THEORY OF THE RAMAN EFFECT IN METALS

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The theory of Raman scattering of light by optical phonons in metals is presented. We develop a detailed theory of the inelastic scattering of light from a metallic surface and discuss the mechanisms that contribute to the Raman effect.

In recent experiments Feldman, Parker, and Ashkin[1] have observed the first order Raman scattering of light by the optical vibration modes in the monatomic metals Be, Zn, Mg, and Bi, and in the alloy $AuAl_2$. In this Letter we present the theory of the Raman effect in metals. We first present a detailed account of the theory of inelastic light scattering from a metallic surface, in the frequency range where the dielectric constant of the metal is negative. We apply this theory to a discussion of the Raman effect, concluding with estimates of the scattering strength of the various mechanisms.

The mechanism responsible for the scattering of light is the modulation of the electronic susceptibility $\chi_{\mu\nu}(\omega)$ of the metal within the skin depth by the optical vibration modes. Both even- and odd-parity phonons can scatter light, but the scattering mechanisms in the two cases are different. In the case of Raman-active even-parity phonons, i.e., those whose symmetries would allow them to be Raman active in nonmetallic crystals, there are two possible scattering mechanisms: (1) the change in $\chi_{\mu\nu}(\omega)$ to first order in the displacements of the atoms in a primitive unit cell, and (2) the change in $\chi_{\mu\nu}(\omega)$ due to the change in the electronic occupation numbers associated with the relative displacements of the sublattices. A microscopic theory of these mechanisms is described elsewhere.[2] Both mechanisms allow scattering of light by modes of zero wave vector. In the case of infrared-active odd-parity phonons, i.e., those whose symmetries allow them to exhibit a linear dipole moment, the scattering mechanism is the change in the electronic susceptibility resulting from the change in the charge-carrier density accompanying the displacements of the sublattices.[3] In contrast with the matrix element for the scattering by even-parity modes, which is independent of the magnitude of the phonon wave vector, the matrix element for scattering by the charge-density fluctuations accompanying odd-parity modes is proportional to the magnitude of the phonon wave vector. The susceptibilities which are being modulated contain both intraband and interband contributions. In crystals lacking an inversion center, the optical phonons will have mixed parity, and all three mechanisms will contribute to the scattering.

We consider first the formal theory of the scattering of light from the surface of a metal at frequencies of the incident radiation for which the dielectric constant of the metal is negative.

If ω_0 is the incident light frequency, and τ is the electronic relaxation time, then for ω_0 in the visible range of frequencies one has $\omega_0\tau \gg 1$ in the usual case. In this circumstance, the imaginary part of the dielectric constant is small compared with the real part, which is negative when the metallic surface (which we assume to be the xy plane) is reflecting. Thus, in the metal ($z < 0$), we assume that the dielectric constant has the form

$$\epsilon_{\mu\nu}(\vec{x}t) = -|\epsilon_0|\delta_{\mu\nu} + \delta\epsilon_{\mu\nu}(\vec{x}t), \tag{1}$$

where $|\epsilon_0|$ is real, and $\delta\epsilon_{\mu\nu}$ is the change in $\epsilon_{\mu\nu}$ induced by a phonon. We suppose that the dielectric constant of the undeformed crystal is isotropic, but this is an unessential simplification and can readily be removed.

To first order in the phonon amplitude, we write

$$\delta\epsilon_{\mu\nu}(xt) = \sum_{n\vec{q}} \frac{\partial\epsilon_{\mu\nu}}{\partial Q_{n\vec{q}}} Q_{n\vec{q}}(t)\exp(i\vec{x}\cdot\vec{q}) + \text{c.c.}, \tag{2}$$

with $Q_{n\vec{q}}$ the normal coordinate of the $n\vec{q}$ normal mode of the crystal.

The vector potential $\vec{A}(\vec{x}t)$ may be determined from Maxwell's equations, employing the form for $\epsilon_{\mu\nu}$ described above. One may write Maxwell's equation in integral form by introducing a suitably defined Green's function:

$$A_\alpha(\vec{x}t) = A_\alpha^{(0)}(\vec{x}t) + \left(\frac{\omega_0}{c}\right)^2 \sum_{\beta\gamma}\int d^3x'dt'\, G_{\alpha\beta}(\vec{x}\vec{x}';t-t')\delta\epsilon_{\beta\gamma}(\vec{x}'t')A_\gamma(\vec{x}'t'), \tag{3}$$

where $\vec{A}^{(0)}$ is the solution when $\delta\epsilon_{\beta\gamma}=0$. The Green's matrix satisfies

$$\sum_{\gamma}\left\{[\nabla\times(\nabla\times)]_{\alpha\gamma}+\delta_{\alpha\gamma}\frac{\epsilon_0(z)}{c^2}\frac{\partial^2}{\partial t^2}\right\}G_{\gamma\beta}(\vec{x}\vec{x}',t-t')=\delta_{\alpha\beta}\delta(\vec{x}-\vec{x}')\delta(t-t'), \tag{4}$$

where the notation in the first term is defined by the relation $[\nabla\times(\nabla\times)]_{\alpha\beta}F_\beta=[\nabla\times(\nabla\times\vec{F})]_\alpha$; $\epsilon_0(z)=1$ for $z>0$, and $\epsilon_0(z)=-|\epsilon_0|$ for $z<0$. In Eqs. (3) and (4), we have assumed the light frequency ω_0 large compared with the phonon frequencies.

The amplitude of the scattered wave to first order in the phonon amplitude may be found from Eq. (1) by inserting the function $A_\gamma^{(0)}$ into the integral on the right-hand side. We write the Green's matrix in the form

$$G_{\alpha\beta}(\vec{x}\vec{x}';t-t')=\int\frac{d^2k_\parallel d\Omega}{(2\pi)^3}\mathcal{G}_{\alpha\beta}(\vec{k}_\parallel\Omega,zz')\exp[i\vec{k}_\parallel\cdot(\vec{x}-\vec{x}')]e^{i\Omega(t-t')}, \tag{5}$$

where $\vec{k}_\parallel$ is the two-dimensional wave vector $\vec{k}_\parallel=(k_x,k_y,0)$. To find the amplitude of the scattered wave, one requires $\mathcal{G}_{\alpha\beta}$ for $z>0, z'<0$. For this case $\mathcal{G}$ may be written in the form

$$\mathcal{G}_{\alpha\beta}(\vec{k}_\parallel\Omega,zz')=(\Omega/c)g_{\alpha\beta}(\vec{k}_\parallel\Omega)\exp(ik_z z)\exp(-\gamma z'), \tag{6a}$$

where

$$\gamma^2=(\Omega/c)^2|\epsilon_0|+k_\parallel^2,\quad k_z^2=(\Omega/c)^2-k_\parallel^2. \tag{6b}$$

It will be useful to discuss briefly the kinematics of the scattering process. Consider the interaction of the light with a phonon of wave vector $\vec{q}$. In the presence of the metallic surface, the z component of wave vector (normal to the surface) is not conserved. However, the component of wave vector parallel to the surface is conserved. Let $\vec{k}^{(S)}$ and $\vec{k}^{(I)}$ be the wave vectors of the scattered and incident light outside the medium. By consideration of the equations that describe conservation of energy and wave vector, one finds that light scattered in a given direction $\hat{k}^{(S)}$ contains contributions from the interaction of the incident light with phonons with a range of values of q_z, but with wave vector component $\vec{q}_\parallel=\vec{k}_\parallel^{(S)}-\vec{k}_\parallel^{(I)}$ parallel to the surface. This is true in the limit that the photon frequency is large compared with phonon frequencies. This remark simplifies construction of the cross section.

One may then derive an expression for the differential cross section. The details of the procedure will be presented elsewhere.[2] Let $\varphi^{(S)}$ be the flux of energy scattered inelastically by the metal. We find that the flux scattered per unit solid angle per unit frequency may be written

$$\frac{d^2\varphi^{(S)}}{d\Omega d\omega}=\frac{cV}{2(2\pi)^4}\left(\frac{\omega_0}{c}\right)^4\cos\theta_S\sum_n\int\frac{dq_z}{2\pi}\frac{\langle Q_{n\vec{q}}^{*}Q_{n\vec{q}}\rangle}{(\gamma_S+\gamma_I)^2+(q_z)^2}\frac{\Gamma_n}{\Gamma_n^2+[\omega-\omega_n(q)]^2}$$

$$\times\sum_\alpha\left|\sum_{\beta\lambda}\sum_\lambda g_{\alpha\beta}(\vec{k}^{(S)}\omega_0)\frac{\partial\epsilon_{\beta\gamma}}{\partial Q_{n\vec{q}}}\Gamma_\gamma^{\ \lambda}(\vec{k}^{(I)})E_\lambda^{(0)}\right|^2. \tag{7}$$

In this result V is the crystal volume, ω is the frequency shift experienced by the light, θ_S the angle between $\vec{k}^{(S)}$ and the normal to the surface, γ_I and γ_S the inverse of the skin depth for the incident and scattered radiation, respectively, and Γ_n the intrinsic width of the phonon of frequency $\omega_n(\vec{q})$. $E_\lambda^{(0)}$ is the amplitude of the component of the incident electric field of polarization λ, and $\Gamma_\gamma^{\ \lambda}(\vec{k}^{(I)})$ is a "transfer function" which gives the amplitude of the incident field in the metal when $E_\lambda^{(0)}$ assumes the value of unity.

When the skin depth δ is much less than the light wavelength λ, the incident field produces an electric field inside the metal nearly parallel to the surface, regardless of the incident polarization. Similarly, after the phonon "beats" with the incident field to produce the scattered light, only the component parallel to the surface is transmitted through with efficiency. Thus, when $\delta\ll\lambda$, one obtains information about those components of $\partial\chi_{\mu\nu}/\partial Q_n$ for which both μ and ν re-

fer to directions parallel to the surface. For example, if the incident field is plane polarized in the plane of incidence (the xz plane), one finds, to lowest order in δ/λ,

$$\vec{E}^{(S)} \propto [(\partial\chi_{xx}/\partial Q_0)(\hat{y}\times\hat{k}^{(S)}) - (\partial\chi_{yx}/\partial Q_0)(\hat{x}\times\hat{k}^{(S)})].$$

We first apply the result of Eq. (7) to the Raman scattering of light by odd-parity phonons. The ionic motion associated with an odd-parity, LO phonon of long wavelength generates a macroscopic electric field. In the metal, this field is screened out by the conduction electrons. Thus, one has macroscopic fluctuations in conduction-electron density associated with excitation of a long-wavelength LO phonon of odd parity. Since the dielectric function depends on the electron density, the presence of such an LO phonon modulates the dielectric function. In particular, the $\vec{k}=0$ dielectric function contains a term $-(\omega_p/\omega_0)^2$, where $\omega_p^2=(4\pi ne^2/m^*)$ is the plasma frequency of the electrons. Since ω_p^2 is proportional to n, this term is modulated. We consider the scattering that comes from this term. If δn_q is the amplitude of the density fluctuation,

$$\delta\epsilon_{\mu\nu} = -\delta_{\mu\nu}(\omega_p/\omega_0)^2(1/n)\delta n_q. \tag{8}$$

If $\vec{u}(\vec{q}k)$ is the amplitude of the displacement for sublattice κ, then in the long-wavelength limit

$$\delta n_q = i(VV_c)^{-1/2}\sum_\kappa z_\kappa \vec{q}\cdot\vec{u}(q\kappa), \tag{9}$$

where V_c is the volume of the unit cell and z_κ the charge on the ion cores of sublattice κ, measured in units of the electronic charge e. There is also an interband contribution to $\delta\epsilon_{\mu\nu}$; however, it is difficult to estimate its magnitude, since it depends on the details of the electronic band structure.

When Eqs. (8) and (9) are combined with Eq. (7), one may compute the scattering cross section. Since the details are described elsewhere,[2] in the present note we shall simply quote the result, after pointing out some important steps in the computation. Notice from Eq. (11) that δn_q and hence $\partial\epsilon_{\mu\nu}/\partial Q_{n\vec{q}}$ are proportional to the phonon wave vector $\vec{q}$ for this scattering mechanism. From the structure of the integral in Eq. (7), it is clear that the important values of q_z are $\gg k^{(I)}$, since $\gamma^{(I)},\gamma^{(S)}\gg k^{(I)}$. The integrand then becomes proportional to $\{q_z^2/[(\gamma_S+\gamma_I)^2+q_z^2]\}\times\{\Gamma_n/(\Gamma_n^2+[\omega-\omega_n(q)]^2)\}$ in the important region of the integration. Let ω be near the $\vec{q}=0$ LO optical phonon frequency ω_{LO}. For large q_z, the first factor in the integrand approaches unity. However, because of dispersion in the phonon branch, as q_z increases, one will have $|\omega-\omega_n(q)|\gg\Gamma_n$, so the second factor will fall off with increasing q_z. If one assumes that $\omega(\vec{q})$ varies quadratically with q near $\vec{q}=0$, the resulting integral converges. We suppose $\omega(\vec{q})=\omega_{LO}[1-\beta(\pi q/a_0)^2]$, where the dimensionless number β measures the curvature of the phonon branch near $\vec{q}=0$, and a_0 is the lattice constant. β may be either positive or negative, and is of order unity for most materials. For a two-sublattice material, with φ_0 the incident flux, we find for the Stokes radiation

$$\frac{1}{\varphi_0}\frac{d^2\varphi_S}{d\Omega d\omega} = 2\sqrt{2}(r_*)^2\left(\frac{\hbar}{V_c\omega_{LO}^2\mu}\right)\left(z_A\frac{\mu}{M_A}-z_B\frac{\mu}{M_B}\right)^2\frac{(1+\bar{n}_{LO})f(\theta^{(S)},\varphi^{(S)})}{a_0(|\beta|)^{1/2}(1+|\epsilon_0|)^2}g(\omega), \tag{10}$$

where the shape function $g(\omega)$ is plotted in Fig. 1, and f, a function of $\hat{k}^{(S)}$, is of order unity. In Eq. (10), $r_*=(e^2/m_*c^2)$, where m_* is the effective mass, μ is the reduced mass of the unit cell, and Γ_0 in Fig. 1 is the intrinsic width of the $\vec{q}=0$ LO phonon. We have replaced Γ_n by Γ_0 in the integral.

From Fig. 1, one can see that $g(\omega)$ is strongly asymmetric. The sense of the asymmetry in $g(\omega)$ provides a measure of the sign of the curvature of the phonon branch near $\vec{q}=0$. One can estimate the integrated strength of the peak in Fig. 1 by noting that the maximum value of g is $\sim(\omega_{LO}/\Gamma_0)^{1/2}$, while the half-width of the peak is $\sim(2-3)\Gamma_0$. Then we estimate that the differential cross section is of the order of

$$\frac{1}{\varphi_0}\frac{d\varphi_S}{d\Omega}\sim 15\frac{(r_*)^2}{a_0}\left(\frac{\hbar}{V_c\omega_{LO}\mu}\right)\times\left(\frac{\Gamma_0}{\omega_{LO}}\right)^{1/2}\frac{1}{(1+|\epsilon_0|)^2}.$$

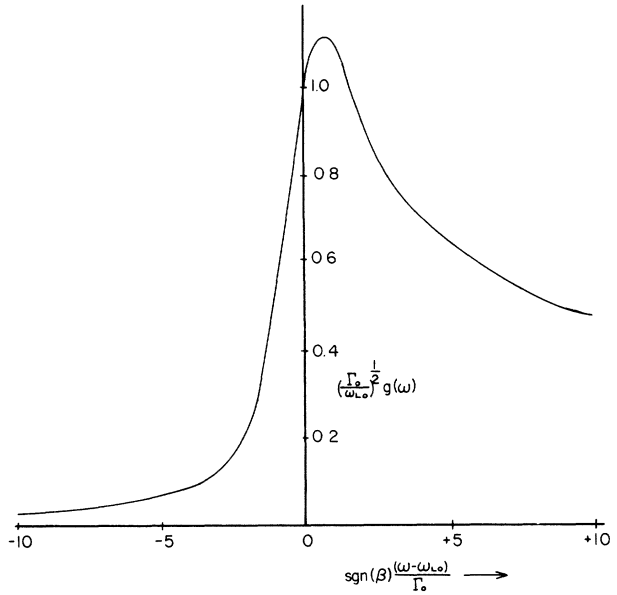

FIG. 1. The shape function $g(\omega)$.

If we take $r_* \sim 2.5\times10^{-13}$ cm, $a_0 = 3$ Å, $V_c \sim 10^{-23}$ cm^3, $\mu \sim 40\times10^{-24}$ g, $\omega_{LO} \sim 200$ cm^{-1}, $\Gamma_0/\omega_{LO} \sim 0.05$, and $(\gamma_I k^{(I)}) \sim 10$, we find $(1/\varphi_0)(d\varphi_S/d\Omega) \sim 10^{-13}$. This estimate indicates that scattering from phonon-induced density fluctuations is strong enough to be readily observed.

If one has two identical atoms in the unit cell, as in the metals Be, Zn, Mg, and Bi, then $M_A = M_B$ and $z_A = z_B$, and the mechanism described above produces no scattering. Near $\vec{q} = 0$, the two equivalent sublattices move out of phase, and no macroscopic electric field results from the motion of the ions. However, in the alloy $AuAl_2$, which has the CaF_2 structure, an odd-parity LO phonon exists at $\vec{q} = 0$, so the scattering from density fluctuations may be observed in this material. Since the Raman line reported by Parker, Feldman, and Ashkin in this material is symmetric, it is unlikely that the observed line is associated with the odd-parity modes.

An even-parity optical phonon can modulate the dielectric tensor at $\vec{q} = 0$, by the mechanisms described at the beginning of this note. We next consider the scattering produced by such a mode. The quantity $\partial\epsilon_{\mu\nu}/\partial Q_{n\vec{q}}$ is insensitive to $\vec{q}$ near $\vec{q} = 0$, so this quantity may be removed from the integration. Similarly, $\Gamma_n/\{\Gamma_n^2 + [\omega - \omega_n(\vec{q})]^2\}$ varies slowly with q_z, compared with $[(\gamma_S+\gamma_I)^2 + q_z^2]^{-1}$. Thus we replace $\Gamma_n(\vec{q})$ and Γ_n by their values ω_{0p}, Γ_0 at $\vec{q} = 0$. The remaining integral is then easily evaluated. We let $\epsilon_{\mu\nu} = \delta_{\mu\nu} + 4\pi\chi_{\mu\nu}$ and then obtain

$$\frac{d^2\varphi_S}{d\Omega d\omega} = \frac{cV}{2\pi}\left(\frac{\omega_0}{c}\right)^4 \frac{\cos\theta_S}{(\gamma_S+\gamma_I)} \langle Q_0^* Q_0\rangle \frac{\Gamma_0}{\Gamma_0^2 + (\omega-\omega_{0p})^2} \sum_\alpha \left| \sum_{\beta\gamma}\sum_\lambda g_{\alpha\beta} \frac{\partial\chi_{\beta\gamma}}{\partial Q_0} \Gamma_\gamma^{(\lambda)} E_\lambda^{(0)} \right|^2 . \tag{11}$$

The Raman line is a symmetric line, centered about ω_{0p} with half-width Γ_0, in contrast with the earlier result. Also, as ω_0 approaches ω_p, and the skin depth increases, the factor $(\gamma_S+\gamma_I)$ approaches zero, so the cross section is enhanced. Thus, one can greatly increase the cross section by working with frequencies near the reflection minimum, i.e., near ω_p.

We have also applied the theory to describe Raman scattering by the $\vec{q} = 0$ modes of a hcp crystal. Upon displacing the sublattice κ by the amount $u_\alpha(\kappa)$, the change in $\chi_{\mu\nu}$ may be written

$$\delta\chi_{\mu\nu} = V_c \sum_{\alpha\kappa} \chi_{\mu\nu,\alpha}(\kappa) u_\alpha(\kappa).$$

When symmetry considerations are combined with the condition $\chi_{\mu\nu,\alpha}(1) = -\chi_{\mu\nu,\alpha}(2)$ that results from translational invariance, only one independent element of $\chi_{\mu\nu,\alpha}(\kappa)$ exists. If the c axis of the crystal is parallel to $\hat{z}$, we find $\chi_{xx,x}(1) = -\chi_{yy,x}(1) = -\chi_{xy,y}(1) = -\chi_{yx,y}(1) \equiv a$, with all other $\chi_{\mu\nu,\alpha} = 0$. This result indicates that the mode with displacements parallel to the c axis does not contribute to the first-order spectrum. The doubly degenerate $q = 0$ optical modes with sublattice displacements perpendicular to the c axis do contribute, however.

We estimate that the magnitude of the cross section is of the order of

$$(1/\varphi_0)(d\varphi_S/d\Omega) \sim 2\pi a^2 \delta(\omega_0/c)^4(\hbar/MV_c\omega_{0p}|\epsilon_0|^2).$$

For diamond, $|a| \approx 4$ Å^2.[4] Comparison of the scattering rate with the experimental estimates[1] suggests that in metals the polarizability derivative is somewhat smaller than in insulators.

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[1]See D. W. Feldman, J. H. Parker, and M. Ashkin, Phys. Rev. Letters 21, 607 (1968). This work will be discussed at the International Conference on Light Scattering, New York, September, 1968.

[2]D. L. Mills, A. A. Maradudin, and E. Burstein (to be published).

[3]A. Mooradian and A. McWhorter, Phys. Rev. Letters 19, 849 (1967).

[4]E. Anastassakis et al., Phys. Rev. Letters 17, 1051 (1966).