Surface electronic fluctuations in metals and Raman light scattering

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(Received 7 February 1994; revised manuscript received 17 May 1994)

The effect of a 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 consisting of the Boltzmann equation for electronic fluctuations and the Maxwell equations for the interaction field is solved with appropriate boundary conditions. The cross section of inelastic light scattering is calculated. The scattered light observed out of the metal is a result of the collective electron interaction with 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 an infinite metal only in the effect of the penetration of radiation in the 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 with a peak).

I. INTRODUCTION

Inelastic light scattering is a known method for experimental studies of electronic fluctuations. Recently, the inelastic electronic light scattering has been observed[1–5] in various high-temperature superconductors (HTSC's) in order to determine the superconducting energy 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 $\omega \simeq 2\Delta \simeq 200$–$400\ \mathrm{cm}^{-1}$. However, more surprising is the fact that at a larger frequency transfer, i.e., $\omega \simeq 10^2$–$10^4\ \mathrm{cm}^{-1}$, the cross section depends neither on ω nor on temperature; on this background there are phonon peaks which are not considered here. The flat Raman continuum exists also in rare-earth metals.[6] According to theory the electronic contribution to the inelastic light scattering should diminish with increasing ω. In a pure superconductor or a normal metal[7,8] this occurs at $\omega > v/\delta \simeq 10$–$100\ \mathrm{cm}^{-1}$ if $\Delta \ll v/\delta$ and at $\omega > \Delta$ if $\Delta \gg v/\delta$ (see Ref. 9), where δ is the skin depth and v is the Fermi velocity. In a dirty metal the cross section decreases[10,11] at $\omega \gg \tau^{-1}$ if the scattering rate $\tau^{-1} > \Delta$. The estimation of τ based on various experimental data for HTSC's (see, e.g., Ref. 12) gives $\tau^{-1} \simeq 10^{13}$–$10^{14}\ \mathrm{s}^{-1} \simeq 10^2$–$10^3\ \mathrm{cm}^{-1}$ for temperature $T \simeq 100$ K. Thus we should like to find a collisionless mechanism of such nondecreasing behavior in the range $\omega \simeq 10^3$–$10^4\ \mathrm{cm}^{-1}$, where the superconducting properties are not essential. The normal properties of the high-temperature superconductors have been the most basic problems of theoretical and experimental research.

We note that the abnormal behavior of the cross section at large frequencies is explained by nesting on the Fermi surface[13] and by the strong electron-phonon interaction.[14] In Ref. 15 a conclusion has been made that the Raman continuum is unlikely to come from conduction electrons because it is observed also in the insulating phases.

The metal surface was ignored in the above mentioned papers. However, the typical distances of fluctuations in the optical frequency range are of the order of the skin depth. For such distances the presence of a surface is especially significant, because specified excitations exist nearby. A contribution of the surface excitations arises in the observable quantities.

A large number of papers has been devoted to the surface excitations in the electron system. The historical background of the field is given in a recent review[16] in the context of electron energy loss spectroscopy. Several review articles have been published in Ref. 17.

In this paper we focus on the effect of the surface in Raman light scattering, taking into account the electron-electron interaction. We shall see that the bulk and surface plasmons may play an important role apart from the electron-hole excitations. So far as the plasmon dispersion is concerned, our treatment differs from the known theories in accounting for the anisotropy of the electron properties. We are interested in high-frequency transfer $\tau^{-1} \ll \omega$ and low-momentum transfer $k \simeq \omega_p/c \ll p_F$ (ω_p is the plasma frequency, p_F is the Fermi momentum). For such transfers the dispersion of the surface plasmons is important. Therefore the retardation of the Coulomb interaction should be included. Apart from that we can use the Boltzmann equation in dealing with the fluctuations.

The plan of this paper is as follows. In Sec. II we calculate the modified density-density correlation function in terms of the generalized susceptibility by applying the general fluctuation-dissipation theorem. The generalized susceptibility is calculated taking into consideration the electron-electron interaction which is described by the Maxwell equations. In order to find the generalized susceptibility we will use the Boltzmann kinetic equation in the collisionless limit, including the scattering rate only for the estimation of the peak width. On the electromagnetic field and the kinetic equation we apply the appropriate boundary conditions leading to all the surface effects considered in this paper. The integral of the correlation function describing the inelastic light scattering cross section is obtained taking into account the distribution of the incident and scattered light in the metal (the connection between this integral and the Raman cross section is given in the Appendix). In Sec. III the bulk and surface electronic fluctuations are found. In Sec. IV the contributions of the electron-hole excitations, the bulk plasmons, and the surface nonradiative and radiative plasmons to the Raman cross section are discussed.

II. THEORETICAL FRAMEWORK

We calculate the density-density correlation function

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

where the density fluctuation

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

is modified by the vertex factor $\gamma(\mathbf{p})$, and $\delta f_{\mathbf{p}}(\mathbf{r},t)$ is the nonequilibrium part of the electron distribution function. The correlation function (1) determines the cross section of the inelastic light scattering. The factor

$$\gamma(\mathbf{p}) = e_{\alpha}^{(i)}e_{\beta}^{(s)}\left[\delta_{\alpha\beta} + \frac{1}{m}\sum_{n}\left(\frac{p_{fn}^{\beta}p_{nf}^{\alpha}}{\epsilon_f(\mathbf{p}) - \epsilon_n(\mathbf{p}) + \omega^{(i)}} + \frac{p_{fn}^{\beta}p_{nf}^{\alpha}}{\epsilon_f(\mathbf{p}) - \epsilon_n(\mathbf{p}) - \omega^{(s)}}\right)\right] \quad (3)$$

in the framework of band theory represents a sum of two Feynman diagrams describing the light scattering.[18] The first one is quadratic in the vector potential $\mathbf{A}$ in the Hamiltonian and is taken in the first order of perturbation theory. The second one is calculated in the second order of perturbation theory on the term linear in $\mathbf{A}$ in the Hamiltonian. 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, and $\omega^{(i)}$ and $\omega^{(s)}$ are the frequencies of the incident and scattered light, respectively. In the expression (3) the light momentum is neglected in comparison with the electron momentum.

For the infinite space $\mathbf{e}^{(i)}, \mathbf{e}^{(s)}$ are the polarization vectors of the incident and scattered light, and the correlation function (1) depends on the differences $\mathbf{r}-\mathbf{r}', t-t'$. Hence the Fourier component of the correlation function is directly related to the cross section of the inelastic light scattering. However, if metal occupies the $z > 0$ 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. As shown in the Appendix [see (A14) and Ref. 19], the cross section is expressed by an integral over z and z' of two functions. One of them is $U^*(\mathbf{k_s}, z;\omega)U(\mathbf{k_s}, z';\omega)$, determined by the distribution of the incident $A^{(i)}$ and scattered $A^{(s)}$ fields in the metal:

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

where $U(\mathbf{k_s}, z;\omega)$ is given by (A16) and (A17), $\omega = \omega^{(i)} - \omega^{(s)}$, and $\mathbf{k_s} = \mathbf{k_s}^{(i)} - \mathbf{k_s}^{(s)}$ are the frequency and momentum transfers, respectively. The second function 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 $t-t'$. We get the parameters $\mathbf{e}^{(i)}$ and $\mathbf{e}^{(s)}$ which are complex and given by (A15). The factor $\gamma(\mathbf{p})$ could be complex also, since the damping for the intermediate states can be included in the denominator of the expression (3). The specific form of $\gamma(\mathbf{p})$ does not play any important role because its dependence on the momentum transfer is not essential for our calculations.

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

$$K_{\gamma*\gamma}(\mathbf{k_s}, z, z';\omega) = \frac{2}{1-\exp(-\omega/T)}\mathrm{Im}\,\alpha(\mathbf{k_s}, z, z';\omega), \quad (5)$$

where α is the generalized susceptibility in an external field $U(\mathbf{k_s}, z;\omega)$ (4), $\hbar = k_B = 1$, and

$$\langle \delta n_{\gamma^*}(\mathbf{k_s}, z;\omega)\rangle = 2\int \frac{d^3p}{(2\pi)^3}\gamma^*(\mathbf{p})\langle \delta f_{\mathbf{p}}(k_x, z;\omega)\rangle = -2\int_0^{\infty} dz'\alpha(\mathbf{k_s}, z, z';\omega)U(\mathbf{k_s}, z';\omega). \quad (6)$$

We calculate the nonequilibrium part of the electron distribution function by using the kinetic equation

$$\mathbf{v}\frac{\partial \delta f_{\mathbf{p}}(\mathbf{r},\omega)}{\partial \mathbf{r}} - i\omega\delta f_{\mathbf{p}}(\mathbf{r},\omega) = [i\omega\gamma(\mathbf{p})U(\mathbf{r},\omega) - e\mathbf{v}\cdot\mathbf{E}(\mathbf{r},\omega)]\frac{df_0}{d\epsilon}, \quad (7)$$

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 a self-consistent determination of the field we apply the Maxwell equation

$$\mathrm{rotrot}\mathbf{E}(\mathbf{r},\omega) - \left(\frac{\omega}{c}\right)^2\mathbf{D}(\mathbf{r},\omega) = \frac{4\pi i\omega}{c^2}\mathbf{j}(\mathbf{r},\omega), \quad (8)$$

where the electric current density

$$\mathbf{j}(\mathbf{r},\omega)=\frac{2e}{(2\pi)^3}\int d^3p\mathbf{v}\langle\delta f_{\mathbf{p}}(\mathbf{r},\omega)\rangle, \tag{9}$$

and $D_\alpha(\mathbf{r},\omega)=\epsilon^0_{\alpha\beta}E_\beta(\mathbf{r},\omega)$, where $\epsilon^0_{\alpha\beta}$ is the contribution of the filled bands.

To solve Eqs. (7) and (8) we take the Fourier transform with respect to spatial coordinates parallel to the surface $\mathbf{s}$ (the x axis is directed along $\mathbf{k_s}$, k_y=0): $\mathbf{E}(\mathbf{r},\omega)\rightarrow\mathbf{E}(k_x,z;\omega)$. Conservation of tangential components of the electric and magnetic fields implies boundary conditions at the surface $z=0$ for the Maxwell equations (8). We apply the boundary condition for the kinetic equation (7) in the form of the specular reflection of electrons,

$$\begin{gathered}[\delta f_{\mathbf{p}}(\mathbf{r},\omega)]_{v_z>0}=[\delta f_{\mathbf{p}}(\mathbf{r},\omega)]_{v_z<0}\,,\\ \epsilon(\mathbf{p_s},v_z>0)=\epsilon(\mathbf{p_s},v_z<0),\end{gathered} \tag{10}$$

for $z=0$. A more realistic boundary condition for the distribution function (see Ref. 20) does not essentially affect the final results.

We can use the even continuation in the $z<0$ half space for the component $E_x(k_x,z;\omega)$ parallel to the surface and for the field $U(k_x,z,\omega)$. For the perpendicular component $E_z(k_x,z;\omega)$ we apply the odd continuation.

The solution of the kinetic equation (7) has the form

$$\delta f_{\mathbf{p}}(\mathbf{k},\omega)=\frac{i}{\omega-\mathbf{k}\cdot\mathbf{v}}[i\gamma(\mathbf{p})\omega U(\mathbf{k},\omega)-e\mathbf{v}\cdot\mathbf{E}(\mathbf{k},\omega)]\frac{df_0}{d\epsilon}. \tag{11}$$

One can immediately see that the expression (11) satisfies the boundary condition (10) since

$$\delta f_{\mathbf{p}}(k_x,z=0,\omega)=\int\frac{dk_z}{2\pi}\delta f_{\mathbf{p}}(k_x,k_z,\omega) \tag{12}$$

and we can change the signs of v_z and k_z conserving the value of the integral (12). We assume that the coordinate planes described above are the symmetry planes of the crystal. Hence $\gamma(\mathbf{p})$ does not vary if the component v_z changes its sign.

By using Eq. (11) we obtain the current density

$$j_\alpha(\mathbf{k},\omega)=\sigma_{\alpha\beta}(\mathbf{k},\omega)E_\beta(\mathbf{k},\omega)+\Gamma_\alpha(\mathbf{k},\omega)U(\mathbf{k},\omega), \tag{13}$$

where

$$\sigma_{\alpha\beta}(\mathbf{k},\omega)=\frac{2ie^2}{(2\pi)^3}\int\frac{dS}{v}\frac{v_\alpha v_\beta}{\omega-\mathbf{k}\cdot\mathbf{v}}, \tag{14}$$

$$\Gamma_\alpha(\mathbf{k},\omega)=\frac{2e\omega}{(2\pi)^3}\int\frac{dS}{v}\frac{v_\alpha}{\omega-\mathbf{k}\cdot\mathbf{v}}\gamma(\mathbf{p}). \tag{15}$$

Here the integration is taken over the Fermi surface, since we assume $T\ll\epsilon_F$.

Substituting (13) into the Maxwell equation (8), we arrive at the equations determining the electric field in a metal:

$$\left(k_z^2-\frac{\omega^2}{c^2}\epsilon_{xx}\right)E_x-k_xk_zE_z=\frac{4\pi i\omega}{c^2}U\Gamma_x-2\frac{i\omega}{c}H_y(k_x,z=0;\omega), \tag{16}$$

$$-k_xk_zE_x+\left(k_x^2-\frac{\omega^2}{c^2}\epsilon_{zz}\right)E_z=\frac{4\pi i\omega}{c^2}U\Gamma_z, \tag{17}$$

$$\left(k_x^2+k_z^2-\frac{\omega^2}{c^2}\epsilon_{yy}\right)E_y=\frac{4\pi i\omega}{c^2}U\Gamma_y-2\frac{dE_y(k_x,z=0;\omega)}{dz}, \tag{18}$$

where $\epsilon_{\alpha\beta}(\mathbf{k},\omega)$ is linked to the conductivity tensor,

$$\epsilon_{\alpha\beta}(\mathbf{k},\omega)=\epsilon^0_{\alpha\beta}+\frac{4\pi i}{\omega}\sigma_{\alpha\beta}(\mathbf{k},\omega). \tag{19}$$

For simplicity, we assume that $\epsilon_{\alpha\beta}$ has the diagonal form in the coordinate system connected with the metal surface plane (x,y) and the scattering plane (x,z) and we omit in (16)–(18) the arguments $\mathbf{k},\omega$ of E_α,Γ_α, U, and $\epsilon_{\alpha\beta}$.

Before the Fourier transformation (with respect to z) the Maxwell equation (18) contains the second derivative $-\frac{d^2}{dz^2}E_y(k_x,z;\omega)$. After the even continuation this term reveals a δ-like singularity at $z=0$ and the additional last term of the right side appears in the Fourier transform (18). Also in the coordinate representation of Eq. (16) the derivative term has the form $-\frac{d^2}{dz^2}E_x(k_x,z;\omega)+ik_x\frac{d}{dz}E_z(k_x,z;\omega)$ and it gives $-2\frac{d}{dz}E_x(k_x,z=0^+;\omega)+2ik_xE_z(k_x,z=0^+;\omega)$ for the Fourier transform (16). By means of the Maxwell equation one can see that the derivative term gives the magnetic field on the right side of (16).

We find the solution of the Maxwell equations (16) and (17):

$$E_x=\frac{4\pi i\omega U(\mathbf{k},\omega)}{c^2\mathcal{D}(\mathbf{k},\omega)}\left[\left(k_x^2-\frac{\omega^2}{c^2}\epsilon_{zz}(\mathbf{k},\omega)\right)\Gamma_x(\mathbf{k},\omega)+k_xk_z\Gamma_z(\mathbf{k},\omega)\right]-\frac{2i\omega H_y(k_x,0;\omega)}{c\mathcal{D}(\mathbf{k},\omega)}\left(k_x^2-\frac{\omega^2}{c^2}\epsilon_{zz}(\mathbf{k},\omega)\right), \tag{20}$$

with

$$\mathcal{D}(\mathbf{k},\omega)=\frac{\omega^2}{c^2}\left(\frac{\omega^2}{c^2}\epsilon_{xx}(\mathbf{k},\omega)\epsilon_{zz}(\mathbf{k},\omega)-k_x^2\epsilon_{xx}(\mathbf{k},\omega)-k_z^2\epsilon_{zz}(\mathbf{k},\omega)\right), \tag{21}$$

and an analogous expression for E_z. The axes of our coordinate system are chosen along the crystal symmetry axes and $k_y=0$; hence $\Gamma_y(\mathbf{k},\omega)=0$ and $E_y(\mathbf{k},\omega)=0$ [see (15) and (18)].

In vacuum ($z < 0$) the electric field $E_x(k_x, z; \omega) = E_x(k_x, z = 0; \omega) \exp(-iq_z z)$, $q_z = [(\omega/c)^2 - k_x^2]^{\frac{1}{2}}$, and the electric and magnetic fields are interrelated by the expression

$$E_x(k_x, z = 0; \omega) = -\frac{c}{\omega} q_z H_y(k_x, z = 0; \omega). \qquad (22)$$

The fields $E_x(k_x, z; \omega)$ and $H_y(k_x, z; \omega)$ are continuous at the surface $z = 0$. Hence by using the Fourier transform

$$E_x(k_x, z = 0; \omega) = \int \frac{dk_z}{2\pi} E_x(\mathbf{k}, \omega)$$

and the formulas (20) and (22), we find

$$H_y(k_x, z = 0; \omega) = \frac{4\pi}{c} I_1(k_x, \omega) \left(iq_z \frac{c^2}{\omega^2} + 2I_2(k_x, \omega) \right)^{-1}, \qquad (23)$$

where

$$I_1(k_x, \omega) = \int \frac{dk_z}{2\pi} \frac{U(\mathbf{k}, \omega)}{\mathcal{D}(\mathbf{k}, \omega)} \left[\left(k_x^2 - \frac{\omega^2}{c^2} \epsilon_{zz}(\mathbf{k}, \omega) \right) \Gamma_x(\mathbf{k}, \omega) + k_x k_z \Gamma_z(\mathbf{k}, \omega) \right], \qquad (24)$$

$$I_2(k_x, \omega) = \int \frac{dk_z}{2\pi} \frac{1}{\mathcal{D}(\mathbf{k}, \omega)} \left(k_x^2 - \frac{\omega^2}{c^2} \epsilon_{zz}(\mathbf{k}, \omega) \right). \qquad (25)$$

As long as the field H_y (23) is known, we can find the field E_α (20) and calculate the generalized susceptibility (6):

$$\langle \delta n_{\gamma^*}(k_x, z; \omega) \rangle = \int \frac{dk_z}{2\pi} e^{ik_z z} I_3(\mathbf{k}, \omega), \qquad (26)$$

$$I_3(\mathbf{k}, \omega) = 2 \int \frac{dS}{(2\pi)^3 v} \frac{\gamma^*(\mathbf{p})}{\omega - \mathbf{k} \cdot \mathbf{v}} \times [\omega \gamma(\mathbf{p}) U(\mathbf{k}, \omega) + ie\mathbf{v} \cdot \mathbf{E}(\mathbf{k}, \omega)], \qquad (27)$$

where $\mathbf{E}(\mathbf{k}, \omega)$ is given by (20) and (23). As mentioned above [see text before Eq. (4) and (A14)], we are interested in the integral

$$\int_0^\infty dz \int_0^\infty dz' U^*(k_x, z; \omega) U(k_x, z'; \omega) K_{\gamma*\gamma}(k_x, z, z'; \omega). \qquad (28)$$

According to (5), (15), and (26), this integral is proportional to

$$\Sigma(k_x, \omega) = -\text{Im} \int \frac{dk_z}{2\pi} U^*(\mathbf{k}, \omega) I_3(\mathbf{k}, \omega). \qquad (29)$$

III. THE BULK AND SURFACE CONTRIBUTIONS TO THE ELECTRONIC FLUCTUATIONS

A. The bulk excitations

The first term of the expression (29) [see (27)] represents the bulk unscreened electron-hole fluctuations. Separating the imaginary part we get this contribution,

$$\Sigma_1(k_x, \omega) = 2 \int \frac{dk_z}{2\pi} |U(\mathbf{k}, \omega)|^2 \times \int \frac{dS}{(2\pi)^3 v} |\gamma(\mathbf{p})|^2 \mathbf{k} \cdot \mathbf{v} \pi \delta(\omega - \mathbf{k} \cdot \mathbf{v}). \qquad (30)$$

The imaginary part appears because ω in (29) contains an infinitesimally small imaginary quantity. An expression similar to (30) has been obtained for superconductors by applying the Green function method in Ref. 7 (see also Ref. 8).

The integral over the Fermi surface in (30) differs from zero if $\omega < \max(\mathbf{k} \cdot \mathbf{v})$ on the Fermi surface. If $\omega \ll kv$,

$$\int \frac{dS}{(2\pi)^3 v} |\gamma(\mathbf{p})|^2 \pi \delta(\omega - \mathbf{k} \cdot \mathbf{v}) = \frac{\pi}{k} \overline{|\gamma(\mathbf{p})|^2 v^{-1} \delta(\mu)} \int \frac{dS}{(2\pi)^3 v}, \qquad (31)$$

where $\mu = \cos(\mathbf{k}, \mathbf{v})$, and the bar denotes averaging over the Fermi surface,

$$\bar{a} = \int \frac{dS}{(2\pi)^3 v} a(\mathbf{p}) \left(\int \frac{dS}{(2\pi)^3 v} \right)^{-1}.$$

For normal incidence and scattering by using (A17) we obtain the following asymptotic form of (30):

$$\Sigma_1(k_x = 0, \omega) = 2 \overline{|\gamma(\mathbf{p})|^2 v^{-1} \delta(\mu)} \int \frac{dS}{(2\pi)^3 v} \times \begin{cases} \frac{\omega}{|\zeta|^2} \left(\ln \frac{|\zeta| v}{\omega} + \frac{\pi \zeta_1}{\zeta_2} \right) & \text{for } v|\zeta| \gg \omega, \\ \simeq \frac{|\zeta|^2 v^4}{\omega^3} & \text{for } v|\zeta| \ll \omega, \end{cases} \qquad (32)$$

where $\zeta = \lambda^{(i)} + \lambda^{(s)} = \zeta_1 + i\zeta_2$ [see (A10) and (A11) with $k_x = 0$].

The second term in the parentheses of the upper formula in (32) becomes important at small absorption ζ_2 of the incident and scattered light. The expression (32) has the form of a wide maximum with a height given by the upper expression in (32) at $\omega \simeq v|\zeta|$.

If in the field $\mathbf{E}(\mathbf{k}, \omega)$ (20), only terms proportional to $U(\mathbf{k}, \omega)$ are left, the second term in the square brackets in the expression (29) represents also the bulk effect. To analyze this term we consider normal incidence and scattering, i.e., $k_x = 0$. Hence $\Gamma_x(\mathbf{k}, \omega) = 0$ and

$$\Sigma_2(k_x=0,\omega) = -\frac{8\pi e}{\omega}\,\mathrm{Im}\int\frac{dk_z}{2\pi}|U(k_z,\omega)|^2 \times\frac{\Gamma_z(k_z,\omega)}{\epsilon_{zz}(k_z,\omega)}\int\frac{dS}{(2\pi)^3 v}\frac{\gamma^*(\mathbf{p})v_z}{\omega-k_z v_z}, \tag{33}$$

where

$$\Gamma_z(k_z,\omega) = 2e\omega\int\frac{dS}{(2\pi)^3 v}\frac{\gamma(\mathbf{p})v_z}{\omega-k_z v_z}, \tag{34}$$

$$\epsilon_{zz}(k_z,\omega) = \epsilon^0_{zz} - \frac{8\pi e^2}{\omega}\int\frac{dS}{(2\pi)^3 v}\frac{v_z^2}{\omega-k_z v_z}. \tag{35}$$

Let us consider two limiting cases. If $k_z v \gg \omega$, the imaginary part (33) appears due to $(\omega - k_z v_z)$ in the denominators of (33)–(35), giving the δ function. This is the contribution of the electron-hole excitations. Extracting the imaginary part and performing the integration we arrive at an expression similar to (30) and (31). As a result we obtain for $\Sigma_1(k_x=0,\omega)+\Sigma_2(k_x=0,\omega)$ the expression (32) in which the substitution $|\gamma(\mathbf{p})|^2 \to |\gamma(\mathbf{p})-\overline{\gamma(\mathbf{p})}|^2$ should be made. This means that in the range $\omega \simeq v|\zeta|$ (32) the density fluctuations are screened due to the Coulomb electron-electron interaction. Hence, Raman scattering by electron-hole excitations exists only if $\gamma(\mathbf{p})$ is anisotropic. A similar result was obtained by the Green function method in Ref. 21.

In the second limiting case $k_z v \ll \omega$, the imaginary part (33) appears due to the zero of $\epsilon_{zz}(k_z,\omega)$. It is related to excitations of the bulk plasmon. Near zero the dielectric function (35) has the known form

$$\epsilon_{zz}(k_z,\omega) = \epsilon^o_{zz} - \frac{8\pi e^2}{\omega^2}\int\frac{dS}{(2\pi)^3 v}v_z^2\left(1+\frac{k_z^2 v_z^2}{\omega^2}\right) = \frac{\epsilon^0_{zz}}{\omega^2}[\omega^2-\omega^2_{pzz}(k_z)], \tag{36}$$

where the dispersion relation for bulk plasmons

$$\omega^2_{pzz}(k_z) = \omega^2_{pzz}(0) + u^2 k_z^2 \tag{37}$$

is introduced. The formula (37) determines the electron plasma frequency

$$\omega^2_{pzz}(0) = \frac{e^2}{\pi^2\epsilon^o_{zz}}\int\frac{dS}{v}v_z^2$$

and the dispersion parameter u,

$$u^2 = \int\frac{dS}{v}v_z^4\left(\frac{dS}{v}v_z^2\right)^{-1},$$

which is of order of the Fermi velocity, $u^2 \simeq \overline{v_z^2}$.

In the same limit $k_z v \ll \omega$ we have

$$\Gamma_z(k_z,\omega) = \frac{2ek_z}{\omega}\int\frac{dS}{(2\pi)^3 v}\gamma(\mathbf{p})v_z^2. \tag{38}$$

Substituting (36)–(38) into (33) we obtain

$$\Sigma_2(k_x=0,\omega) = M\mathcal{J}(\omega)\mathrm{sgn}\omega, \tag{39}$$

where

$$M = \frac{16\pi^2 e^2}{\epsilon^o_{zz}}\left|\int\frac{dS}{(2\pi)^3 v}\gamma(\mathbf{p})v_z^2\right|^2 \simeq m^2 v u^2\omega^2_{pzz}(0)\overline{\gamma}^2/\pi^2,$$

$$\mathcal{J}(\omega) = \frac{1}{\omega^2}\int\frac{dk_z}{2\pi}|U(k_z,\omega)|^2 k_z^2\delta(\omega^2-\omega^2_{pzz}(k_z)). \tag{40}$$

At this point we need to remember that a plasmon has damping. For weak scattering $(1/\tau \ll \omega)$ by a short-range impurity potential, it is easy to see that damping can be accounted for by the substitution $\omega \to \omega + i/\tau$ in the kinetic equation (7). Hence the plasmon dispersion law has the form $\omega = \omega_{pzz}(k_z) - i/2\tau$ and the δ function in (40) is replaced,

$$\delta(\omega^2-\omega^2_{pzz}(k_z)) \to \frac{1}{4\pi\tau\omega_{pzz}(0)\left\{[\omega-\omega_{pzz}(k_z)]^2+(2\tau)^{-2}\right\}}, \tag{41}$$

where $\omega_{pzz}(k_z)$ is given by (37).

The integral (40) with (41) and U (A17) can be evaluated explicitly. Its value is determined by the relation between the widths of the integrand functions. In the case when the width of the function U (A18) is less than the width of (41), i.e., $u^2|\zeta|\zeta_2 \ll \omega_{pzz}(0)/\tau$, we must integrate in (40) only $|U|^2$ taking the other factors at $k_z = \zeta_1$. We obtain

$$\mathcal{J}(\omega) = \frac{|\zeta|^2}{4\pi\omega^3_{pzz}(0)\tau\zeta_2\left\{[\omega-\omega_{pzz}(\zeta_1)]^2+(2\tau)^{-2}\right\}}. \tag{42}$$

Here the location of the maximum $\omega = \omega_{pzz}(0) + u^2\zeta_1^2/2\omega_{pzz}(0)$ is determined by the condition that the plasmon wave vector equals the sum of the incident and scattered light vectors. The maximum value of (42) is $\tau|\zeta|^2/2\pi\omega^3_{pzz}(0)\zeta_2$.

In the opposite case, i.e., $u^2|\zeta|^2\zeta_2 \gg \omega_{pzz}(0)/\tau$, the width of U is larger than the plasmon damping. Then the integral (40)

$$\mathcal{J}(\omega) = \frac{2}{\pi\omega^2_{pzz}(0)u^2}\frac{|\zeta|^2 k_z}{(\zeta_1^2-\zeta_2^2-k_z^2)^2+4\zeta_1^2\zeta_2^2}, \tag{43}$$

where $k_z = \{2\omega_{pzz}(0)[\omega-\omega_{pzz}(0)]\}^{1/2}/u$. The expression (43) has the form of a sharp peak. The maximum value of (43) is equal to $C|\zeta|/2\pi u^2\omega^2_{pzz}(0)\zeta_2^2$; $C=1$ for $\zeta_1 \gg \zeta_2$ and $C = 3^{3/2}/4$ for $\zeta_1 \ll \zeta_2$.

B. The surface excitations

If we substitute the terms proportional to H_y (20) in (29) for $\mathbf{E}(\mathbf{k},\omega)$ we obtain the surface contribution of the electronic fluctuations. The imaginary part (29) arises in the parentheses of (23) at $kv \ll \omega$, as we will see. Putting $\mathbf{k}=\mathbf{0}$ in $\epsilon_{\alpha\beta}$ [(19) and (14)] we integrate (25):

$$I_2(k_x,\omega) = \frac{c^2}{2\omega^2}\left(\frac{k_x^2 - \epsilon_{zz}(0,\omega)\omega^2/c^2}{\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)}\right)^{1/2}, \quad (44)$$

where $\epsilon_{zz}(0,\omega)$ is given by Eq. (35) with $k_z = 0$, and ϵ_{xx} is obtained from ϵ_{zz} by the substitution $v_z^2 \to v_x^2$. The expression in the parentheses in (23) is proportional to

$$\mathcal{G}(k_x,\omega) = \left[i\left(\frac{\omega^2}{c^2} - k_x^2\right)^{1/2} + \left(\frac{k_x^2 - \epsilon_{zz}(0,\omega)\omega^2/c^2}{\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)}\right)^{1/2}\right]^{-1}. \quad (45)$$

Now we substitute in Eq. (29) for $\mathbf{E}(\mathbf{k},\omega)$ the terms proportional to H_y (20) with $\Gamma_\alpha(\mathbf{k},\omega)$ given by an expression similar to (38). We obtain

$$\Sigma_3(k_x,\omega) = -\frac{8\pi e^2 k_x^2}{c^4}\mathrm{Im}\mathcal{G}(k_x,\omega)|J(k_x,\omega)|^2 \times\left(\int\frac{dS}{4\pi^3 v}\right)^2,$$

$$J(k_x,\omega) = \int\frac{dk_z}{2\pi}\frac{U(\mathbf{k},\omega)}{\mathcal{D}(\mathbf{k},\omega)} \times\left[\left(k_x^2 - \frac{\omega^2}{c^2}\epsilon_{zz}(0,\omega)\right)\overline{\gamma(\mathbf{p})v_x^2} + k_z^2\overline{\gamma(\mathbf{p})v_z^2}\right]. \quad (46)$$

The imaginary part of $\mathcal{G}(k_x,\omega)$ arises 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. Then $\mathcal{G}(k_x,\omega)$ has a pole which determines the dispersion law of the surface plasmons:

$$k_x^2(\omega) = \frac{\omega^2}{c^2}\frac{\epsilon_{zz}(0,\omega)[1-\epsilon_{xx}(0,\omega)]}{1-\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)}. \quad (47)$$

In the isotropic case Eq. (47) gives the well known dispersion relation[22]

$$k_x^2(\omega) = \frac{\omega^2}{c^2}\frac{\epsilon(\omega)}{1+\epsilon(\omega)} = \frac{\omega^2}{c^2}\frac{\omega_p^2-\omega^2}{\omega_p^2-2\omega^2}, \quad (48)$$

where the plasma frequency of electrons is $\omega_p = (4\pi\rho_{\mathrm{el}}e^2/m)^{1/2}$.

We do not know reliable experimental data about $\epsilon_{\alpha\beta}(\omega)$ for HTSC's in the interesting frequency interval $\omega = 0.01$–1 eV. For example, we have taken the parameters $\omega_{pxx}(0)$, $\omega_{pzz}(0)$, ϵ_{xx}^0, ϵ_{zz}^0 from Ref. 23 for $YBa_2Cu_3O_{7-\delta}$. The experiments in the cited papers were interpreted by the 1–2 Drude and the 7–13 Lorentz terms. In Figs. 1 and 2 the function (47) is shown for two cases: Fig. 1 for $\epsilon_{xx}(0,\omega) = 3-(1.5/\omega)^2$ and $\epsilon_{zz}(0,\omega) = 3-(0.6/\omega)^2$; Fig. 2 for $\epsilon_{xx}(0,\omega) = 3-(0.6/\omega)^2$ and $\epsilon_{zz}(0,\omega) = 3-(1.5/\omega)^2$. The first set corresponds to the c axis orientation along the normal to a metal surface. In the second case the normal is directed the along the a axis. The upper branches existing in the expression (47) are not shown since the Green function (45) has no pole on these branches actually.

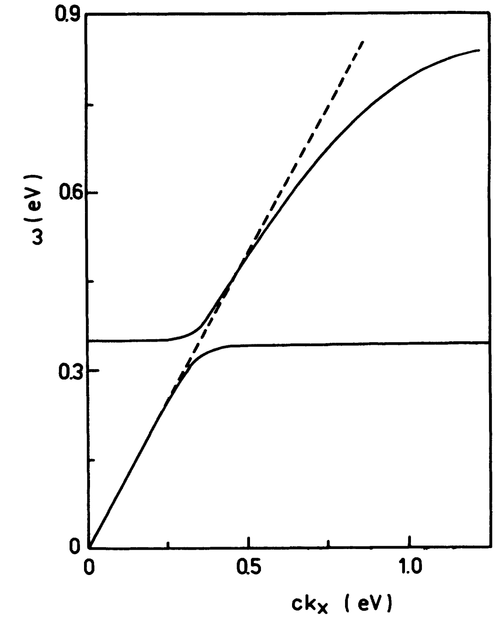

FIG. 1. The dispersion (47) of the surface plasmon for $\epsilon_{xx}(0,\omega) = 3-(1.5/\omega)^2$ and $\epsilon_{zz}(0,\omega) = 3-(0.6/\omega)^2$.

For low frequencies $\omega \ll \omega_1$, where $\omega_1 \simeq \omega_p$ is the lowest zero of the denominator of (47),

$$k_x(\omega) = \frac{\omega}{c}\left(1 - \frac{\omega^2}{2\omega_{pxx}^2(0)\epsilon_{xx}^0}\right). \quad (49)$$

Near the threshold $\omega \to \omega_1$

$$k_x(\omega) \simeq \frac{\omega_1}{c}\left(\frac{\omega_1}{\omega_1-\omega}\right)^{1/2}. \quad (50)$$

In the integral (25) and (44) the essential value of k_z is of the order of

$$k_z(\omega) \simeq \frac{\omega}{c}|\epsilon_{xx}(0,\omega)|\left(\frac{1-\epsilon_{zz}(0,\omega)}{\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)-1}\right)^{1/2}.$$

Due to the small factor v/c, the expansion in powers of $\mathbf{k}\cdot\mathbf{v}/\omega$, applied above, is valid outside the very narrow region near ω_1.

Separating the imaginary part at the pole of $\mathcal{G}(k_x,\omega)$

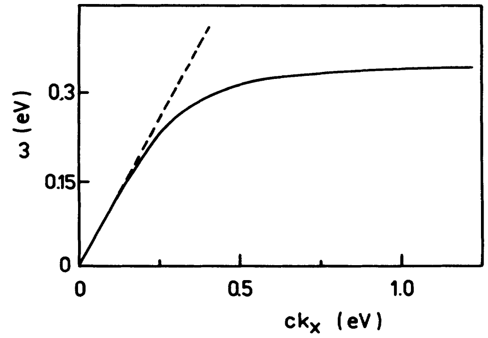

FIG. 2. The dispersion (47) of the surface plasmon for $\epsilon_{xx}(0,\omega) = 3-(0.6/\omega)^2$ and $\epsilon_{zz}(0,\omega) = 3-(1.5/\omega)^2$.

(45) we get

$$-\mathrm{Im}\mathcal{G}(k_x,\omega)=2\frac{\omega}{c}\frac{\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)[1-\epsilon_{zz}(0,\omega)]^{1/2}}{[\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)-1]^{3/2}}\times\pi\delta(k_x^2-k_x^2(\omega)), \quad (51)$$

where $k_x^2(\omega)$ is given by (47).

Damping of the surface plasmon can be accounted by the collision frequency τ^{-1}. Thus we get the shape of the peak (51):

$$\delta(k_x^2-k_x^2(\omega))\to\frac{1}{\pi\tau_1\left\{[k_x^2-k_x^2(\omega)]^2+\tau_1^{-2}\right\}}, \quad (52)$$

where for $\omega<\omega_1$

$$\tau_1^{-1}\simeq\frac{|\omega|^3\omega_1^2}{\tau c^2(\omega_1^2-\omega^2)^2}.$$

The surface plasmon is the well defined excitation at small damping

$$\tau^{-1}\ll 4(\omega_1-\omega). \quad (53)$$

The imaginary part of $\mathcal{G}(k_x,\omega)$ (45) 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. In Figs. 1 and 2 this region is on the left side of the dashed line. In a metal the electromagnetic field decreases for the same frequency range $\omega<\omega_1$. We define this excitation as the surface radiative plasmon. Here the imaginary part

$$-\mathrm{Im}\mathcal{G}(k_x,\omega)=\left(\frac{\omega^2}{c^2}-k_x^2\right)^{1/2}\times\left(\frac{\omega^2}{c^2}-k_x^2+\frac{k_x^2-\epsilon_{zz}(0,\omega)\omega^2/c^2}{\epsilon_{xx}(0,\omega)\epsilon_{zz}(0,\omega)}\right)^{-1}\times\mathrm{sgn}\omega. \quad (54)$$

If $\omega\ll\omega_1$ we obtain

$$-\mathrm{Im}\mathcal{G}(k_x,\omega)=(\omega^2/c^2-k_x^2)^{1/2}\times\left(\frac{\omega^2}{c^2}-k_x^2+\frac{\omega^4}{c^2\omega_{pxx}^2(0)\epsilon_{xx}^0}\right)^{-1}\mathrm{sgn}\omega. \quad (55)$$

Using $\mathcal{D}(\mathbf{k},\omega)$ (21) with $\epsilon_{\alpha\beta}(0,\omega)$ and $U(\mathbf{k},\omega)$ (A17) we integrate over k_z in (46),

$$J(k_x,\omega)=\left(\frac{a_1}{a_3}-\frac{i\zeta a_2}{\sqrt{-\epsilon_{zz}}}\right)\left(a_3-i\zeta\sqrt{-\epsilon_{zz}}\right)^{-1}, \quad (56)$$

where

$$a_1=\frac{c^2}{\omega^2}\left(k_x^2-\epsilon_{zz}\omega^2/c^2\right)\overline{\gamma(\mathbf{p})v_x^2},\quad a_2=\frac{c^2}{\omega^2}\overline{\gamma(\mathbf{p})v_z^2},$$

$$a_3=\left(\frac{\omega^2}{c^2}\epsilon_{xx}\epsilon_{zz}-k_x^2\epsilon_{xx}\right)^{1/2},$$

and arguments of $\epsilon_{\alpha\beta}(0,\omega)$ are omitted. ζ is given in (A16), (A10) and (A11).

IV. SUMMARY AND CONCLUSIONS: THE RAMAN SCATTERING CROSS SECTION

By using (5), (6), (26), and (29), the Raman cross section (A14) can be rewritten in the form

$$d\sigma(k_x,\omega)=\left(\frac{8\pi e^2}{mc\hbar\omega^{(i)}}\right)^2\frac{\Sigma(k_x,\omega)}{1-\exp(-\omega/T)}\times\frac{k_z^{(s)}\omega^{(s)}d\omega^{(s)}d\Omega^{(s)}}{c(2\pi)^3}. \quad (57)$$

Let us discuss the frequency dependence of the cross section taking into account the results of Sec. III. Below we will discuss only the Stokes case $\omega>0$; however, the consideration can be transferred for $\omega<0$ keeping in mind the Bose factor in (57). If the incident and scattered light frequencies are in the optical frequency range, $\omega^{(i)}\simeq\omega^{(s)}$, the parameter ζ [see (15), (A10), and (A11)] has the value $|\zeta|\simeq\omega^{(s)}\sqrt{\epsilon(\omega^{(s)})}/c$. The electron-hole excitations give a continuum around the low-frequency transfer $\omega_{\max}\simeq v|\zeta|\simeq(v/c)\omega^{(s)}\sqrt{\epsilon(\omega^{(s)})}$ [see (32)] of a width $\Delta\omega^{eh}\simeq\omega_{\max}$. The maximum in the cross section (57) is determined by

$$d\sigma(\omega_{\max})=\frac{4}{\pi^3}\left(\frac{e^2v}{\hbar c^2}\right)^2\frac{\mathcal{S}}{1-\exp(-\omega/T)}\frac{d\omega^{(s)}d\Omega^{(s)}}{\Delta\omega}, \quad (58)$$

where

$$\mathcal{S}=\mathcal{S}^{eh}\simeq\left(\pi\frac{\zeta_1}{\zeta_2}+C_1\right)\overline{|\gamma(\mathbf{p})-\overline{\gamma(\mathbf{p})}|^2} \quad (59)$$

and C_1 is of the order of unity.

In the range of a large frequency transfer, $\omega\simeq\omega_p$, there is a contribution of the bulk plasmons, which has the form of a sharp peak [see (39)–(43)]. The function $\mathcal{J}(\omega)$ (40) possesses the following maximum value and width $\Delta\omega$:

$$\mathcal{J}(\omega_{\max})\simeq|\zeta|^2\tau/2\pi\omega_{pzz}^3(0)\zeta_2$$

and (60)

$$\Delta\omega^{\rm BP}=\omega_{\max}-\omega_p(\zeta_1)\simeq 1/2\tau$$

for $u^2|\zeta|\zeta_2\ll\omega_{pzz}(0)/\tau$,

$$\mathcal{J}(\omega_{\max})\simeq|\zeta|/2\pi u^2\omega_{pzz}^2(0)\zeta_2^2$$

and (61)

$$\Delta\omega^{\rm BP}=\omega_{\max}-\omega_p(\zeta_1)\simeq u^2|\zeta|\zeta_2/\omega_{pzz}(0)$$

for $u^2|\zeta|\zeta_2\gg\omega_{pzz}(0)/\tau$.

The maximum value of the bulk plasmon peak is given by (58), where

$$\mathcal{S}=\mathcal{S}^{\rm BP}\simeq\frac{|\zeta|^2}{\pi\zeta_2}\frac{v}{\omega_{pzz}(0)}\overline{|\gamma(\mathbf{p})|^2}. \quad (62)$$

There is a surface plasmon contribution in the cross section. Consider for simplicity normal incidence of light.

The wave vector transfer k_x is determined by the scattering angle, $k_x = \frac{\omega^{(s)}}{c}\sin\theta$. The surface plasmon gives a sharp peak at θ defined by the condition $\frac{\omega^{(s)}}{c}\sin\theta_{\rm max} = k_x(\omega_1)$, where $k_x(\omega)$ is given by (47), (49), and (50). For frequencies $\omega \ll \omega_1$ the peak is situated at

$$\sin\theta_{\rm max} = \frac{\omega}{\omega^{(s)}}\left(1 - \frac{\omega^2}{2\omega_{pxx}^2(0)\epsilon_{xx}^0}\right). \qquad (63)$$

The shape of the cross section (57) is described by (46), (51), and (52), where $J(k_x,\omega)$ (56) depends on ζ weakly:

$$J(k_x,\omega) \simeq c^2\overline{\gamma(\mathbf{p})v^2}/\omega_1^2. \qquad (64)$$

Estimating (46) we get the height of the surface plasmon peak in the form (58), where

$$\mathcal{S} = \mathcal{S}^{\rm SP} \simeq \frac{v}{c}\left(\frac{\omega}{\omega_1}\right)^3\left(\frac{\omega_1}{\omega_1-\omega}\right)^{1/2}\overline{|\gamma(\mathbf{p})|^2} \qquad (65)$$

and the width $\Delta\omega^{\rm SP} = \omega^2/2\tau\omega_{pxx}^2(0)$. At the threshold $\omega \to \omega_1$ the peak height (65) is limited by the condition

$$\left(\frac{\omega_1}{\omega_1-\omega}\right)^{1/2} = \frac{\omega^{(s)}}{\omega_1}\sin\theta \ll \left(2(\tau\omega_1)^{1/2};\frac{c}{v}\right), \qquad (66)$$

which means that the surface plasmon damping is small and the expansion in powers of kv/ω is valid.

The line shape of the surface plasmon peak for $\omega \ll \omega^{(s)}$ is described by the expression

$$d\sigma^{\rm SP}(\theta,\omega) = \frac{(\Delta\omega^{\rm SP})^2}{(\omega-\theta\omega^{(s)})^2 + (\Delta\omega^{\rm SP})}d\sigma^{\rm SP}(\omega_{\rm max}), \qquad (67)$$

where $d\sigma^{\rm SP}(\omega_{\rm max})$ is given by (58) and (65).

Now we consider the contribution of the surface radiative plasmons for small frequency transfer $ck_x < \omega \ll \omega_1$. In this case the cross section (57) is described by (46) and (55). This contribution exists for the scattering angles $0 < \omega^{(s)}\sin\theta < \omega$ and reveals a sharp maximum at $\theta_{\rm max} = (\omega/\omega^{(s)})[1 - \omega^3/\omega^{(s)}\omega_{pxx}^2(0)\epsilon_{xx}^0]$. The maximum value of the cross section $d\sigma^{\rm RP}(\omega_{\rm max})$ by surface radiative plasmons is given by (58), where

$$\mathcal{S} = \mathcal{S}^{\rm RP} \simeq 3\sqrt{2}\frac{v}{c}\frac{\omega^3}{\omega_{pxx}^3(0)\epsilon_{xx}^0}\overline{|\gamma(\mathbf{p})|^2} \qquad (68)$$

and the width $\Delta\omega^{\rm RP} = \omega^3/\omega_{pxx}^2(0)\epsilon_{xx}^o$. The angular and frequency dependence of the surface radiative plasmon continuum has the form

$$d\sigma^{\rm RP}(\theta,\omega) = \frac{3\omega^{(s)}}{\sqrt{2}\omega_{pxx}(0)}\frac{\theta^2\left[\left(\frac{\omega}{\omega^{(s)}}\right)^2-\theta^2\right]^{1/2}}{\left(\frac{\omega}{\omega^{(s)}}\right)^2-\theta^2+\frac{\omega\Delta\omega^{\rm RP}}{(\omega^{(s)})^2}}d\sigma^{\rm RP}(\omega_{\rm max}).$$

A comparison between (59), (62), (65), and (68) shows that the scattering by the volume excitations (59) and (62) increases at $\zeta_2 \to 0$. If the sample thickness $d \ll \zeta_2^{-1}$, ζ_2^{-1} should be substituted by d. It that limiting case the scattering cross section is proportional to the sample volume. The scattering by the plasmon-type excitations (62), (65), and (68) implies the small factor v/c. For the scattering by the bulk plasmon this factor can be compensated, increasing the incident and scattered light frequency since $\zeta \propto (\omega^{(i)} + \omega^{(s)})/c$. Inelastic scattering of x rays by the surface and bulk plasmons has been theoretically investigated in Ref. 24. The scattering cross section by the surface plasmon excitations includes the factor $(v/c)[\omega_1/(\omega_1-\omega)]^{1/2}$ which does not exceed unity [see (66)].

The observation of Raman light scattering by the electronic excitations is preferable in the resonant conditions for γ. Due to a large difference between the scattering cross sections by the electron-hole and plasmon-type excitations, the Raman continuum is unlikely to come from plasmons. The consideration of other collective bulk and surface excitations is currently under way.

ACKNOWLEDGMENTS

The authors thank A. R. Ferchmin for critical reading of the manuscript. This research was made possible in part by a grant from the International Science Foundation. One of us (S.K.) thanks the Polish Research Committee of Science for financial support (Grant No. 2 1299 91 01).

APPENDIX: RELATION BETWEEN THE RAMAN CROSS SECTION AND THE GENERALIZED DENSITY-DENSITY CORRELATION FUNCTION

We write the Maxwell equation for a scattered field in the metal as

$$\mathrm{rotrot}\mathbf{E} + \frac{1}{c^2}\frac{\partial^2\mathbf{D}}{\partial t^2} = -\frac{4\pi}{c^2}\frac{\partial\mathbf{j}}{\partial t}, \qquad (A1)$$

where the part of $\mathbf{j}$ proportional to the scattered field is included in the induction $\mathbf{D}$. On the right side of (A1) only the part proportional to the incident field is retained. By using the effective Hamiltonian

$$\mathcal{H} = \frac{e^2}{mc^2}\int d^3r\int\frac{d^3p}{(2\pi)^3}A_\alpha^{(i)}(\mathbf{r},t)A_\beta^{(s)}(\mathbf{r},t) \times\gamma_{\alpha\beta}(\mathbf{p})f_p(\mathbf{r},t),$$

which describes the scattering, we find the electric current

$$j_\alpha(\mathbf{r},t) = -c\frac{\delta\mathcal{H}}{\delta A_\alpha} = -\frac{e^2}{mc}\delta n_{\alpha\beta}(\mathbf{r},t)A_\beta^{(i)}(\mathbf{r},t), \qquad (A2)$$

where

$$\delta n_{\alpha\beta}(\mathbf{r},t) = \int\frac{d^3p}{(2\pi)^3}\gamma_{\alpha\beta}(\mathbf{p})\delta f_p(\mathbf{r},t) \qquad (A3)$$

and the tensor $\gamma_{\alpha\beta}(\mathbf{p})$ is given by the expression in square brackets in (3).

For the Fourier transform with respect to the coordinates $\mathbf{s}$ parallel to the surface and time t,

$$\mathbf{E}(\mathbf{k}_s^{(s)}, z; \omega^{(s)}) = \int d^2s\int dt e^{i(\omega^{(s)}t - \mathbf{k}_s^{(s)}\mathbf{s})}\mathbf{E}(\mathbf{r},t), \qquad (A4)$$

the Maxwell equations have the form $(z > 0)$

$$-\frac{d^2E_x}{dz^2} + ik_x^{(s)}\frac{dE_z}{dz} - \left(\frac{\omega^{(s)}}{c}\right)^2 \epsilon_{xx}E_x = \frac{4\pi i\omega^{(s)}}{c^2}j_x, \tag{A5}$$

$$ik_x^{(s)}\frac{dE_x}{dz} + \left[k_x^{(s)2} - \left(\frac{\omega^{(s)}}{c}\right)^2 \epsilon_{zz}\right] E_z = \frac{4\pi i\omega^{(s)}}{c^2}j_z, \tag{A6}$$

$$-\frac{d^2E_y}{dz^2} + \left[k_x^{(s)2} - \left(\frac{\omega^{(s)}}{c}\right)^2 \epsilon_{yy}\right] E_y = \frac{4\pi i\omega^{(s)}}{c^2}j_y, \tag{A7}$$

where the x axis is directed along $\mathbf{k}_s^{(s)}$ and we omit the arguments $(\mathbf{k}_s^{(s)}, z; \omega^{(s)})$ of E_α and j_α. If the frequency $\omega^{(s)}$ is in the normal skin range, $\epsilon_{\alpha\beta}$ depends on $\omega^{(s)}$ only.

Determining E_z from (A6) and substituting into (A5), we get an equation for the parallel polarization $[\mathbf{E} = (E_x, 0, E_z)]$ of the scattered field,

$$-\frac{d^2E_x}{dz^2} - \lambda_l^{(s)2}E_x = \frac{4\pi i\omega^{(s)}}{c^2}\mathcal{J}, \tag{A8}$$

$$\mathcal{J} = \frac{c^2}{\omega^{(s)2}}\left(\lambda_l^{(s)2}\frac{\epsilon_{zz}}{\epsilon_{xx}}j_x + ik_x^{(s)}\frac{dj_z}{dz}\right), \tag{A9}$$

$$\lambda_l^{(s)2} = \left[\left(\frac{\omega^{(s)}}{c}\right)^2 \epsilon_{zz}(\omega^{(s)}) - k_x^{(s)2}\right]\frac{\epsilon_{xx}(\omega^{(s)})}{\epsilon_{zz}(\omega^{(s)})}. \tag{A10}$$

The equation (A7) for the perpendicular polarization $[\mathbf{E} = (0, E_y, 0)]$ has the form of Eq. (A8) with $\lambda_l^{(s)2}$ substituted by

$$\lambda_t^{(s)2} = \left[\left(\frac{\omega^{(s)}}{c}\right)^2 \epsilon_{yy}(\omega^{(s)}) - k_x^{(s)2}\right]. \tag{A11}$$

The solutions of Eqs. (A7) and (A8) decreasing for $z \to +\infty$ are of the form

$$E(z) = Ce^{i\lambda z} - \frac{2\pi\omega^{(s)}}{\lambda c^2}\int_0^\infty dz'\mathcal{J}(z')e^{i\lambda|z-z'|}. \tag{A12}$$

For both polarizations the scattered field in vacuum $(z < 0)$

$$E(z) = D\exp(-ik_z^{(s)}z), \tag{A13}$$

with $k_z^{(s)} = \left[\left(\frac{\omega^{(s)}}{c}\right)^2 - k_x^{(s)2}\right]^{1/2}$.

The constants C and D are determined from the conditions of continuity of the tangential components of the electric and magnetic fields at $z = 0$. They are expressed by the integrals of the current density operators over the half space $z > 0$.

The normal component of the scattered energy flux into vacuum is proportional to $|D|^2\omega^{(s)}/ck_z^{(s)}$ for the parallel polarization and to $|D|^2ck_z^{(s)}/\omega^{(s)}$ for the perpendicular polarization. The current density (A2) entering in (A12) is proportional to the incident field in the metal $A^{(i)}$. For the normal skin range we have $A^{(i)} = Be^{i\lambda^{(i)}z}$. Here $\lambda^{(i)}$ is given by (A10) or (A11) depending on the polarization of the incident field with the substitution $\omega^{(s)} \to \omega^{(i)}$. Relating the constant B to the amplitude of the incident field in the vacuum and dividing by the energy flux in the incident field, we obtain the Raman cross section

$$d\sigma = \int_0^\infty dzdz'K_{\gamma*\gamma}(\mathbf{k}_s, z, z'; \omega)U^*(\mathbf{k}_s, z; \omega) \times U(\mathbf{k}_s, z'; \omega)\left(\frac{8\pi e^2}{mc\omega^{(i)}}\right)^2 \frac{k_z^{(s)}\omega^{(s)}d\omega^{(s)}d\Omega^{(s)}}{c(2\pi)^3}, \tag{A14}$$

where $K_{\gamma*\gamma}(\mathbf{k}_s, z, z'; \omega)$ is the Fourier transform of (1) with respect to $\mathbf{s} - \mathbf{s}', t - t'$. The components $e_\alpha^{(s)}$ are given by

$$e_x^{(s)} = \frac{\lambda_l(ck_z^{(s)}/\omega^{(s)})^{1/2}}{\lambda_l + \epsilon_{xx}k_z^{(s)}},$$
$$e_z^{(s)} = -k_x^{(s)}\frac{\epsilon_{xx}}{\epsilon_{zz}}\frac{(ck_z^{(s)}/\omega^{(s)})^{1/2}}{\lambda_l + \epsilon_{xx}k_z^{(s)}}, \tag{A15}$$
$$e_y^{(s)} = \frac{(\omega^{(s)}k_z^{(s)}/c)^{1/2}}{\lambda_t + k_z^{(s)}},$$

for the scattered frequency $\omega^{(s)}$, where $\epsilon_{\alpha\beta} = \epsilon_{\alpha\beta}(\omega^{(s)})$, $\lambda_l = \lambda_l^{(s)}$, and $\lambda_t = \lambda_t^{(s)}$. The components $e_\alpha^{(i)}$ are obtained by the substitution $\omega^{(s)} \to \omega^{(i)}$.

In (A14) $U(\mathbf{k}_s, z; \omega)$ denotes the product of two exponents describing the distribution of the incident and scattered fields in the metal,

$$U(\mathbf{k}_s, z; \omega) = \exp(i\zeta z), \quad \zeta = \zeta_1 + i\zeta_2 = \lambda^{(i)} + \lambda^{(s)}, \tag{A16}$$

and has the Fourier transform

$$U(\mathbf{k}, \omega) = \int_0^\infty dzU(\mathbf{k}_s, z; \omega)(e^{ik_zz} + e^{-ik_zz}) = \frac{2i\zeta}{\zeta^2 - k_z^2}. \tag{A17}$$

If the incident and scattering frequencies are below the transparency threshold, then $\zeta_1 \ll \zeta_2 \simeq 2/\delta$, where δ is the skin depth for the frequency $\omega^{(i)}$. If the incident and scattering frequencies are in the transparency range, then $\zeta_1 \gg \zeta_2$ and the expression (A17) has a pole if the momentum transfer k_z equals the sum of the wave vectors of the incident and scattered light in the metal ζ_1. Near the pole the expression (A17) takes the form

$$U(k_z, \omega) = \frac{i}{\zeta_1 - k_z + i\zeta_2}. \tag{A18}$$

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