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INELASTIC LIGHT SCATTERING AT METAL-INSULATOR TRANSITION: RIPPLE AND ELASTO-OPTIC MECHANISMS

L.A.Falkovsky, E.G.Mishchenko

Institute for Theoretical Physics L.D.Landau RAS

117334 Moscow, Russia

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The inelastic light scattering in metals and insulators by acoustic and optical phonons is considered. The ripple and elasto-optic mechanisms are taken into account. The phonon damping and skin effect are analyzed. The surface contribution into the cross section is found to be not sensitive to the skin depth. Influence of carriers on the bulk contribution through the skin effect is essential as well as through the phonon damping. The recent experimental data for fullerides are discussed.

1. The inelastic light scattering is a widespread experimental tool in investigating phonon spectra of various systems [1-3]. But despite the large number of papers devoted to the subject the appropriate theory is still far from completion. The surface effects seems to be an important problem. Although its significance was recognized for a long time a thorough description has not been given until now.

Several papers contain the theory of Brillouin scattering from acoustic phonons in insulators in more or less transparent manner for different models taking into account a surface presence [4-7]. On the other hand the inelastic light scattering by phonons in metals has been investigated less extensively. A few attempts [8,9] devoted to Raman scattering used the Green function formalism had failed to consider a sample surface. The theory of Brillouin scattering in metals appears to be proposed firstly by present authors [10,11] using the straightforward semiclassical approach. The similar theory for the Raman light scattering from optical phonons was presented too [12].

Our main purpose is to compare the inelastic light scattering from phonons in metals and insulators. Since the skin depth in metals is small, the scattering by the movements on the surface (ripples) has to be taken into consideration. The surface contribution from the ordinary elasto-optic mechanism should to be included too.

Let us consider the incident light wave with the frequency $\omega^{(i)}$ propagating normally to the surface (along the z-axis) and light wave with the frequency $\omega^{(s)}$ scattered in the xz-plane. If $\omega^{(i)}$ and $\omega^{(s)}$ are in the normal skin range and the polarizations are perpendicular to the xz-plain, the spatial distribution of the field in metal is determined by the z-component of wave vectors:

$$\zeta^{(i,s)} = \left(\epsilon(\omega^{(i,s)})\omega^{(i,s)2}/c^2 - k_x^{(i,s)2}\right)^{1/2}.$$

There are two mechanisms of light scattering in metal. One (elasto-optic) associated with the electronic density fluctuations results the following cross section [13]:

$$\frac{d^2\sigma_{el}}{d\omega^{(s)}do^{(s)}} = \frac{(\omega_P/\omega^{(i)})^4}{2\pi^3c^5}\,\frac{k_z^{(i)}k_z^{(s)2}\omega^{(i)3}\omega^{(s)2}}{\left|k_z^{(i)}+\zeta^{(i)}\right|^2\left|k_z^{(s)}+\zeta^{(s)}\right|^2}.$$

$$\int_0^\infty \int_0^\infty dz\ dz'\ U(z)\ U^*(z') << \delta n_\gamma(z, \mathbf{k}_s, \omega) \delta n_{\gamma *}(z', \mathbf{k}_s, \omega) >>, \tag{1}$$

here $\omega_P^2 = 4\pi e^2 n_e/m$, n_e being the density of electrons. The vector components $\mathbf{k}_s$ are along the surface, $k_z^{(i)}$ and $k_z^{(s)}$ are the normal components of wave vectors for incident and scattered light in the vacuum. We introduce also the frequency and momentum transfer $\omega = \omega^{(i)} - \omega^{(s)}$, $\mathbf{k}_s = \mathbf{k}_s^{(i)} - \mathbf{k}_s^{(s)}$. For the considered geometry $\mathbf{k}_s^{(i)} = 0$. The operator δn_γ can be expressed through the electronic distribution function $\delta f_p(\mathbf{r}, t)$

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

and the effective electron-photon vertex

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

where the sum is taken over all zones n. The subscript f denotes the conduction band, $\epsilon_{fn} = \epsilon_f - \epsilon_n$. The factor $U(z) = \exp(i\zeta_1 z - \zeta_2 z)$ describes the light penetration into the crystal, where the complex quantity $\zeta_1 + i\zeta_2 = \zeta^{(i)} + \zeta^{(s)}$.

The ripple contribution is given by the electromagnetic boundary conditions at the surface moving due to phonons. As a result the inelastic light scattering becomes possible without any elasto-optic interaction. The scattering cross section by ripples has the form:

$$\frac{d^2\sigma_{rip}}{d\omega^{(s)} do^{(s)}} = \frac{|\epsilon_{yy}(\omega^{(i)}) - 1|^2}{2\pi^3 c^5} \frac{k_z^{(i)} k_z^{(s)2} \omega^{(i)3} \omega^{(s)2}}{\left|k_z^{(i)} + \zeta^{(i)}\right|^2 \left|k_z^{(s)} + \zeta^{(s)}\right|^2} << u_z^{sur}(\mathbf{k}_s, \omega) u_z^{sur*}(\mathbf{k}_s, \omega) >>, \tag{4}$$

here u_z^{sur} denotes the surface displacement. The connection of u_z^{sur} with the acoustic $u(\mathbf{r}, t)$ and optical $w(\mathbf{r}, t)$ phonon displacements is determined by the surface orientation respect to the crystal axes. The result is expressed in terms of the correlators $<< u_z(\mathbf{s}, z = 0, t) u_z(\mathbf{s}, z = 0, t) >>$ and $<< w_z(\mathbf{s}, z = 0, t) w_z(\mathbf{s}, z = 0, t) >>$, where the statistical average is taken.

2. The correlator (1) as well as the correlator (4) was evaluated in our recent papers [10-13] with the help of fluctuation-dissipation theorem, the Boltzmann equation and equation of dynamical theory of elasticity [14]. The following designation will be used:

$$\frac{\begin{Bmatrix} \Sigma_{el}(\mathbf{k}_s, \omega) \\ \Sigma_{rip}(\mathbf{k}_s, \omega) \end{Bmatrix}}{1 - \exp(-\omega/T)} = \begin{cases} \int_0^\infty \int_0^\infty dz\ dz'\ U(z)\ U^*(z') << \delta n_\gamma(z, \mathbf{k}_s, \omega) \delta n_{\gamma *}(z', \mathbf{k}_s, \omega) >> \\ |\epsilon(\omega^{(i)}) - 1|^2 << u_z^{sur}(\mathbf{k}_s, \omega) u_z^{sur*}(\mathbf{k}_s, \omega) >> \end{cases} \tag{5}$$

Both the elasto-optic and ripple mechanisms have the same resonant factors at the frequency of interband transition, since γ_{yy} (3) and dielectric function ϵ_{yy} have the same singularities. For example, in a Drude–Lorentz model:

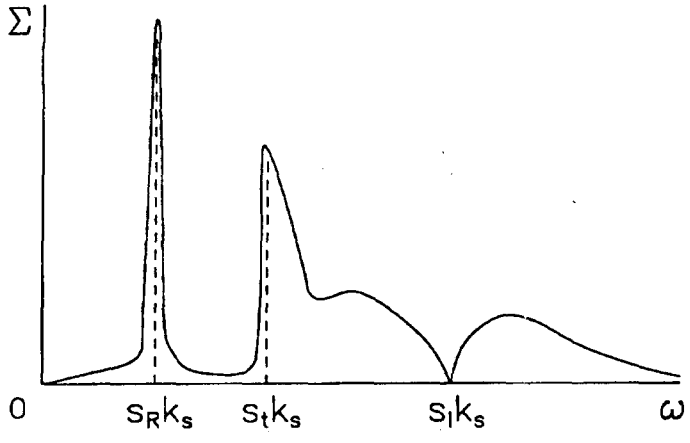
$$\epsilon(\omega^{(i)}) \simeq 1 - \frac{\omega_P^2}{\omega^{(i)2}} + \sum_n \frac{\Omega_n^2}{\epsilon_{fn}^2 - \omega^{(i)2}}. \tag{6}$$

In the following we omit these resonant factors.

The correlator Σ_{rip} for isotropic crystal has the form:

$$\Sigma_{rip}(\mathbf{k}_s,\omega) = \frac{1}{\rho\omega^2}\ \mathrm{Im}\ \left(\frac{k_s^2}{\kappa_t} - \kappa_l - \frac{\omega^4\kappa_l/s_t^4}{(k_s^2+\kappa_t^2)^2 - 4k_s^2\kappa_l\kappa_t}\right), \tag{7}$$

where ρ is the crystal density, κ_l and κ_t describe the z-dependence of the longitudinal and transverse mode amplitude: the real κ indicates the mode decaying into the bulk. The correlator Σ_{el} contains the contributions from electron-hole excitations and from optical and acoustic phonons via the electron-phonon interaction [10-13,15]. We pay our attention to phonon contributions only.



Cross section for the ripple Brillouin scattering. The left peak at $\omega = s_R k_s$ is associated with the Rayleigh wave (8). The nonsymmetric maximum near $\omega = s_t k_s$ is related with the transverse phonon slipping along the surface. The continuum between $\omega = s_t k_s$ and $\omega = s_l k_s$ involves the "mixed" phonon mode. The right continuum at $\omega > s_l k_s$ follows from the bulk phonons reflected from the surface

Let us consider initially the Brillouin scattering, i.e. the scattering with excitation or absorption of acoustic phonons (Fig.). For acoustic phonons $\kappa_{l,t}^{ac} = (k_s^2 - \omega^2/s_{l,t}^2)^{1/2}$, where s_l and s_t are the longitudinal and transverse sound velocity. In the range $\omega < s_t k_s$ the imaginary part in (7) arises only from the third term and has the peak related to Rayleigh wave (the same peak appears in the elasto-optic contribution):

$$\left.\begin{matrix}\Sigma_{el}^{ac}(\mathbf{k}_s,\omega)\\ \Sigma_{rip}^{ac}(\mathbf{k}_s,\omega)\end{matrix}\right\} \simeq \frac{\Gamma_{ac}}{\rho s((\omega - s_R k_s)^2 + \Gamma_{ac}^2)}, \tag{8}$$

where s_R is the Rayleigh wave velocity. The acoustic phonon damping includes the contribution from the electron-phonon interaction

$$\Gamma_{ac}(\mathbf{k}) = \frac{k^2}{2\rho}\mathrm{Im}\int < \frac{\lambda^2(\mathbf{p})}{\mathbf{vk} - i\tau_p^{-1}} > \frac{dS_F}{v(2\pi)^3}, \tag{9}$$

where $\lambda(\mathbf{p})$ is the deformation potential and τ_p^{-1} is the electron collision rate, the integral is taken over the Fermi surface. For small carrier concentration n, Γ_{ac} is proportional to n, since the average of λ over the Fermi surface is equal to zero. One can see from (8) both the elasto-optic and ripple mechanisms give the similar contributions which are virtually independent of the skin depth. This result contradicts to the paper [7].

In the domain $s_t k_s < \omega < s_l k_s$ the narrow continuum associated with "mixed" mode (with decaying longitudinal wave and nondecaying transverse one) appears in both electronic and ripple cross section:

$$\left.\begin{matrix}\Sigma^{ac}_{el}(\mathbf{k}_s,\omega)\\ \Sigma^{ac}_{rip}(\mathbf{k}_s,\omega)\end{matrix}\right\} \simeq (s_l^2 k_s^2 - \omega^2)(\omega^2 - s_t^2 k_s^2)^{1/2}/\rho s^5 k_s^4. \tag{10}$$

The first term in (7) gives the additional ripple contribution (nonsymmetric transverse resonance) absent in Σ_{el}:

$$\Sigma^{ac}_{rip}(\mathbf{k}_s,\omega) \simeq \frac{s_t k_s^2}{\rho\omega^2}\mathrm{Re}\ (\omega^2 - s_t^2 k_s^2 + 2i\Gamma_{ac}\omega)^{-1/2}. \tag{11}$$

It is produced by transverse phonons slipping along the surface. Finally, in the range $\omega > s_l k_s$ we have wide nonsymmetric longitudinal resonance due to the electron-phonon interaction and the continuum by the ripples:

$$\left.\begin{matrix}\Sigma^{ac}_{el}(\mathbf{k}_s,\omega)\\ \Sigma^{ac}_{rip}(\mathbf{k}_s,\omega)\end{matrix}\right\} \simeq \begin{cases} \dfrac{s_l k_s^4}{\rho\omega^2(\zeta_1^2+\zeta_2^2)}\mathrm{Re}\ (\omega^2 - s_l^2 k_s^2 + 2i\Gamma_{ac}\omega)^{-1/2}, \\ (\omega^2 - s_l^2 k_s^2)^{1/2}/\rho s\omega^2. \end{cases} \tag{12}$$

The first and second terms in the brackets (7) are absent in [6,7]. We derive them from the "bulk" part of the phonon Green function. The last term in (7) arises from the "surface" part. The entire Green function obeys the elastic equation for the semi-space $z > 0$ and the boundary condition at $z = 0$.

The elasto-optic cross section contains also the contribution from bulk phonons. For the normal incidence and scattering the only longitudinal phonons are involved. The corresponding peak is sharp when the skin depth is small $\zeta_1 >> \zeta_2$:

$$\Sigma^{ac}_{el}(\mathbf{k}_s,\omega) \simeq \begin{cases} \dfrac{\zeta_1}{\rho[(\omega - s_l\zeta_1)^2 + s_l^2\zeta_2^2]} & \text{for } s_l\zeta_2 >> \Gamma_{ac}, \\ \dfrac{\zeta_1\Gamma_{ac}}{\rho s_l\zeta_2[(\omega - s_l\zeta_1)^2 + \Gamma_{ac}^2]} & \text{for } s_l\zeta_2 << \Gamma_{ac}. \end{cases} \tag{13}$$

For the nonperpendicular incidence and scattering the bulk transverse phonons are excited too giving the peak with the same form (13) multiplied on $\min(k_s^2/\zeta_1^2, \zeta_1^2/k_s^2)$.

3. The Raman light scattering from optical phonons can be analyzed similarly. To find the optical part of the correlator (4) we apply the elasto-optic equation taking into account the electron- optical-phonon interaction [11,12]. After the evaluation we obtain the expression (7) with $\kappa^{op}_{l,t} = (k_s^2 - (\omega^2 - \omega^2_{l,t})/a_{l,t})^{1/2}$. Here $\omega_{l,t}$ and $a_{l,t}$ define the bulk optical spectrum $\omega_{l,t}(\mathbf{k})^2 = \omega^2_{l,t} + a_{l,t}k^2$. The dispersion parameters $a_{l,t}$ are of the order of s^2 and may get an arbitrary sign. The surface optical phonons exist when κ_l^{op} and κ_l^{op} are both real. On the contrary to the acoustic case there are two branches of optical surface phonons [12] for the case of two atoms in an elementary cell. Each of them results a strong Lorentzian peak:

$$\left.\begin{matrix}\Sigma^{op}_{el}(\mathbf{k}_s,\omega)\\ \Sigma^{op}_{rip}(\mathbf{k}_s,\omega)\end{matrix}\right\} \simeq \frac{\Gamma_{op}}{\rho s((|\omega| - \omega_s(k_s))^2 + \Gamma_{op}^2)} \begin{cases} \min(p_F^2/|\zeta|^2, p_F^2/k_s^2) \\ 1 \end{cases} \tag{14}$$

were $\omega_s(k_s)$ are their spectra. The optical phonon damping was evaluated selfconsistently [12] and has the form:

$$\Gamma_{op}(\mathrm{k}) = -\frac{1}{2\rho}\mathrm{Im}\int < \frac{\xi^2(\mathrm{p})}{\omega - \mathrm{vk} + i\tau_p^{-1}} > \frac{dS_F}{v(2\pi)^3}, \tag{15}$$

where $\xi(\mathrm{p})$ is the optical deformation potential. The electron-phonon interaction gives also the optical frequency shift:

$$\delta\omega = \frac{1}{2\rho\omega}\mathrm{Re}\int \frac{(i\tau_p^{-1} - \mathrm{vk})\xi^2(\mathrm{p})}{\omega - \mathrm{vk} + i\tau_p^{-1}} \frac{dS_F}{v(2\pi)^3}. \tag{16}$$

The various nonsymmetric resonances and continua appear near the frequencies which obey $\kappa_l = 0$ or $\kappa_t = 0$. The detailed analysis is rather sophisticated and depends on the relations of spectrum parameters.

The optical bulk peaks arise only in elasto-optic contribution. For example, the shape of the longitudinal phonon peak has the form:

$$\Sigma_{el}^{op}(\mathrm{k}_s, \omega) \simeq \begin{cases} \dfrac{p_F\Gamma_{op}}{\rho s\zeta_2[(\omega - (\omega_l^2 + a_l\zeta_1^2)^{1/2})^2 + \Gamma_{op}^2]} & \text{for } s\zeta_2 << \Gamma_{op}p_F/\zeta_1, \\ \dfrac{p_F^2}{\rho\zeta_1[(\omega - (\omega_l^2 + a_l\zeta_1^2)^{1/2})^2 + s_l^2\zeta_2^2]} & \text{for } s\zeta_2 >> \Gamma_{op}p_F/\zeta_1. \end{cases} \tag{17}$$

In the last case, when $s\zeta_2 >> \Gamma_{op}p_F/\zeta_1$, an additional peak controlled by the singularity of the phonon density of states appears:

$$\Sigma_{el}^{op}(\mathrm{k}_s, \omega) \simeq \frac{p_F^2}{\rho s(\zeta_1^2 + \zeta_2^2)}\ \mathrm{Re}\ (\omega^2 - \omega_l^2 + 2i\Gamma_{op}\omega_t)^{-1/2} \tag{18}$$

This peak has the nonsymmetric shape. Its symmetry changes simultaneously with the sign of a.

4. In the experiments the incident light frequency is taken usually in the transparency range to increase the penetration depth. Now let us imagine that the number of carriers grows in a sample. The experimental results on fullerides [16] show that the most of vibrational modes disappear for the metallic phase A_3C_{60} in comparison with the Raman spectra for the insulator phases C_{60} and A_6C_{60}. One can propose the two explanations for this phenomenon. The first one suggests the strong influence of carriers on the skin depth: the doping can make the dielectric function (6) to be negative at incident or scattered frequency. In this case $\zeta_2 \sim \zeta_1$ and all the bulk peaks (13), (17)-(18) became unobservable. The acoustic surface resonances (8)-(12) and optical surface ones are still exist.

The alternative explanation involves the effect of carriers on the phonon damping. As one can see from (9), (15)-(16) the interaction of carriers with phonons results the broadening and shift of the peaks. The electron-phonon damping can be forbidden by selection rules. For example, if the optical phonon polarization is perpendicular to the vector of deformation potential, the damping and shift are equal to zero (15)-(16). Indeed, the experimental data demonstrate the broadening and shift of most peaks. Complementary data to the Raman studies come from inelastic neutron scattering. Here the skin depth should not affect the neutron spectra. To our view the data [17] seem to be unable to choose the scenario.

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