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Surface Inelastic Scattering of Light†

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A semiclassical study of surface inelastic scattering of light is presented here. The relation between calculated and experimental cross sections, i.e., the derivation of the Fresnel correction factors, is given. The fluctuation-dissipation theorem is used to relate the fluctuation of the dielectric constant, and therefore the scattering cross section, to the imaginary part of a generalized susceptibility.

Apresenta-se um estudo semi-clássico do espalhamento inelástico da luz numa superfície. Obtém-se a relação entre a seção de choque calculada e a experimental, isto é, obtém-se os fatores corretivos de Fresnel. Emprega-se o teorema de ilutuação-dissipação para relacionar a flutuação da constante dielétrica, e portanto da seção de choque de espalhamento, à parte imaginária da suscetibilidade generalizada.

1. Introduction

Surface scattering of light in condensed media has long been under consideration and use[1]. This applies to narrow gap semiconductors, semimetals and metals. The technique of scattering from semiconductor surfaces seems to have been used first by Russell[2]. Feldman *et al.*[3] were the first to report first order Raman scattering of light by optical vibrations of metals. The theory was given by D. L. Mills *et al.*[4]. Study of the energy gap in superconductors in photoluminiscence experiments has recently been done[5]. Theoretical studies of light scattering by a superconducting surface were made by Abrikosov and Falkovskii[6].

However, due to experimental difficulties this technique has not been widely employed and this kind of study is only beginning. Basically, the scattering intensity is greatly reduced if the scattering volume is restricted to the

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skin depth. Although this generally implies that the scattering efficiency is near the threshold of detectability, it can be expected that improvements in experimental techniques will produce a revival of this aspect of Raman spectroscopy. Furthermore, interest in this and related problems will certainly increase as a result of the growing use of thin films in physical experiments and devices.

We consider in this paper a semiclassical treatment of light scattering from the surface of an opaque material. We remark that microscopic calculations of scattering cross sections consistently use the effective field inside the material whereas the ones measured are those outside it. To connect the calculated cross section to the experimental cross section, one solves the usual boundary value problem at the material surface. This will be the subject of next section, where we also solve the inhomogeneous wave equation for the vector potential of the electromagnetic field. The source of inhomogeneities can be fluctuations associated whith elementary excitations in the material (phonons, magnons, quasiparticle excitations, plasmons, etc.) which are responsible for the scattering process[7,8,9]. The Green function tensor that connects the flutuations with the scattered field for arbitrary experimental geometry is obtained.

In Section **3,** the scattering cross section is derived and related through the fluctuation-dissipation theorem to the imaginary part of the generalized susceptibility associated with the "current" which is the source of the inhomogeneous term in the wave equation for the vector potential.

2. The Scattered Field

Let us consider a semi-infinite crystal filling the half space $z < 0$ as shown in Fig. 1. One can think of an extended slab of width L much larger than the skin depth δ, so that reflections from the back surface can be neglected. Eletromagnetic radiation incident on this material will be scartered within the skin depth. One can describe the process as the absorption of one photon (o,, k,, μ_1) by the system and simultaneous emission of another photon (ω_2, $\mathbf{k}_2$, μ_2); o , k and μ stand for frequency, wavevector and polarization of the photons. The frequency ***o,*** can be greater or smaller than ***o, ,***giving rise to the so-called Stokes and antiStokes bands, respectively. The difference o = ***o,*** – o, is the so-called Raman frequency shift.

Fom a macroscopic point of view, scattering results from fluctuations of the optical properties of the media, characterized by the deviation

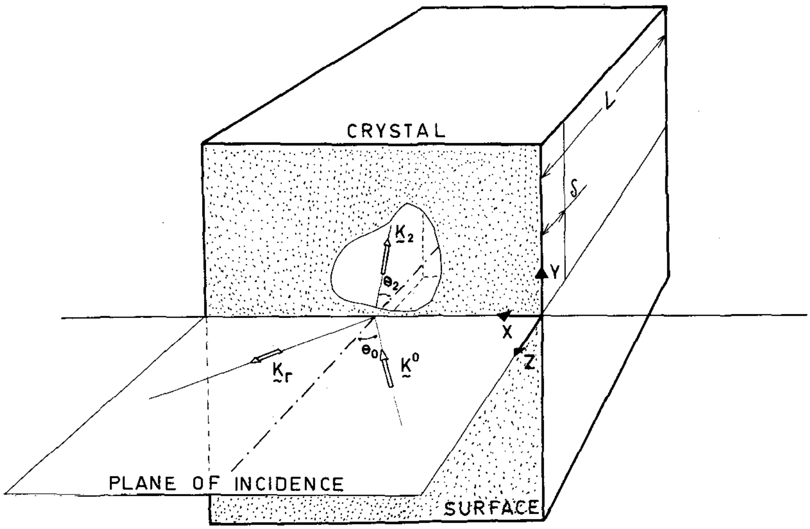

Fig. 1 - Schematic of a typical crystal situation, whose surface is in the (x, y)-plane, with the reference frame and the wave vectors $\mathbf{k}^0$ of the incident field, $\mathbf{k}_r$ of the reflected field and $\mathbf{k}_2$ of the transmitted field.

$\delta\varepsilon$ of the local instantaneous value of the dielectric tensor with respect to its averaged value[7]. We write

$$\varepsilon_{ij}(\mathbf{r}, t) = \varepsilon^0(\mathbf{r}, t)\delta_{ij} + \delta\varepsilon_{ij}(\mathbf{r}, t) \tag{2-1}$$

for the dielectric constant of the material ($z < 0$). In fact, $\delta\varepsilon$, can be considered as an effect of modulation of the dielectric tensor by periodic motions in the system. If $\{Q_\mu e^{i\omega_\mu t}\}$ denotes a set of coordinates which describe the motion that causes the scattering, one can write, in first approximation,

$$\delta\varepsilon_{ij} = \sum \frac{\partial\varepsilon_{ij}}{\partial Q_\mu} Q_\mu e^{i\omega_\mu t} = \sum_\mu \alpha_{ij,\mu} Q_\mu e^{i\omega_\mu t} \tag{2-2}$$

where $\alpha_{ij,\mu}$ is the (third rank) polarizability tensor[8,9].

In order to find the scattered intensity, we must find the scattered field. To do so, we proceed to solve the Maxwell equation for the vector potential $\mathbf{A}(\mathbf{r}, t)$:

$$\nabla \times \nabla \times \mathbf{A}(\mathbf{r}, t) - \frac{1}{c^2}\frac{\partial}{\partial t}\hat{\varepsilon}(\mathbf{r}, t)\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} = 0, \tag{2-3}$$

where the dielectric tensor $\hat{\varepsilon}$ is

$$\hat{\varepsilon}(\mathbf{r}, t) = \begin{cases} 1 & \text{for } z > 0, \\ \hat{\varepsilon}^0(\mathbf{r}, t) + \delta\hat{\varepsilon}(\mathbf{r}, t) & \text{for } z < 0, \end{cases} \tag{2-4}$$

which properly includes the modulation effect responsible for the scattering phenomena. Furthermore, we will assume that the exciting laser radiation is in the optical region and therefore it is safe to replace $\hat{\varepsilon}^0(\mathbf{r}, t)$ by a constant background dielectric tensor $\hat{\varepsilon}^0$, i.e. $\varepsilon^0_{\alpha\beta}(\mathbf{r}, t) = \varepsilon^0 \delta_{\alpha\beta}$ (for $z<0$). For simplicity we have considered a cubic material.

Equation (2-3) can be rewritten:

$$\sum_\gamma \square_{\alpha\gamma} A_\gamma(\mathbf{r}, t) = -\frac{1}{c} \mathscr{I}_\alpha(\mathbf{r}, t) \tag{2-5}$$

where $\square$ is the D'Alembertian operator

$$\square_{\alpha\gamma} = \sum_\rho \text{curl}_{\alpha\rho} \text{curl}_{\rho\gamma} + \theta(-z)\delta_{\alpha\gamma}\left(\frac{\varepsilon^0}{c^2}\right)\frac{\partial^2}{\partial t^2} \tag{2-6}$$

and

$$\text{curl}_{\alpha\rho} = \sum_\beta \varepsilon_{\alpha\beta\rho} \frac{\partial}{\partial x_\beta}, \tag{2-7}$$

where $\varepsilon_{\alpha\beta\rho}$ are the Levi-Civita symbols[10,11]. Finally, $\mathscr{I}$ is the "current"

$$\mathscr{I}(\mathbf{r}, t) = \frac{\theta(-z)}{c} \frac{\partial}{\partial t}\left[\delta\hat{\varepsilon}(\mathbf{r}, t)\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t}\right]. \tag{2-8}$$

In order to solve Eq. (2-5), we will find the matrix Green function G which satisfies

$$\sum_\gamma \square_{\alpha\gamma} G_{\gamma\beta}(\mathbf{r}, \mathbf{r}'; t - t') = \delta_{\alpha\beta}\delta(t - t')\delta(\mathbf{r} - \mathbf{r}'). \tag{2-9}$$

As is well known, the complete solution to Eq. (2-5) is of the form

$$A_\alpha(\mathbf{r}, t) = A_\alpha^{(h)}(\mathbf{r}, t) + \frac{1}{c}\sum_\beta \int d^3r'\, dt'\, G_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t - t')\mathscr{I}_\beta(\mathbf{r}', t'), \tag{2-10}$$

where $A_\alpha^{(h)}$ is the solution of the homogeneous equation, i.e. with $\delta\varepsilon = 0$ (Ref. 11). The second term in Eq. (2-10) is the scattered field which we will designate as $\mathbf{A}^s(\mathbf{r}, t)$. The first order approximation in the fluctuation $\delta\varepsilon$ is obtained by replacing $\mathscr{I}_\beta(\mathbf{r}', t')$ on the right hand side of Eq. (2.10) by

$$\mathscr{I}_\beta^{(h)}(\mathbf{r}', t') = \frac{\theta(-z')}{c} \frac{\partial}{\partial t'} \left[\delta\hat{\varepsilon}(\mathbf{r}', t') \frac{\partial A_\beta^{(h)}(\mathbf{r}', t')}{\partial t'} \right] \tag{2-11}$$

The scattered field is then given by

$$E_\alpha^s(\mathbf{r}, t) = -\frac{1}{c} \frac{\partial A_\alpha^s(\mathbf{r}, t)}{\partial t} = \frac{1}{c} \sum_\beta \int d^3 r' \, dt' \frac{\partial}{\partial t} [G_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; \; t - t')] \mathscr{I}_\beta^{(h)}(\mathbf{r}', t'). \tag{2-12}$$

At this point, it is convenient to introduce the Fourier transforms defined by the equations

$$G_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; \; t - t') = \int \frac{d^2 k_{||} \, d\omega}{(2\pi)^3} \mathscr{G}_{\alpha\beta}(\mathbf{k}_{||}, \omega; \; z, z') \cdot \exp \{ i[\mathbf{k}_{||} \cdot (\mathbf{r} - \mathbf{r}') - \omega(t - t')] \}, \tag{2-13a}$$

$$E_\alpha^{(h)}(\mathbf{r}, t) = \mathscr{E}_\alpha \exp (i[\mathbf{k}_2 \cdot \mathbf{r} - \omega_0 t]) \tag{2-13b}$$

and

$$\delta\varepsilon_{\alpha\beta}(\mathbf{r}, t) = \sum_{\mathbf{q}} \delta\varepsilon_{\alpha\beta}(\mathbf{q}) \exp [i(\mathbf{q} \cdot \mathbf{r} - \omega_a t)]. \tag{2-13c}$$

Here, $\mathbf{k}_{||}$ and $\mathbf{q}_{||}$ are the components of the wavevector parallel to the sample surface. Since the plane (x, y) contains the sample surface, translational invariance implies that G depends only on the diferences $x - x'$ and $y - y'$. The fluctuation $\delta\varepsilon$ is assumed to be produced by excitations of wavevector q and frequency ω_a. After replacement of Eqs. (2-13a), (2-13b) and (2-13c) into Eq. (2-12), one gets

$$E_\alpha^s(\mathbf{r}, t) = \frac{\omega_0 \omega_s}{c^2} \sum_{\mathbf{q}} \int_{-\infty}^{0} dz' \sum_{\beta\gamma} \mathscr{G}_{\alpha\beta}(\mathbf{k}_{||}^s, \; \omega_s; \; z, z') \cdot$$

$$\delta\varepsilon_{\beta\gamma}(\mathbf{q}) \mathscr{E}_\gamma \exp \{ i[z(k_{2z} + q_z) + \mathbf{r} \cdot \mathbf{k}_{||}^s - \omega_s t] \}, \tag{2-14}$$

where
$$k_{||}^s = \mathbf{k}_{||}^0 + \mathbf{q}_{||}, \tag{2.15a}$$

$$\omega_s = \omega_0 + \omega_a, \tag{2-15b}$$

which are the laws of parallel momentum and energy conservation. (Let us observe that $\mathbf{k}_{||}^0 = \mathbf{k}_{2||}$).

Next we have to obtain the relationship between the unperturbed field $\mathbf{E}^{(h)}$ in the medium and the incident field $\mathbf{E}_0$, i.e., the Fresnel coefficients.

Let $\mathbf{E}_0$, $\mathbf{E}^{(h)}$ and E, be incident, transmitted and reflected fields respectively. We shall consider separately the cases:

i) incident wave polarized with $\mathbf{E}(E_0^{(\perp)})$ normal to the plane of incidence (x, z).
ii) incident wave polarized with $\mathbf{E}(E_0^{(\|)})$ in the plane of incidence (x, z).

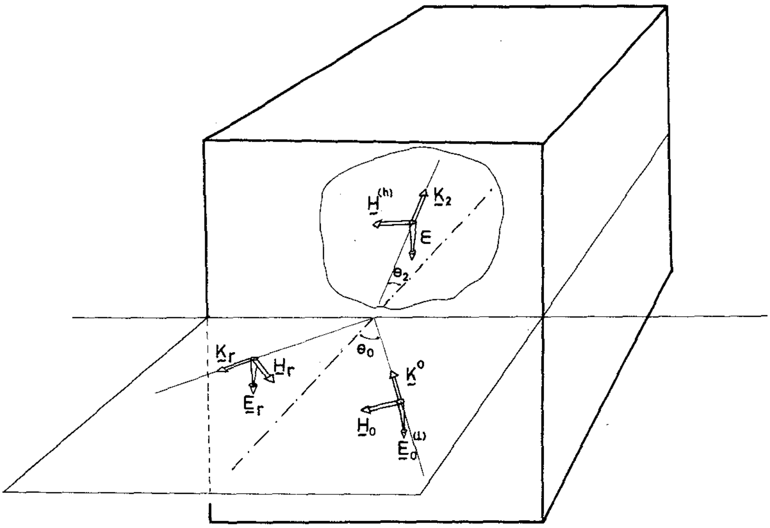

Fig. 2 - Case of incident wave with electric field normal to the plane of incidence (x, z).

(i) In the conditions of Fig. 2, the continuity of the tangential components of the eletric and the magnetic fields implies[12]

$$E_0^{(\perp)} + E,. = \mathscr{E}_y, \tag{2-16a}$$

$$H_0 \cos\theta_i - H,.\cos\theta_i = H^{(h)} \cos O,, \tag{2-16b}$$

or

$$(E_0^{(\perp)} + E,)\cos\theta_i = \left(\frac{\varepsilon_2\mu_1}{\varepsilon_1\mu_2}\right)^{1/2} \mathscr{E}_y \cos\theta_t, \tag{2-16c}$$

since $H = (\varepsilon\mu)^{1/2} E$. Solving this system of equations, one obtains the well known Fresnel equation[12]

$$\mathscr{E}_y = \frac{2(\varepsilon_1/\mu_1)^{1/2}\cos\theta_i}{(\varepsilon_2/\mu_2)^{1/2}\cos\theta_t + (\varepsilon_1/\mu_1)^{1/2}\cos\theta_i} E_0^{(\perp)} \tag{2-17}$$

On the other hand, the dispersion relation

$$c^2(k_{2x}^2 + k_{2z}^2) = \omega_0^2 \varepsilon^0,$$

together with Snells' law $\dfrac{\sin\theta_i}{\sin\theta_t} = \left(\dfrac{1}{\varepsilon^0}\right)^{1/2}$, with $\varepsilon_1 = 1$ and $\varepsilon_2 = \varepsilon^0$,

allows us to obtain the relationship

$$ck_{2z} = -k_2 \cos\theta_t = \omega_0(\varepsilon^0 - \sin^2\theta_i)^{1/2},$$

and finally

$$\mathscr{E}_y = \frac{2(\omega_0/c)\cos e,}{(\omega_0/c)\cos\theta_i - k_{2z}} E_0^{(\perp)}$$

or

$$\mathscr{E}_y \equiv \mathscr{F}_y^{(\perp)} E_0^{(\perp)} \tag{2-18}$$

(ii) In the conditions of Fig. **3,** the continuity relations read:

$$H_0 - H, = H^{(h)}, \tag{2-19a}$$

$$\mathscr{E}_x = (E_0^{(\|)} + E,)\cos 0,, \tag{2-19b}$$

$$(D_0 - D,)\sin\theta_i = D_z^{(h)}, \tag{2-19c}$$

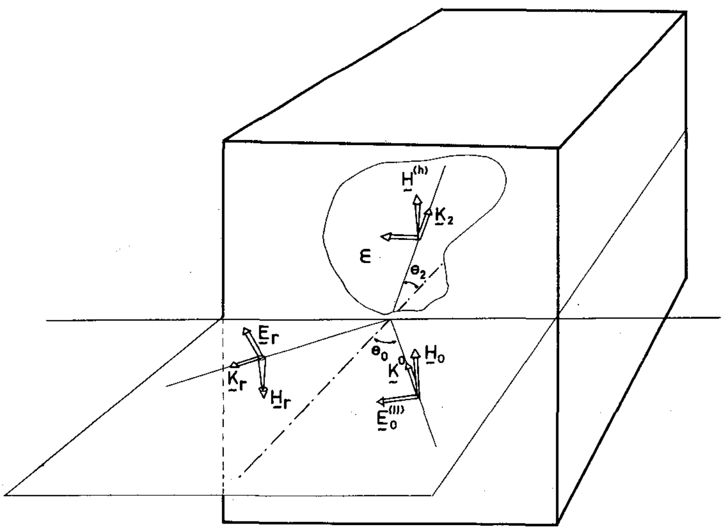

Fig. 3 - Case of incident wave with electric field parallel to the plane of incidence (x, z).

and

$$k_{2x}\mathscr{E}_x + k_{2z}\mathscr{E}_z = 0, \qquad (2\text{-}19d)$$

since div $\mathbf{E}^{(h)} = 0$.

This gives a system of four equations for the four quantities **E,,** $\mathscr{E}_z$, H, and $H^{(h)}$. Straightforward but tedious algebra, whose details we omit here, permits us to obtain the solutions

$$\mathbf{E}, = \frac{2(\omega_0/c)\sin\theta_i\cos\theta_i}{(\omega_0\varepsilon^0/c)\cos\theta_i - k_{2z}} E_0^{(\|)}$$

or

$$\mathscr{E}_z \equiv \mathscr{F}_z^{(\|)} E_0^{(\|)}, \qquad (2\text{-}20)$$

and

$$\mathscr{E}_x = \frac{2\cos\theta_i k_{2z}}{\mathbf{k},, - (\omega_0\varepsilon^0/c)\cos\theta_i} E_0^{(\|)}$$

or

$$\mathscr{E}_x \equiv \mathscr{F}_x^{(\|)} E_0^{(\|)}. \qquad (2\text{-}21)$$

In short notation, Equations (2-18), (2-20) and (2-21) can be written, using equation (2-13*b*), as

$$\mathscr{E}_\alpha = \sum_\lambda \mathscr{F}_\alpha^\lambda E_0^\lambda$$

where $\lambda = \|$ (parallel), **i** (perpendicular).

We proceed now to obtain the Fourier transform of the matrix Green function. To simplify the mathematical handling of Eq. (2-9) we will choose $k_\|$ along the x-direction. Later on we will remove this restriction by performing a rotation in the (x, y) plane. Using Eq. (2-13*a*) and the integral representation of the 6-function, we have

$$\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t') = \frac{1}{(2\pi)^4}\int d^3k \int d\omega \exp\{i[\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}') - \omega(t-t')]\}.$$

Therefore, the system of equations (2-9) becomes

$$ik_\| \frac{\mathbf{a}}{\partial z}\mathscr{G}_{zx} - \left[\frac{\partial^2}{\partial z^2} + \frac{\omega^2}{c^2}\varepsilon^0(z)\right]\mathscr{G}_{xx} = \delta(z-z'), \qquad (2\text{-}22a)$$

$$\left[k_{\|}^{2}-\frac{\omega^{2}}{c^{2}}\varepsilon^{0}(z)\right]\mathscr{G}_{yx}-\frac{\partial^{2}}{\partial z^{2}}\mathscr{G}_{yx}=0, \tag{2-22b}$$

$$ik_{\|}\frac{\partial}{\partial z}\mathscr{G}_{xx}+\left[k_{\|}^{2}-\frac{\omega^{2}}{c^{2}}\varepsilon^{0}(z)\right]\mathscr{G}_{zx}=0, \tag{2-22c}$$

$$ik_{\|}\frac{\partial}{\partial z}\mathscr{G}_{zy}-\left[\frac{\partial^{2}}{\partial z}+\frac{\omega^{2}}{c^{2}}\varepsilon^{0}(z)\right]\mathscr{G}_{xy}=0, \tag{2-22d}$$

$$\left[k_{\|}^{2}-\frac{\omega^{2}}{c^{2}}\varepsilon^{0}(z)\right]\mathscr{G}_{yy}-\frac{\partial^{2}}{\partial z^{2}}\mathscr{G}_{yy}=\delta(z-z'), \tag{2-22e}$$

$$ik_{\|}\frac{\partial}{\partial z}\mathscr{G}_{xy}+\left[k_{\|}^{2}-\frac{\omega^{2}}{c^{2}}\varepsilon^{0}(z)\right]\mathscr{G}_{zy}=0, \tag{2-22f}$$

$$ik_{\|}\frac{\partial}{\partial z}\mathscr{G}_{zz}-\left[\frac{\partial^{2}}{\partial z^{2}}+\frac{\omega^{2}}{c^{2}}\varepsilon^{0}(z)\right]\mathscr{G}_{xz}=0, \tag{2-22g}$$

$$\left[k_{\|}^{2}-\frac{\omega^{2}}{c^{2}}\varepsilon^{0}(z)\right]\mathscr{G}_{yz}-\frac{\partial^{2}}{\partial z^{2}}\mathscr{G}_{yz}=0, \tag{2-22h}$$

$$ik_{\|}\frac{\partial}{\partial z}\mathscr{G}_{xz}+\left[k_{\|}^{2}-\frac{\omega^{2}}{c^{2}}\varepsilon^{0}(z)\right]\mathscr{G}_{zz}=\delta(z-z'). \tag{2-22i}$$

The components $\mathscr{G}_{xy}$, $\mathscr{G}_{yx}$, $\mathscr{G}_{yz}$ and **9,** are zero in the chosen system of cartesian axes. To solve this system of differential equations we must establish the boundary conditions. Eq. (2-10) tells us that $G_{\alpha\beta}$ satisfies the same boundary conditions at the sample surface ($z = 0$) as the field components ***A*,,** for any β. This is so because of the arbitrariness of the "source" $\mathscr{I}$ which depends on the material and the exciting radiation; therefore

$$\mathscr{G}^{<}_{xx}=\mathscr{G}^{>}_{xx}, \quad \mathscr{G}^{<}_{zz}=\mathscr{G}^{>}_{zz} \tag{2-23a}$$

and

$$\varepsilon^{0}\mathscr{G}^{<}_{zx}=\mathscr{G}^{>}_{zx}, \quad \varepsilon^{0}\mathscr{G}^{<}_{xz}=\mathscr{G}^{>}_{xz} \tag{2-23b}$$

are the continuity laws for the tangential component of E and transverse component of D, respectively. The signs $<$ and $>$ stand for values of $\mathscr{G}$ at the interface, in the material medium and in the vacuum, respectively. These sets of conditions allow us to determine the two integration coefficients of the system of Equations (2-22a) and (2-22c) and the system of Equations (2-22*g*) and (2-22i).

The component $\mathscr{G}_{yy}$ satisfies by itself a second order differential equation. The boundary conditions for it are

$$\mathscr{G}_{yy}^{<} = \mathscr{G}_{yy}^{>} \tag{2-24a}$$

(continuity of tangential component of E)

and

$$\frac{\partial \mathscr{G}_{yy}^{<}}{\partial z} = \frac{\partial \mathscr{G}_{yy}^{>}}{\partial z} \tag{2-24b}$$

which involves the continuity of the tangential component of the magnetic field related to $\mathscr{G}$ through the Maxwell equation $(\nabla \times E)_x = \frac{\partial E_y}{\partial z} = \left(\frac{\omega\mu}{c}\right) H_x$ and Eq. (2-10).

Appendix I contains the calculations involved in the solution of system (2-22).

In matrix form, we can write

$$\hat{\mathscr{G}}(z, z' ; \mathbf{x} k_{||}, \omega) = \left(\frac{c}{\omega}\right)^2 \hat{\Gamma}(\mathbf{x} k_{||}, k_z, \kappa_z ; \omega) \cdot \frac{\exp\{i(zk_z + z'\kappa_z)\}}{\kappa_z - \varepsilon^0 k_z} \tag{2-25}$$

where

$$\hat{\Gamma}(\mathbf{x} k_{||}, k_z, \kappa_z ; \omega) = \begin{pmatrix} ik_z\kappa_z & 0 & ik_{||} k_z \\ 0 & -i\left(\frac{\omega}{c}\right)^2 \frac{\kappa_z - \varepsilon^0 k_z}{\kappa_z - k_z} & 0 \\ -ik_{||}\kappa_z & 0 & -ik_{||}^2 \end{pmatrix} \tag{2-26}$$

Let us recall the fact that this result corresponds to the particular geometry in which $\mathbf{k}_{||}$ is in x-direction. Generalization to arbitrary orientation of $\mathbf{k}_{||}$ can be done simply by performing a rotation of angle Φ in the (x, y) plane, the transformation matrix being

$$R(\Phi) = \begin{pmatrix} \frac{k_x}{k_{||}} & -\frac{k_y}{k_{||}} & 0 \\ \frac{k_y}{k_{||}} & \frac{k_x}{k_{||}} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{2-27}$$

with $\tan \Phi = k_y/k_x$.

The matrix Γ of Eq. (2-26) in the new reference frame, i.e., after performing the similarity transformation $R\Gamma R^{-1}$, becomes

$$\Gamma(k_{||}, k_z, \kappa_z;\ \omega) = R\Gamma R^{-1}, \tag{2-28}$$

whose matrix elements are

$$\Gamma_{11} = i\frac{\kappa_z k_z k_x^2}{k_{||}^2} - i\left(\frac{\omega k_y}{k_{||} c}\right)^2 \frac{\kappa_z - \varepsilon^0 k_z}{\kappa_z - k_z},$$

$$\Gamma_{12} = i\frac{\kappa_z k_z k_x k_y}{k_{||}^2} + i\left(\frac{\omega}{c}\right)^2 \frac{k_x k_y}{k_{||}^2} \frac{\kappa_z - \varepsilon^0 k_z}{\kappa_z - k_z} = \Gamma_{21},$$

$$\Gamma_{13} = ik_x k_z;$$

$$\Gamma_{22} = \frac{i\kappa_z k_z k_y^2}{k_{||}^2} - i\left(\frac{\omega}{c}\right)^2 \frac{k_x}{k_{||}} \frac{\kappa_z - \varepsilon^0 k_z}{\kappa_z - k_z}, \quad \Gamma_{23} = ik_y k_z;$$

$$\Gamma_{31} = -ik_x\kappa_z, \quad \Gamma_{32} = -ik_y\kappa_z, \quad \Gamma_{33} = -ik_{||}^2$$

The condition of transversality of the scattered electromagnetic field is contained in matrix Γ since it has the property

$$\sum_\alpha k_\alpha \Gamma_{\alpha\beta} = 0, \tag{2-29}$$

which implies (cf. Eq. 2-14)

$$\sum_\alpha k_\alpha E_\alpha^s = 0.$$

Inserting Equations (2-25), (2-18), (2-20) and (2-21) into **Eq. (2-14)**, we obtain

$$E_\alpha^s(r, t) = (\omega_0/c)^2 \sum_q \sum_{\beta\gamma} \sum_\lambda (c/\omega_s)^2\, \Gamma_{\alpha\beta}(k_{||}^s, k_z^s, \kappa_z^s;\ \omega_s).$$

$$\cdot\, \delta\varepsilon_{\beta\gamma}(q) \mathscr{F}_\gamma^\lambda E_{oi}^\lambda \frac{\exp\{i(\mathbf{r}\cdot\mathbf{k}^s - \omega_s t)\}}{i(\kappa_z^s - \varepsilon^0 k_z^s)(q_z + \kappa_z^s + k_{2z})}, \tag{2-30}$$

where we used

$$\int_{-\infty}^0 dz' \exp(iz'(q_z + \kappa_z^s + k_{2z})) = -i(q_z + \kappa_z^s + k_{2z})^{-1}.$$

We recall the fact that in Eq. (2-30) the conservation laws of Eqs. (2-15a) and (2-15b) are implicit. The latter contains a dependence, through w„ on the z-component of the wavenumber of the crystal excitation. Since for most cases, *o,* can be neglected in comparison with the frequency of the exciting radiation, we can write $|k_{||}^{s}| \simeq |k_{||}^{0}|$. Using this fact and considering Fig. 4 one easily finds the angle θ_s between the propagation

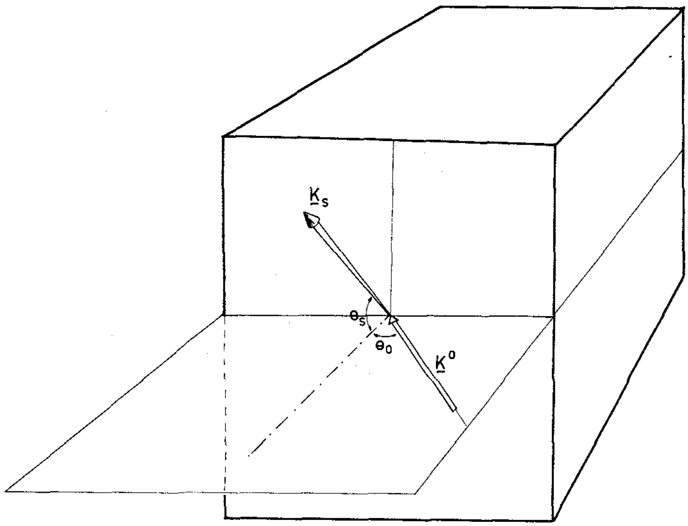

Fig. 4 - The scattering geometry. The relation between the angle of incidence and the angle of emergence of the scattered radiation is given in Eq. (2-31).

direction of the scattered radiation and the normal to the material surface in terms of the parallel components of q, which results in

$$\sin^2 \theta_s \simeq \left(\frac{cq_y}{\omega_0}\right)^2 + \left(\sin \theta_i + \frac{cq_x}{\omega_0}\right)^2 \qquad (2\text{-}31)$$

3. The Scattering Cross Section

We shall now calculate the scattering cross section, i.e., the ratio of energy scattered per unit time, per solid angle (in direction $\mathbf{k}^s$), per unit frequency and unit area, to the flux of incident energy,

$$\frac{V|E^s|^2/4\pi}{c|E^0|^2/4\pi} \qquad (3\text{-}1)$$

Using Eqs. (2-30) and (2-2), one obtains

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{V^2}{(2\pi)^3}\left(\frac{\omega_0}{c}\right)^4 \cos\theta_s \frac{1}{c|\mathbf{E}_0|^2} \int dq_z \sum_{\alpha\mu}$$

$$\cdot \left| \sum_{\beta\gamma} \sum_{\lambda} \Gamma_{\alpha\beta}(k^s_{||}, k^s_z, \kappa_z;\ \omega_s)\alpha_{\beta\gamma\mu} \frac{(c\omega_0/\omega_s^2)}{(\kappa^s_z - \varepsilon^0 k^s_z)}\right.$$

$$\left. \cdot \frac{\mathscr{F}^\lambda_\gamma E^\lambda_{oi}}{(q_z + \kappa^s_z + k_{2z})} \right|^2 \langle Q^*_\mu(q) Q_\mu(q)\rangle_\omega . \quad (3\text{-}2)$$

We have used the fact that, for radiation scattered in the $\mathbf{k}^s$ direction, within a solid angle $d\Omega$, $q_{||}$ remains constant. The number of modes for fixed q_z is $(d^2 q_{||}/(2\pi)^2)A$, with A the area of the laser beam incident on the sample. Considering the conservation law for the parallel components of momentum and transforming to spherical coordinates we have

$$d^2 q_{||} \simeq \left(\frac{\omega_0}{c}\right)^2 \cos\theta_s d\Omega. \quad (3\text{-}3)$$

In Eq. (3-2), the wavevector κ_z in the media have real and imaginary parts $\kappa'_z + i\kappa''_z$. The integral

$$\int \frac{dq_z}{2\pi} \frac{1}{[(\kappa^{s'}_z + k'_{2z} + q_z)^2 + (\kappa^{s''}_z + k''_{2z})^2]} \quad (3\text{-}4)$$

is the so called scattering coherence length.

Let us stress the fact that we have been considering materials with finite skin depth much smaller than the sample thickness. That implies that k''_{2z} is not zero and that coherence length of Eq. (3-4) is finite. In case of Raman scattering by transparent materials, conservation of the normal component of the wavevector removes the singularity at $q_z = \kappa^{s'}_z + k'_{2z}$.

Futhermore, when $\delta \ll \lambda$, i.e., $k''_{2z} \gg k^0$ and $|\varepsilon| \gg 1$, an analysis of Fresnel coeffícients shows that, for any orientation of the incident field, the transmitted field is nearly parallel to the surface and, consequently, the same happens to the scattered field. This is important to take into account when considering the experimental set up.

Finally, we will make some considerations regarding the quantity $(Q^* Q)$, in Eq. (3-2) by means of the approach of Landau and Lifshitz[13]. This quantity is the Fourier transform (in space and time) of the time dependent correlation function $\phi(t-t') = \langle Q^*(t)Q(t')\rangle$ (Ref. 14). In fact, since $Q^*(t)$ and $Q(t)$ are quantum mechanical operators defined at different times, they do not commute generally. Thus, it is more convenient to write

$$\phi(t-t') = (1/2)\langle[Q(t),\ Q(t')]_+\rangle\,; \tag{3-5}$$

the average refers to a particular stationary state.

Let us assume that the system is in the presence of a harmonic externa1 perturbation, the interaction energy being

$$V(t) = -(1/2)[F_0 Q^*(t)\exp\{-i o t) + F_0^* Q(t)\exp\{i o t)]. \tag{3-6}$$

Under the action of this pertubation, the transition probability per unit time from state $|n)$ to state $|m)$, at T = 0"K, is

$$W_{nm} = \frac{\pi|F_0|^2}{2}|Q_{nm}|^2\{\delta(\omega+\omega_{nm}) + \delta(\omega+\omega_{mn})\}, \tag{3-7}$$

where $o_{,,} =$ E, $- E_m(h = 1)$.

The mean energy dissipation A per unit time is

$$A = \sum_m \omega_{mn} W_{nm} = \frac{|F_0|^2}{2}\alpha(\omega) = \frac{|F_0|^2}{2}\omega\chi''(\omega), \tag{3-8}$$

where $\alpha(\omega)$ is the so called absorption coefficient and χ'' is the imaginary part of the generalized susceptibility:

$$\chi(\omega) = \sum_m |Q_{nm}|^2\left\{\frac{1}{\omega+\omega_{nm}-is} + \frac{1}{\omega+\omega_{mn}+is}\right\}. \tag{3-9}$$

At finite temperatures T $\neq$ 0, the previous derivations continue to be valid except for the fact that, because the system is no longer in a pure quantum mechanical state but in mixed states, the average values in Eq. (3-5) must be replaced by the statistical average

$$(\ldots) = \mathrm{Tr}(\ldots p), \tag{3-10a}$$

where ρ is the density matrix

$$\rho = \frac{e^{-\beta H_0}}{Z_0}, \tag{3-10b}$$

with Z_0 the partition function

$$Z_0 = \operatorname{Tr}\{e^{-\beta H_0}\}. \tag{3-10c}$$

A straightfonvard calculation lead us to the relationship

$$\chi''(\omega) = \pi[1 - e^{-\beta\omega}] \sum_{mn} w_n |Q_{nm}|^2 \delta(\omega + \omega_{nm}), \tag{3-11}$$

where

$$w_n = \frac{e^{-\beta E_n}}{Z_0}.$$

Similarly, one easily finds that

$$\langle Q^* Q \rangle_\omega = (1/2)[1 + e^{-\beta\omega}] \sum_{mn} w_n |Q_{nm}|^2 \delta(\omega + \omega_{nm}). \tag{3-12}$$

Comparing Eqs. (3-11) and (3-12), we can write

$$\langle Q^* Q \rangle_\omega = (1/\pi)\{(1/2) + [e^{a..} - 1]^{-1}\}\chi''(\omega). \tag{3-13}$$

This important formula (the *fluctuation-dissipation* theorem) connects the fluctuation of physical quantities with dissipative properties of the system[14,15].

Introducing **Eq.** (3-13) into Eq. (3-2), we obtain a formula for the Raman scattering cross section (RSCS):

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{V^2}{(2\pi)^3}\left(\frac{\omega_0}{c}\right)^4 \cos\theta_s \frac{1}{c|\mathbf{E}_0|^2}[n(\omega) + 1].$$

$$\int \frac{dq_z}{\pi} \sum_\alpha \sum_\mu \Bigg| \sum_{\beta\gamma} \sum_\lambda \Gamma_{\alpha\beta}(\mathbf{k}_{||}^s, k_z^s, \kappa_z^s;\ \omega_s) \frac{c\omega_0}{\omega_s^2}.$$

$$\cdot\, \alpha_{\beta\gamma,\mu} \frac{\mathscr{F}_\gamma^\lambda E_{oi}^\lambda}{(\kappa_z^s - \varepsilon^0 k_z^s)(q_z + \kappa_z^s + k_{2z})}\Bigg|^2 \operatorname{Im}\chi_\mu(\omega, \mathbf{q}), \tag{3-14}$$

where $n(\omega) = [e^{\beta\omega} - 1]^{-1}$ and $\omega = \mathbf{o,} - \omega_0$.

It is important to notice that in writing **Eq. (3-14)**, we have replaced the term (1/2) in Eq. (3-13) by 1. This is so because Stokes and antiStokes processes do not get lumped together and the thermal factor in the fluctuation-dissipation theorem is $[n(\omega) + 1]$ (Ref. 16). This factor correctly appears when the Raman spectra is obtained using the Green's function formalism'[7].

4. Conclusions

Eq. (3-14) directly connects the RSCS with a correlation function or imaginary part of a generalized susceptibility. This correlation function, in fact the line-shape function, contains practically all the information on the Raman scattering spectra of materials. This, once again, shows the importance and inevitability of the use of correlation functions to describe physical measurements[14]. This formulation is also very convenient since it allows for immediate connection with field theoretical methods. This is not always necessary, but very often convenient, mainly in cases of a system of strongly interacting particles, so that relaxation effects, collective excitation, final state interactions, etc., can be dealt with more easily.

To end this presentation, we would like to emphasize that surface inelastic scattering of light could be in a near future an important tool in the study of a number of interesting problems like electronic excitation in normal and non-normal metals, semiconductor-semimetal transitions, thin film superconductors, etc..

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Appendix: Solution of the system (2-23)

The matrix elements $\mathcal{G}_{zx}$ and $\mathcal{G}_{xx}$ are coupled together by Eqs. (2-22a) and (2-22*c*). The boundary conditions are given by Eqs. (2-23*a*) and (2-236). Using Eq. (2-22*c*), one may write Eq. (2-22*a*) as an equation for $\mathcal{G}_{xx}$ alone, i.e.,

$$\mathcal{G}_{zx} = -i \frac{k_{\|} \frac{\partial}{\partial z} \mathcal{G}_{xx}}{k_{\|}^2 - (\omega/c)^2 \varepsilon^0} \tag{A-1}$$

and

$$\left[\frac{\partial^2}{\partial z^2} + \left(\frac{\omega}{c}\right)^2 \varepsilon^0 - k_{\|}^2\right] \mathcal{G}_{xx} = -\frac{c^2}{\omega^2 \varepsilon^0} \left[\left(\frac{\omega}{c}\right)^2 \varepsilon^0 - k_{\|}^2\right] \delta(z - z'). \tag{A-2}$$

Defining

$$\left(\frac{\omega}{c}\right)^2 \varepsilon^0 - k_{\|}^2 = \left(\frac{\omega}{c}\right)^2 \varepsilon^0 - k_x^2 = \kappa_z^2$$

and

$$\left(\frac{\omega}{c}\right)^2 - k_{\|}^2 = k_z^2\,,$$

one can write

$$\left[\frac{\partial^2}{\partial z^2} + \kappa_z^2\right]\mathscr{G}_{xx} = -\frac{c^2\kappa_z^2}{\omega^2\varepsilon^0}\,\delta(z-z') \tag{A-3}$$

for $z < 0$. For $z > 0$, the equation is

$$\left[\frac{\partial^2}{\partial z^2} + k_z^2\right]\mathscr{G}_{xx} = 0, \tag{A-4}$$

which has the simple solution

$$\mathscr{G}_{xx} = A\,\exp\{izk_z\} \tag{A-5}$$

when using outgoing-wave boundary condition.

The solution to Eq. (A-3) is a superposition of the solution of the homogeneous equation, i.e.,

$$\mathscr{G}_{xx}^{(h)} = B\,\exp\{iz\kappa_z\} \tag{A-6}$$

and a particular solution, $\mathscr{G}_{xx}^{(p)}$. To find this we introduce the Fourier transforms

$$\mathscr{G}_{xx}^{(p)} = \int_{-\infty}^{+\infty}\frac{dk}{2\pi}\,\tilde{\mathscr{G}}_{xx}(k)\,\exp\{ik(z-z')\}$$

and

$$\delta(z-z') = \int_{-\infty}^{+\infty}\frac{dz}{2\pi}\,\exp\{ik(z-z')\}$$

Substituting these expressions into Eq. (A-3), we obtain

$$\mathscr{G}_{xx}^{(p)} = \frac{c^2\kappa_z^2}{\omega^2\varepsilon^0}\int\frac{dk}{2\pi}\,\frac{\exp\{ik(z-z')\}}{(k^2-\kappa_z^2)}\,, \tag{A-7}$$

which after integration (recalling that for an absorptive media $\operatorname{Im}\kappa_z < 0$) gives

$$\mathscr{G}_{xx}^{(p)} = -i\,\frac{c^2\kappa_z}{2\omega^2\varepsilon^0}\exp\{-i\kappa_z(z-z')\}\,. \tag{A-8}$$

Substituting Eqs. (A-5), (A-6) and (A-8) into Eq. (A-1), one obtains

$$\mathscr{G}_{zx} = \begin{cases} -A\,\dfrac{k_{\|}}{k_z}\exp\{izk_z\}\,, & (z > 0) \\[2ex] -B\,\dfrac{k_{\|}}{\kappa_z}\exp\{iz\kappa_z\} - i\,\dfrac{c^2k_{\|}}{2\omega^2\varepsilon^0}\exp\{-i(z-z')\kappa_z\}\,. & (z < 0). \end{cases} \tag{A-9}$$

The boundary conditions of Eqs. (2-23*a*) and (2-23b) allow us to determine the parameters *A* and B. In fact, since we are interested in the scattered wave (for $z > 0$), we only need to determine ***A*.** Straight-forward algebra produces

$$\mathscr{G}_{xx} = -\frac{ic^2 k_z \kappa_z}{\omega^2(\kappa_z - \varepsilon^0 k_z)} \exp\{i(z'\kappa_z + zk_z)\}, \tag{A-9a}$$

$$\mathscr{G}_{zx} = -\frac{ic^2 k_{\parallel} \kappa_z}{\omega^2(\kappa_z - \varepsilon^0 k_z)} \exp\{i(z'\kappa_z + zk_z)\}. \tag{A-9b}$$

Next, we consider the element $\mathscr{G}_{yy}$, which satisfies

$$\left[k_{\parallel}^2 - \frac{\omega^2}{c^2}\varepsilon^0\right]\mathscr{G}_{yy} - \frac{\partial^2}{\partial z^2}\mathscr{G}_{yy} = \delta(z - z').$$

Using the same method as before and the boundary conditions, Eqs. (2-24*a*) and (2-24*b*), we obtain

$$\mathscr{G}_{yy} = \frac{i}{k_z - \kappa_z} \exp\{i(zk_z - z'\kappa_z)\}. \tag{A-10}$$

Finally, we need to calculate the terms $\mathscr{G}_{xz}$ and $\mathscr{G}_{zz}$, Fourier transforming Eqs. (2-22*i*) and (2-22*g*) one obtains

$$k_{\parallel} k \tilde{\mathscr{G}}_{zz} + \kappa_z^2 \tilde{\mathscr{G}}_{zz} = -1 \tag{A-11a}$$

and

$$k_{\parallel} k \tilde{\mathscr{G}}_{zz} + \left[\frac{\omega^2}{c^2}\varepsilon^0 - k^2\right]\tilde{\mathscr{G}}_{xz} = 0. \tag{A-11b}$$

By substitution, we find

$$\tilde{\mathscr{G}}_{xz} = -\frac{c^2}{\omega^2 \varepsilon^0}\,\frac{k_{\parallel} k}{(k^2 - \kappa_z^2)},$$

whose inverse transformation is

$$\mathscr{G}_{xz}^{(p)} = -\frac{ic^2 k_{\parallel}}{2\omega^2 \varepsilon^0} \exp\{i(z - z')\kappa_z\}; \tag{A-12}$$

therefore,

$$\mathscr{G}_{xz} = \begin{cases} E \exp\{izk_z\} & \text{for } z > 0, \\ F \exp\{iz\kappa_z\} - i\dfrac{c^2 k_{\parallel}}{2\omega^2 \varepsilon^0} \exp\{i(z - z')\kappa_z\} & \text{for } z < 0, \end{cases}$$

and

$$\mathscr{G}_{zz} = \begin{cases} -E\left(\dfrac{k_{\parallel}}{k_z}\right) \exp\{izk_z\} & \text{for } z > 0, \\ F\left(\dfrac{k_{\parallel}}{\kappa_z}\right) \exp\{iz\kappa_z\} - i\dfrac{c^2 k_{\parallel}^2}{2\kappa_z \omega^2 \varepsilon^0} \exp\{-i(z - z')\kappa_z\} & \text{for } z < 0. \end{cases}$$

With the help of boundary conditions Eqs. (2-22a) and (2-22b), the coefficient E can be found:

$$E = \frac{c^2 k_{\|} k_z}{\omega^2} \frac{\exp\{iz'\kappa_z\}}{\kappa_z - \varepsilon^0 k_z}; \tag{A-13}$$

hence,

$$\mathscr{G}_{zz} = -i\frac{c^2 k_{\|}^2}{\omega^2} \frac{\exp\{i(z'\kappa_z + zk_z)\}}{\kappa_z - \varepsilon^0 k_z} \tag{A-14a}$$

and

$$\mathscr{G}_{xz} = i\frac{c^2 k_{\|} k_z}{\omega^2} \frac{\exp\{i(z'\kappa_z + zk_z)\}}{\kappa_z - \varepsilon^0 k_z}, \tag{A-14b}$$

which completes the determination of the matrix elements of Eq. (2-25).

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