence of a surface is especially important, because specified surface excitations exist nearby. We include the electron–electron interaction. Usually it is treated as the Coulomb interaction and described in the theory of the plasma fluctuations by the Poisson equation.[14] With this approach one loses the dispersion of the surface plasmons. The retardation of electromagnetic interaction should therefore be considered.

2. We calculate here the density–density correlation function

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

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

If metal occupies the half-space, the electrodynamic problem should be solved in order to connect the incident (scattered) radiation in vacuum ($z<0$) with the incident (scattered) radiation in the metal ($z>0$). We see[16] that the cross section is expressed by an integral over z and z' of the two functions. One of them is the Fourier transform $K_{\gamma^*\gamma}(\mathbf{k}_s,z,z';\omega)$ of (1) with respect to the spatial coordinates, which are parallel to the surface $s-s$, 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 field $A^{(i)}$ and the scattered field $A^{(s)}$ in the 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 transfer are $\omega=\omega^{(i)}-\omega^{(s)}$ and $\mathbf{k}_s=\mathbf{k}_s^{(i)}-\mathbf{k}_s^{(s)}$. 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 the frequency and the polarization. We consider the normal incidence ($\mathbf{k}_s^{(i)}=0$), direct the x axis along $\mathbf{k}_s$, and assume that the coordinate planes are the symmetry planes of the 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 obtain

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

respectively.

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

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

where α is the generalized susceptibility in the field $U(\mathbf{k}_s,z;\omega)$ [Eq. (4)]:

$$\langle\delta n_{\gamma^*}(\mathbf{k}_s,z;\omega)\rangle=2\int\frac{d^3p}{(2\pi)^3}\gamma^*(\mathbf{p})\langle\delta f\mathbf{p}(k_x,z;\omega)\rangle$$

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

We derive the generalized susceptibility by means of the Boltzmann equation

$$\mathbf{v}\frac{\partial\delta f_{\mathbf{p}}(\mathbf{r},\omega)}{\partial\mathbf{r}}-i\omega\delta f\mathbf{p}\,(\mathbf{r},\omega)=-[\gamma(\mathbf{p})\mathbf{v}\nabla U(\mathbf{r},\omega)+e\mathbf{v}\mathbf{E}(\mathbf{r},\omega)]\frac{df_0}{d\epsilon},\tag{9}$$

where $\mathbf{v}$ is the electron velocity, and f_0 is the nonfluctuating part of the distribution function which gives the Fermi distribution function for electrons in the 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 a Maxwell's equation. Conservation of the tangential components of the electric and magnetic fields implies boundary conditions at the surface $z=0$ for Maxwell's 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

$$j_\alpha(\mathbf{k},\omega)=\frac{2e}{(2\pi)^3}\int d^3pv_\alpha\langle\delta f\mathbf{p}(\mathbf{k},\omega)\rangle=\sigma_{\alpha\beta}(\mathbf{k},\omega)E_\beta(\mathbf{k},\omega)+\Gamma_\alpha(\mathbf{k},\omega)U(\mathbf{k},\omega),\tag{10}$$

where

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

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

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

3. Substituting (10) into Maxwell's equations, we obtain the equations determining the electric field in a metal. One of the equations has the form

$$\left[k_z^2-\frac{\omega^2}{c^2}\epsilon_{xx}(\mathbf{k},\omega)\right]E_x(\mathbf{k},\omega)-k_xk_zE_z(\mathbf{k},\omega)$$

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

where the contribution of the filled bands $\epsilon^0_{\alpha\beta}$ is included in the dielectric constant

$$\epsilon_{\alpha\beta}(\mathbf{k},\omega)=\epsilon^0_{\alpha\beta}+\frac{4\pi i}{\omega}\sigma_{\alpha\beta}(\mathbf{k},\omega). \tag{14}$$

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 a δ-like singularity at $z=0$ and the additional last term on the right side appears in the Fourier transform. With the help of Maxwell's equations we can see that it gives the magnetic field on the right side of (13).

We find the solution of Maxwell's equations

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

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

where

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

In the vacuum the electric field is $E_x(k_x,z;\omega)=E_x(k_x,z=0;\omega)\exp(-iq_zz)$, 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

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

where

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

$$I_2(k_x,\omega)=\int\frac{dk_z}{2\pi}\frac{1}{\mathscr{D}(\mathbf{k},\omega)}\left[k_x^2-\frac{\omega^2}{c^2}\epsilon_{zz}(\mathbf{k},\omega)\right]. \tag{19}$$

Since the field H_y [Eq. (17)] is known, we can find the field E_x [Eq. (15)] and calculate the generalized susceptibility (8):

$$\langle\delta n_{\gamma^*}(k_x,z;\omega)\rangle=2\int\frac{dk_z}{2\pi}e^{ik_zz}\int\frac{dS}{(2\pi)^3v}\frac{\gamma^*(\mathbf{p})}{\omega-\mathbf{kv}}[\gamma(\mathbf{p})\mathbf{kv}U(\mathbf{k},\omega)+ie\mathbf{v}\mathbf{E}(\mathbf{k},\omega)]. \tag{20}$$

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

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

where the 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 expression (22) represents the bulk, unscreened, electron–hole fluctuations. A similar expression was obtained for superconductors by applying the Green's function method[5] (see also Ref. 6).

The second term in the parentheses in expression (22) represents the volume effect, if in the field $\mathbf{E}(\mathbf{k},\omega)$ only the terms proportional to $U(\mathbf{k},\omega)$ are retained in (15). If $\omega\ll kv$, this term expresses the Coulomb screening of the electron–hole excitations. Therefore they contribute to the Raman scattering only if $\gamma(\mathbf{p})$ is anisotropic. A similar result was obtained by the Green's function method in Ref. 18. For a large frequency transfer, $\omega\gg kv$, this term describes the excitation of plasmons if the transfer is larger than their frequency.

Finally, if we substitute the term proportional to H_y [Eq. (16)] in (22) for $\mathbf{E}(\mathbf{k},\omega)$, we will obtain the surface contribution of the electronic fluctuations. The imaginary part of (22) appears in the parentheses of (17) if the condition $kv\ll\omega$ is satisfied. Setting $\mathbf{k}=0$ in $\epsilon_{\alpha\beta}$, (14) and (11), we integrate (19)

$$I_2(k_x,\omega)=\frac{c^2}{2\omega^2}\left(\frac{k_2^x-\epsilon_{zz}(0,\omega)\omega^2/c^2}{\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)}\right)^{1/2}. \tag{23}$$

The expression in the parentheses in (17) is proportional to

$$\mathcal{G}(k_x, \omega) = \left[i(\omega^2/c^2 - k_2^x)^{1/2} + \left(\frac{k_x^2 - \epsilon_{zz}(0, \omega)\omega^2/c^2}{\epsilon_{xx}(0, \omega)\epsilon_{zz}(0, \omega)} \right)^{1/2} \right]^{-1}. \qquad (24)$$

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

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

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

Separating the imaginary part at the pole we obtain

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

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

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

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

Using $\mathcal{D}(k, \omega)$, (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 find 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 $k_x^{(s)} = (\omega^{(s)}/c)\sin\theta^{(s)}$, $k_z^{(s)} = (\omega^{(s)}/c)\cos\theta^{(s)}$, and $\theta^{(s)}$ is the scattering angle.

We note several qualitative results, leaving the details for future publications. The wide frequency interval $v|\zeta| < \omega < \omega_p$ (between the electron–hole excitations and the volume plasmons) is filled by the surface plasmons. For an anisotropic metal the dielectric constants $\epsilon_{xx}(0, \omega)$ and $\epsilon_{zz}(0, \omega)$ vanish at different values of ω. There are therefore two types of surface plasmons, instead of one in the interval $0 < \omega < \omega_p/\sqrt{2}$. The cross section increases in the case of a large plasma dispersion parameter (usually on the order of the Fermi velocity) and for small damping of the incident light.

One of the authors (L.A.F.) thanks the Russian Foundation for Basic Research.

[1)]e-mail: falk@cpd.landau.free.net

[1]M. Boekholt, M. Hoffman, and G. Güntherodt, Physica C **175**, 127 (1991).
[2]T. Staufer, R. Hackl, and P. Müller, Solid State Commun. **79**, 409 (1991).
[3]F. Slakey, M. V. Klein, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **43**, 3764 (1992).
[4]A. A. Maksimov, A. V. Puchkov, I. I. Tartakovskii *et al.*, Solid State Commun. **81**, 407 (1992).

[5]A. A. Abrikosov and L. A. Falkovsky, Zh. Exp. Teor. Fiz. **40**, 262 (1961) [Sov. Phys. JETP **13**, 179 (1961)].
[6]I. P. Ipatova, M. I. Kaganov, and A. V. Subashiev, Zh. Exp. Teor. Fiz. **84**, 1830 (1983) [Sov. Phys. JETP **57**, 1066 (1983)].
[7]A. A. Abrikosov and L. A. Falkovsky, Physica C **156**, 1 (1988).
[8]A. Zawadowski and M. Cardona, Phys. Rev. B **42**, 10732 (1990).
[9]L. A. Falkovsky, Zh. Exp. Teor. Fiz. **103**, 666 (1993) [Sov. Phys. JETP **76**, 331 (1993)].
[10]J. Kircher, M. Cardona, A. Zibold *et al.*, Phys. Rev. B **48**, 3993 (1993).
[11]K. Kamaras *et al.*, Phys. Rev. Lett. **64**, 84 (1990).
[12]A. Virosztek and J. Ruvalds, Phys. Rev. B **45**, 347 (1992).
[13]V. N. Kostur, Z. Phys. B **89**, 149 (1992).
[14]E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics*, Moscow, Nauka, 1979, Ch. IV (in Russian); (Pergamon, Oxford 1981).
[15]M. V. Klein and S. B. Dierker, Phys. Rev. B **29**, 4976 (1984).
[16]L. A. Falkovsky, Zh. Exp. Teor. Fiz. **100**, 2045 (1991); (Sov. Phys. JETP **73**, 1134 (1991).
[17]L. A. Falkovsky, Adv. in Phys. **32**, 753 (1983).
[18]A. A. Abrikosov and V. M. Genkin, Zh. Exp. Teor. Fiz. **65**, 842 (1973); (Sov. Phys. JETP **38**, 417 (1974)).

Published in English in the original Russian journal. Reproduced here with the stylistic changes by the Translations Editor.