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Electric Field Induced Infrared Absorption and Raman Scattering by Optical Phonons in Centrosymmetric Crystals

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Abstract. An externally applied electric field removes the center of inversion of a centrosymmetric crystal by producing relative displacements of the atoms in the unit cell and by deforming the charge distributions of the atoms. The resulting electrically deformed crystal can exhibit a first order (one phonon) infrared absorption by Raman active normally infrared inactive optical phonons and a first order Raman scattering by infrared active (or inactive) normally Raman inactive optical phonons. A discussion is presented of the nature of the tensor coefficients which determine the strength of the electric field induced first order infrared absorption and Raman scattering by optical phonons. Electric field induced Raman scattering spectra in which the electric field of the incident electromagnetic radiation serves as the 'applied electric field' are also discussed.

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1. Introduction

The effects resulting from the lowering of the symmetry of a crystal by the application of an 'external force', such as an electric field or a stress, are called 'morphic effects' [1, 2]. In optical phenomena morphic effects manifest themselves as changes in the selection rules for photon absorption and scattering processes, and as splittings of the degeneracies of normal mode frequencies. The recent observation of electric field induced first order (one phonon) infrared (IR) absorption in diamond [3] and of electric field induced first order Raman (R) scattering in KTaO_3 [4] and SrTiO_3 [5, 6] are examples of morphic effects in which the removal of the center of inversion of a crystal by an applied electric field leads to new IR absorption and R scattering peaks and, in the case of SrTiO_3 [6], to an appreciable splitting of the degenerate mode frequencies. In this paper we present a discussion of the nature of the tensor coefficients which determine the strength of the electric field induced first order IR absorption and R scattering by optical phonons in centrosymmetric crystal. The electric field induced Raman scattering by optical phonons in which the electric field of the incident electromagnetic (EM) radiation serves as the 'applied electric field' is also discussed.

2. The Absorption and Scattering of EM Radiation

In crystals which have a center of inversion only odd-parity optical phonons can be IR active, and only even-parity optical phonons can be R active, i.e., IR absorption and R scattering of EM radiation by optical phonons in centrosymmetric crystals are complementary [7]. Furthermore, in crystals in which all the atomic sites are centers of inversion, such as NaCl, CsCl and cubic BaTiO_3 type crystals, the optical phonons have only oddparity and are R inactive. In diamond type crystals in which the atoms are not at centers of symmetry, the optical phonons have even-parity and are IR inactive. Odd parity phonons are not necessarily IR active, i.e., the F_{2u} symmetry phonons in cubic BaTiO_3 type crystals are IR as well as R inactive, and even-parity phonons are not necessarily R active. The optical phonons in crystals lacking a center of inversion have mixed-parity and can therefore be both IR and R active.

An applied electric field removes the center of inversion of a centrosymmetric crystal by inducing relative displacements of the sub-lattices (providing the crystal has IR active optical phonons) and by deforming the electron distributions of the atoms. The optical phonons in the 'electrically deformed' crystal have mixed parity, so that R active normally IR inactive phonons can become IR active, IR active normally R inactive phonons can become R active, and phonons which are both IR and R inactive can become IR active and/or R active.

The interaction matrix element which determines the absorption of EM radiation by type j optical phonons is proportional to $|M_j^{(1)} \cdot \hat{\epsilon}_0 E_0|$ where $\hat{\epsilon}_0$ and E_0 are the polarization vector and amplitude of the electric field of the incident radiation, and $M_j^{(1)}$ is the electric moment per unit cell set up by the displacements of the atoms in the unit cell, \mathbf{u}_j , and by the associated macroscopic electric field, \mathbf{E}_j , of the type j optical phonons (see appendix). The requirements of energy and momentum conservation take the form $\omega_j = \omega_0$ and $\mathbf{q}_j = \mathbf{k}_0 \approx 0$, where ω_0 and \mathbf{k}_0 are the frequency and wave

vector of the EM radiation and ω_j and \mathbf{q}_j are the frequency and wave vector of the optical phonons.

The first order electric moment of a type j optical phonon is given by (see appendix)

$$\mathbf{M}_j^{(1)} = \left(\frac{\partial M}{\partial u_{0j}} \right)_{E_j} \mathbf{u}_j + \left(\frac{\partial M}{\partial E_j} \right)_{u_j} \mathbf{E}_j = \tilde{\mathbf{e}}_j^* \mathbf{u}_j + \tilde{\boldsymbol{\alpha}}_j \mathbf{E}_j \quad (2.1)$$

where $\tilde{\mathbf{e}}_j^* = (\partial M / \partial u_j)_{E_j}$ is the effective charge of the type j optical phonon and $\tilde{\boldsymbol{\alpha}}_j = (\partial M / \partial E_j)_{u_j}$ is the contribution to the polarizability per unit cell at $\omega = \omega_\omega$ from electronic interband transitions. $\tilde{\mathbf{e}}_j^*$ like $\tilde{\boldsymbol{\alpha}}_j$ is a second rank tensor. $\tilde{\mathbf{e}}_j^*$ exhibits the symmetry of the type j optical phonon. Its magnitude, which is determined by charge redistribution as well as by the static ionic charge [8], is equal to zero for even-parity optical phonons. \mathbf{E}_j is non-zero for optical phonons with non-zero $\tilde{\mathbf{e}}_j^*$ which have a longitudinal component, and for polaritons [9, 10] (coupled photon-TO phonon modes). It is equal to zero for even-parity optical phonons and for pure transverse optical TO phonons.

The polarization selection rules for the resonance absorption of EM radiation by optical phonons correspond to $\tilde{\mathbf{e}}_j^* \hat{\boldsymbol{\epsilon}}_j \cdot \hat{\boldsymbol{\epsilon}}_0 \neq 0$ where $\hat{\boldsymbol{\epsilon}}_j$ is the polarization vector of the type j phonons. In the case of EM radiation propagating along a general direction in optically anisotropic crystals, $\hat{\boldsymbol{\epsilon}}_0$ will have a longitudinal component, i.e., $\hat{\boldsymbol{\epsilon}}_0 \cdot \mathbf{k}_0$ will not be zero. Correspondingly, the optical phonons with $\mathbf{q}_j = \mathbf{k}_0$ will also have mixed transverse and longitudinal character so that both contributions to \mathbf{M}_j will play a role in the absorption of EM radiation. In the case of EM radiation propagating along directions corresponding to principal axes of the dielectric constant, $\hat{\boldsymbol{\epsilon}}_0$ will be pure transverse and only the transverse component of $\tilde{\mathbf{e}}_j^* \mathbf{u}_j$ will be involved in the absorption of EM radiation. On the other hand, for EM radiation propagating along a symmetry axis of the crystal (or any direction in cubic crystals) $\hat{\boldsymbol{\epsilon}}_0$ will be pure transverse, and the optical phonons with $\mathbf{q}_j = \mathbf{k}_0$ will be pure transverse and pure longitudinal. In this situation only TO phonons with non-zero $\tilde{\mathbf{e}}_j^*$ will participate in the resonance absorption of EM radiation.

The interaction matrix element which determines the scattering of EM radiation by type j optical phonons is proportional to $|\hat{\boldsymbol{\epsilon}}_s \cdot \tilde{\boldsymbol{\alpha}}_j^{(1)} \cdot \hat{\boldsymbol{\epsilon}}_0 E_0|$ where $\hat{\boldsymbol{\epsilon}}_0$ and $\hat{\boldsymbol{\epsilon}}_s$ are the polarization vectors of the incident and scattered EM radiation and $\tilde{\boldsymbol{\alpha}}_j^{(1)}$ is the first order change in the polarizability per unit cell caused by the relative displacements of the atoms and by the macroscopic electric field of the type j optical phonons. The requirements of energy and momentum conservation take the form $\omega_s = \omega_0 \mp \omega_j$ and $\mathbf{k}_s = \mathbf{k}_0 \mp \mathbf{q}_j$ where ω_s and \mathbf{k}_s are the frequency and wave vector of the scattered radiation. (The $-$ applies to Stokes scattering processes in which phonons are created and the $+$ applies to anti-Stokes scattering processes in which phonons are annihilated.)

The first order change in the polarizability which is induced by type j optical phonons is given by [9]

$$\tilde{\boldsymbol{\alpha}}_j^{(1)} = \left(\frac{\partial \alpha}{\partial u_j} \right)_{E_j} \mathbf{u}_j + \left(\frac{\partial \alpha}{\partial E_j} \right)_{u_j} \mathbf{E}_j = \tilde{\mathbf{a}}_j \mathbf{u}_j + \tilde{\mathbf{b}}_j \mathbf{E}_j \quad (2.2)$$

where $\tilde{\mathbf{a}}_j = (\partial \alpha / \partial u_j)_{E_j}$ is the atomic displacement R tensor and $\tilde{\mathbf{b}}_j = (\partial \alpha / \partial E_j)_{u_j}$ is the electro-optic R tensor [11]. $\tilde{\mathbf{a}}_j$ is zero for all odd-parity optical phonons, and $\tilde{\mathbf{b}}_j$ is zero for all centrosymmetric crystals. Because of the form of the scattering matrix elements,

LO phonons as well as TO phonons can take part in R scattering even in cubic crystals.

For completeness we also write out the expressions for the second order electric moment, $\mathbf{M}_{jk}^{(2)}$, which determines the second order (two phonon) absorption of EM radiation, and for the second order polarizability, $\alpha_{jk}^{(2)}$, which determines the second order scattering of EM radiation (the subscripts j and k designate the types of optical phonons involved). For the case where $j \neq k$, $\mathbf{M}_{jk}^{(2)}$ is given by

$$\begin{aligned} \mathbf{M}_{jk}^{(2)} = & \left(\frac{\partial^2 M}{\partial u_j \partial u_k} \right)_{E_j, E_k} \mathbf{u}_j \mathbf{u}_k + \left(\frac{\partial^2 M}{\partial u_j \partial E_k} \right)_{E_j, u_k} \mathbf{u}_j \mathbf{E}_k + \left(\frac{\partial^2 M}{\partial E_j \partial u_k} \right)_{u_j, E_k} \mathbf{E}_j \mathbf{u}_k \\ & + \left(\frac{\partial^2 M}{\partial E_j \partial E_k} \right)_{u_j, u_k} \mathbf{E}_j \mathbf{E}_k. \end{aligned} \quad (2.3)$$

The coefficient $(\partial^2 M / \partial u_j \partial u_k) = (\partial e_j^* / \partial u_k) = (\partial e_k^* / \partial u_j)$ is non-zero only when the j and k phonons have different parities. The coefficient $(\partial^2 M / \partial u_j \partial E_k) = (\partial e_j^* / \partial E_k) = (\partial \alpha_k / \partial u_j)$ has non-zero components only when the j phonon has even-parity and the k phonon has an associated electric field. (Similar considerations apply to its counterpart $(\partial^2 M / \partial u_k \partial E_j)$ in which the roles of the j and k phonons are interchanged.) The coefficient $(\partial^2 M / \partial E_j \partial E_k) = (\partial \alpha_j / \partial E_k) = (\partial \alpha_k / \partial E_j)$ is an electro-optic tensor which is zero in centro-symmetric crystals.

$\alpha_{jk}^{(2)}$ is similarly given by

$$\begin{aligned} \alpha_{jk}^{(2)} = & \left(\frac{\partial^2 \alpha}{\partial u_j \partial u_k} \right)_{E_j, E_k} \mathbf{u}_j \mathbf{u}_k + \left(\frac{\partial^2 \alpha}{\partial u_j \partial E_k} \right)_{E_j, u_k} \mathbf{u}_j \mathbf{E}_k + \left(\frac{\partial^2 \alpha}{\partial E_j \partial u_k} \right)_{u_j, E_k} \mathbf{E}_j \mathbf{u}_k \\ & + \left(\frac{\partial^2 \alpha}{\partial E_j \partial E_k} \right)_{u_j, u_k} \mathbf{E}_j \mathbf{E}_k. \end{aligned} \quad (2.4)$$

The coefficient $(\partial^2 \alpha / \partial u_j \partial u_k) = (\partial a_j / \partial u_k) = (\partial a_k / \partial u_j)$ has non-zero components only when the j and k phonons have the same parity. The coefficient $(\partial^2 \alpha / \partial u_j \partial E_k) = (\partial a_j / \partial E_k) = (\partial b_k / \partial u_j)$ and its counterpart with j and k interchanged have non-zero components only when the j and k phonons have odd-parities and the k (or j) phonon has an associated electric field. The coefficient $(\partial^2 \alpha / \partial E_j \partial E_k) = (\partial b_j / \partial E_k) = (\partial b_k / \partial E_j)$ which occurs when the j and k phonons have odd-parity and have associated electric field, is a quadratic electro-optic tensor which has non-zero components in centro-symmetric crystals.

3. Electric Field Induced IR Absorption

The field induced first order (one phonon) resonance absorption of EM radiation by optical phonons is determined by the field induced first order electric moment, $\mathbf{M}_{jE}^{(1)}$, which, to terms linear in the applied field, is given by

$$\begin{aligned} \mathbf{M}_{jE}^{(1,1)} = & \left(\frac{\partial^2 M}{\partial u_j \partial E_a} \right)_{E_j, d_E} \mathbf{u}_j \mathbf{E}_a + \left(\frac{\partial^2 M}{\partial u_j \partial d_E} \right)_{E_j, E_a} \mathbf{u}_j \mathbf{d}_E + \left(\frac{\partial^2 M}{\partial E_j \partial E_a} \right)_{u_j, d_E} \mathbf{E}_j \mathbf{E}_a \\ & + \left(\frac{\partial^2 M}{\partial E_j \partial d_E} \right)_{u_j, E_a} \mathbf{E}_j \mathbf{d}_E, \end{aligned} \quad (3.1)$$

where \mathbf{E}_a is the applied macroscopic field within the crystal; \mathbf{d}_E is the electric field induced relative displacements of the atoms in the unit cell; and the superscript (1.1) indicates that the terms are first order in the phonons and first order in the applied

electric field. \mathbf{d}_E can be expressed as a superposition of the field induced relative displacements of atoms corresponding to the IR active TO phonons, \mathbf{u}_{kE} . When the electric field is applied along a symmetry axis in optically anisotropic crystals, or along any direction in cubic crystals, the relative displacements of the atoms are parallel to the applied field and \mathbf{d}_E is given by

$$\mathbf{d}_E = \sum_k \mathbf{u}_{kE} = \sum_k \frac{(e_k^*/\mu_k)}{\omega_k^2 - \omega_a^2 - i\omega_a/\tau_k} \mathbf{E}_a, \quad (3.2)$$

where e_k^* , μ_k , τ_k and ω_k are the effective charge, reduced mass, lifetime and resonance frequency of the TO phonons; and ω_a is the frequency of the applied electric field. When \mathbf{E}_a is a static field (i.e., $\omega_a = 0$) \mathbf{d}_E is given by

$$\mathbf{d}_E = \sum_k \frac{e_k^*}{\mu_k \omega_k^2} \mathbf{E}_a. \quad (3.3)$$

On the other hand when $\omega_a \gg \omega_k$, \mathbf{d}_E is given by

$$\mathbf{d}_E = - \sum_k \frac{e_k}{\mu_k \omega_a^2} \mathbf{E}_a \approx 0. \quad (3.4)$$

$\mathbf{M}_{jE}^{(1,1)}$ can also be written in the form

$$\begin{aligned} \mathbf{M}_{jE}^{(1,1)} &= \left[\left(\frac{\partial e_j^*}{\partial E_a} \right)_{d_E} \mathbf{E}_a + \left(\frac{\partial e_j^*}{\partial d_E} \right)_{E_a} \mathbf{d}_E \right] \mathbf{u}_j + \left[\left(\frac{\partial \alpha_j}{\partial E_a} \right)_{d_E} \mathbf{E}_a + \left(\frac{\partial \alpha_j}{\partial d_E} \right)_{E_a} \mathbf{d}_E \right] \mathbf{E}_j \\ &= \mathbf{e}_{jE}^{*(1)} \mathbf{u}_j + \alpha_{jE}^{(1)} \mathbf{E}_j, \end{aligned} \quad (3.5)$$

where $\mathbf{e}_{jE}^{*(1)}$ is the linear induced effective charge of type j optical phonons and $\alpha_{jE}^{(1)}$ is the linear field induced change in α_j . The terms $(\partial e_j^*/\partial E_a)_{d_E} \mathbf{E}_a$ and $(\partial \alpha_j/\partial E_a)_{d_E} \mathbf{E}_a$ represent the changes in \mathbf{e}_j^* and α_j resulting from the electric field induced deformation of the electron distributions of the atoms, and $(\partial e_j^*/\partial \mathbf{u}_{kE})_{E_a} \mathbf{u}_{kE}$ and $(\partial \alpha_j/\partial \mathbf{u}_{kE})_{E_a} \mathbf{u}_{kE}$ represent the changes resulting from the field induced relative displacements of the atoms in the unit cell.

The tensor coefficients that appear in the expression for $\mathbf{M}_{jE}^{(1,1)}$ are the counterparts of the tensor coefficients that appear in the expression for the second order electric moment, $\mathbf{M}_{jk}^{(2)}$, given in Equation (2.3). The coefficient $(\partial e_j^*/\partial E_a)_{\mathbf{u}_{kE}} = (\partial \alpha_a/\partial \mathbf{u}_j)_{E_j}$ (where α_a is the polarizability per unit cell at ω_a) is an atomic displacement R tensor for the IR inactive mode which has non-zero components only when the type j optical phonon is R active. The coefficient $(\partial e_j^*/\partial \mathbf{u}_{kE})_{E_a} = (\partial e_k^*/\partial \mathbf{u}_j)_{E_j}$ which occurs when the crystal has optical phonons which are IR active, has the same non-zero components as the atomic displacement R tensor when the type j optical phonon is R active. The coefficient $(\partial \alpha_j/\partial E_a)_{\mathbf{u}_{kE}} = (\partial \alpha_a/\partial E_j)_{\mathbf{u}_j}$ is an electro-optic R tensor which is equal to zero in centrosymmetric crystals. The coefficient $(\partial \alpha_j/\partial \mathbf{u}_{kE})_{E_a} = (\partial e_k^*/\partial E_j)_{\mathbf{u}_j}$ is also equal to zero in centrosymmetric crystals since IR active type k optical phonons are not R active. Moreover, as noted earlier, \mathbf{E}_j is equal to zero for the type j IR inactive phonons, so that terms linear in \mathbf{E}_j do not occur even in crystals which lack a center of inversion. Thus the expression for $\mathbf{M}_{jE}^{(1,1)}$ for IR inactive type j optical phonons in crystals with or without a center of inversion reduces to

$$\mathbf{M}_{jE}^{(1,1)} = \left(\frac{\partial e_j^*}{\partial E_a} \right)_{\mathbf{u}_{kE}} \mathbf{u}_j \mathbf{E}_a + \sum_k \left(\frac{\partial e_j^*}{\partial \mathbf{u}_{kE}} \right)_{E_a} \mathbf{u}_j \mathbf{u}_{kE} \quad (3.6)$$

which can also be written in the form

$$\mathbf{M}_{jE}^{(1,1)} = \left(\frac{\partial \alpha_a}{\partial u_j} \right) \mathbf{u}_j \mathbf{E}_a + \sum_k \left(\frac{\partial e_k^*}{\partial u_j} \right) \mathbf{u}_j \mathbf{u}_{kE} = \underline{\alpha}_{aj} \mathbf{u}_j \mathbf{E}_a + \sum_k \underline{e}_{kj}^* \mathbf{u}_j \mathbf{u}_{kE}, \quad (3.7)$$

where $\underline{\alpha}_{aj}$ is the first order change in α_a induced by the \mathbf{u}_j of the IR inactive type j phonons, and \underline{e}_{kj}^* is the corresponding change in e_k^* due to the \mathbf{u}_j of the IR inactive type j phonons.

In the case of polar centrosymmetric crystals which have R active optical phonons such as CaF_2 type crystals, both $\underline{\alpha}_{aj}$ and \underline{e}_{kj}^* have non zero components for the R, active type j phonons (and, of course, both are zero for the IR active type k phonons).

In the case of the homopolar diamond type crystals, a field induced relative displacement of the atoms does not occur to first order in \mathbf{E}_a (e.g. $\mathbf{u}_{kE} = 0$ since the optical phonons have $\underline{e}_j^* = 0$), and $\mathbf{M}_{jE}^{(1,1)}$ is given by

$$\mathbf{M}_{jE}^{(1,1)} = \left(\frac{\partial e_j^*}{\partial E_a} \right)_{u_{kE}} \mathbf{E}_a \mathbf{u}_j = \left(\frac{\partial \alpha_a}{\partial u_j} \right)_{E_j} \mathbf{u}_j \mathbf{E}_a. \quad (3.8)$$

The corresponding field induced effective charge to first order in the applied field is given by

$$\underline{e}_{jE}^{*(1)} = \left(\frac{\partial M_{jE}^{(1,1)}}{\partial u_j} \right)_{E_j} = \left(\frac{\partial e_j^*}{\partial E_a} \right)_{u_{kE}} \mathbf{E}_a = \left(\frac{\partial \alpha_a}{\partial u_j} \right)_{E_j} \mathbf{E}_a = \underline{\alpha}_{aj} \mathbf{E}_a. \quad (3.9)$$

Since there is no optical phonon contribution to the polarizability, $(\partial \alpha_a / \partial u_j)_{E_j}$ is essentially independent of ω_a (provided ω_a is well below the absorption edge for interband transitions) and can be set equal to $\underline{\alpha}_j$, the atomic displacement R tensor at optical frequencies. A measurement of the strength of the field induced absorption band in diamond type crystals, which is proportional to $(\underline{e}_{jE}^{*(1)})^2 = (\underline{\alpha}_{aj} \mathbf{E}_a)^2$, can yield quantitative data on the atomic displacement tensor, $\underline{\alpha}_j$.

In the case of optical phonons in polar crystals which are both IR and R inactive, such as the F_{2u} symmetry phonons in cubic BaTiO_3 type crystals, both $\underline{\alpha}_{aj} = (\partial \alpha_a / \partial u_j)$ and $\underline{e}_{kj}^* = (\partial e_k^* / \partial u_j)$ are equal to zero since the modes are R inactive and both \underline{e}_k^* and $\underline{\alpha}_a$ are second rank tensors. Accordingly an electric field induced effective charge does not occur, to first order in the applied electric field, for optical phonons which are both IR and R inactive. A field induced effective charge for F_{2u} symmetry optical phonons does occur to second order in the applied electric field.

The matrix element for the electric field induced absorption of EM radiation by type j optical phonons is proportional to

$$\mathbf{M}_{jE}^{(1,1)} \cdot \hat{\mathbf{e}}_0 E_0 = (\underline{\alpha}_{aj} \mathbf{u}_j \mathbf{E}_a + \sum_k \underline{e}_{kj}^* \mathbf{u}_j \mathbf{u}_{kE}) \cdot \hat{\mathbf{e}}_0 E_0. \quad (3.10)$$

The polarization selection rules are accordingly determined by

$$(\hat{\mathbf{e}}_a \cdot \underline{\alpha}_{aj} \hat{\mathbf{e}}_j \cdot \hat{\mathbf{e}}_0) + \sum_k (\underline{e}_k \cdot \underline{e}_{kj}^* \hat{\mathbf{e}}_j \cdot \hat{\mathbf{e}}_0) \neq 0 \quad (3.11)$$

where $\hat{\mathbf{e}}_a$ is the polarization vector of the applied electric field and $\hat{\mathbf{e}}_k$ is the polarization vector of the field induced relative displacements of the atoms corresponding to the type k IR active optical phonons. For \mathbf{E}_a applied along a symmetry axis (or along any direction in cubic crystals) $\hat{\mathbf{e}}_k$ will be parallel to \mathbf{E}_a , and \underline{e}_k^* will have the same non-

zero components as \underline{a}_{aj} . Under these circumstances the two terms of Equation (3.7) yield identical selection rules. Furthermore the polarization selection rules are the same as those for the first order R scattering by type j optical phonons,

$$(\hat{\epsilon}_s \cdot \underline{a}_j \hat{\epsilon}_j \cdot \hat{\epsilon}_0) + (\hat{\epsilon}_s \cdot \underline{b}_j \hat{\epsilon}_j \cdot \hat{\epsilon}_0) \neq 0 \quad (3.12)$$

with the polarization vectors, $\hat{\epsilon}_a$ and $\hat{\epsilon}_k$ replacing the polarization vector of the scattered radiation $\hat{\epsilon}_s$. One immediate consequence of the electric field modified selection rules is that LO phonons as well as TO phonons can take part in the absorption of EM radiation.

An electric field induced absorption by optical phonons has been observed in diamond by ANASTASSAKIS, IWASA and BURSTEIN [1] (Fig. 1). Their data on the strength of the field induced absorption band yield a value of $4 \times 10^{-16} \text{ cm}^2$ for $|(\partial\alpha/\partial u)|$. More recent measurements indicate that the absorption band exhibits no observable shift in position with electric field for fields up to $2.5 \times 10^5 \text{ V/cm}$ in agreement with theoretical calculations of GANESAN and MARADUDIN [12] which predict a shift of the order of 10^{-4} cm^{-1} at an electric field of $2.5 \times 10^5 \text{ V/cm}$.

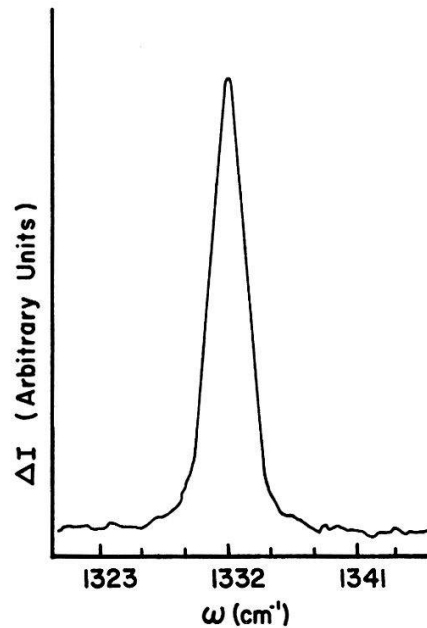


Figure 1

The electric field induced absorption spectrum of diamond at an applied field of $5 \times 10^4 \text{ V/cm AC}$ (peak to peak) superimposed on a DC field of $1 \times 10^5 \text{ V/cm}$. The slit width was 480 microns.

(E. ANASTASSAKIS and E. BURSTEIN to be published).

The magnitude of $(\partial\alpha/\partial u)$ is observed to vary quadratically with the applied field. The absence of a linear dependence of $(\partial\alpha/\partial u)$ on the applied electric field follows from the fact that the relative displacements of the atoms of even-parity optical phonons does not remove the center of symmetry, so that a further change in the polarizability will be quadratic in the applied field. STOICHEFF and co-workers [13] have recently carried out direct measurements of the R scattering efficiency of diamond and obtain a value of $4.4 \times 10^{-16} \text{ cm}^2$ for $|(\partial\alpha/\partial u)|$. It is of interest to note

that the field induced absorption and R scattering data can only provide information about the absolute magnitude of $(\partial\alpha/\partial u)$. MARADUDIN and BURSTEIN [14] have derived the sign and magnitude of $(\partial\alpha/\partial u)$ for diamond type crystals from experimental values of the photoelastic constants type crystals from experimental values of the photoelastic constants using a microscopic lattice theory which relates the photoelastic and Raman tensors. They obtain $(\partial\alpha/\partial u) = -4 \times 10^{-16} \text{ cm}^2$ for diamond. Although the agreement between theoretical and experimental values should be considered fortuitous, it is believed that the negative sign of $(\partial\alpha/\partial u)$ for diamond is correct.

4. Electric Induced Raman Scattering

The electric field induced first order (one phonon) R scattering of EM radiation by R inactive optical phonons is determined by the electric field induced first order polarizability, $\alpha_{jE}^{(1)}$, which, to terms linear in the applied electric field, is given by [15, 16]

$$\alpha_{jE}^{(1,1)} = \left(\frac{\partial^2 \alpha}{\partial u_j \partial E_a} \right)_{E_j, d_E} \mathbf{u}_j \mathbf{E}_a + \left(\frac{\partial^2 \alpha}{\partial u_j \partial d_E} \right)_{E_j, E_a} \mathbf{u}_j \mathbf{d}_E + \left(\frac{\partial^2 \alpha}{\partial E_j \partial E_a} \right)_{u_j, d_E} \mathbf{E}_j \mathbf{E}_a + \left(\frac{\partial^2 \alpha}{\partial E_j \partial d_E} \right)_{u_j, E_a} \mathbf{E}_j \mathbf{d}_E. \quad (4.1)$$

$\alpha_{jE}^{(1,1)}$ can also be written in the form

$$\alpha_{jE}^{(1,1)} = \left[\left(\frac{\partial a_j}{\partial E_a} \right)_{u_{kE}} \mathbf{E}_a + \sum_k \left(\frac{\partial a_j}{\partial u_{kE}} \right)_{E_a} \mathbf{u}_{kE} \right] \mathbf{u}_j + \left[\left(\frac{\partial b_j}{\partial E_a} \right)_{u_{kE}} \mathbf{E}_a + \sum_k \left(\frac{\partial b_j}{\partial u_{kE}} \right)_{E_a} \mathbf{u}_{kE} \right] \mathbf{E}_j = \mathbf{a}_{jE}^{(1)} \mathbf{u}_j + \mathbf{b}_{jE}^{(1)} \mathbf{E}_j \quad (4.2)$$

where $\mathbf{a}_{jE}^{(1)}$ is the electric field induced atomic displacement R tensor of type j R inactive (i.e., $\mathbf{a}_j = 0$) optical phonons, and $\mathbf{b}_{jE}^{(1)}$ is the field induced electro-optic R tensor. ($\mathbf{b}_{jE}^{(1)}$ is a quadratic electro-optic tensor.) It should be noted that the tensor coefficients that appear in the expression for $\alpha_{jE}^{(1,1)}$ are the counterparts of the tensor coefficients that appear in the expression for the second order polarizability, $\alpha_{jk}^{(2)}$ given in Equation (2.4).

The coefficients $(\partial a_j / \partial E_a)_{u_{kE}} = (\partial b_a / \partial u_j)_{E_j}$ and $(\partial a_j / \partial u_{kE})_{E_a} = (\partial a_k / \partial u_j)_{E_j}$ have non-zero components for odd-parity phonons including the F_{2u} symmetry optical phonons in cubic BaTiO₃ crystals. Thus, to terms first order in the applied electric field, optical phonons with F_{2u} symmetry become R active, but remain IR inactive. The coefficients are equal to zero for even-parity phonons such as the R active F_{2g} symmetry optical phonons in CaF₂ and diamond type crystals, i.e., the application of an electric field does not produce any first order change in the atomic displacement R tensor of even parity phonons. (The physical basis for this is that the relative displacements of the atoms, \mathbf{u}_j , corresponding to even-parity optical phonons does not remove the center of inversion of the crystal.) The coefficients $(\partial b_j / \partial E_a)_{u_{kE}} = \partial b_a / \partial E_j)_{u_j}$ and $(\partial b_j / \partial u_{kE})_{E_a} = (\partial a_k / \partial E_j)_{u_j}$ have non-zero components for odd-parity phonons which have a macroscopic electric field, i.e., for LO phonons which have non-zero \mathbf{e}_j^* and for polaritons. They do not occur either for even-parity phonons, or for IR inactive odd-parity phonons such as the F_{2u} symmetry phonons, or the IR active TO phonons.

The polarization selection rules for the linear electric field induced R scattering of EM radiation are given by

$$\hat{\epsilon}_s \cdot \alpha_{jE}^{(1,1)} \cdot \hat{\epsilon}_0 = \hat{\epsilon}_s \cdot \alpha_{jE}^{(1)} \mathbf{u}_j \cdot \hat{\epsilon}_0 + \hat{\epsilon}_s \cdot \mathbf{b}_{jE}^{(1)} \mathbf{u}_j \cdot \hat{\epsilon}_0 \neq 0. \quad (4.3)$$

In the case of IR active phonons in cubic crystals, such as the F_{1u} symmetry phonons in NaCl and cubic BaTiO₃ type crystals, \mathbf{d}_E is parallel to \mathbf{E}_a and in the case of LO phonons and polaritons all four coefficients of $\alpha_{jE}^{(1,1)}$ exhibit the same non-zero components. In the case of the F_{2u} symmetry phonons in cubic BaTiO₃ crystals, $\mathbf{b}_{jE}^{(1)}$ is equal to zero and the tensor coefficients of $\alpha_{jE}^{(1)}$, i.e., $(\partial a_j / \partial E_a)$ and $(\partial a_j / \partial u_{kE})$ have the same non-zero components. (In the case of crystals lacking a center of inversion, such as zincblende type crystals, in which the optical phonons are both IR and Raman active, the major effect of the applied electric field is to modify the polarization selection rules and to split the degeneracy of the TO phonons linearly with the field.)

A lattice theory of the electric field induced Raman scattering by the soft (ferroelectric) mode F_{1u} symmetry optical phonons in cubic BaTiO₃ (perovskite) type

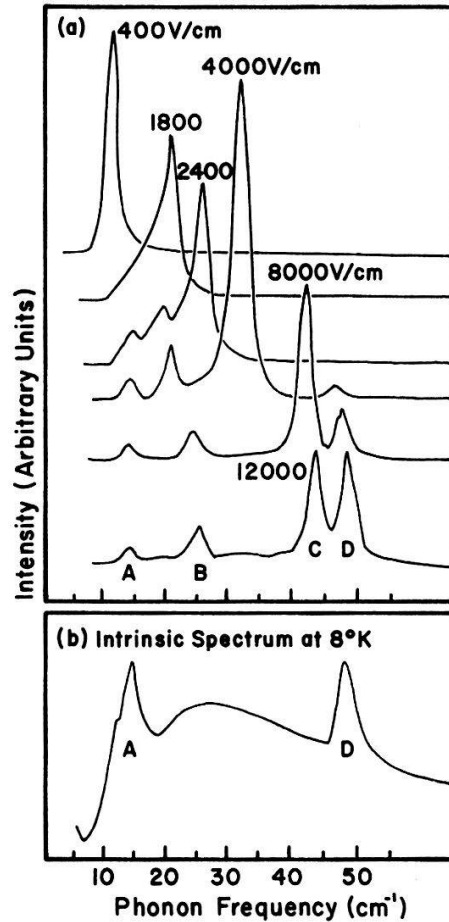


Figure 2

Low temperature (8°K) and low frequency (0–60 cm⁻¹) Raman spectra of SrTiO₃.

- Electric field induced spectra at various values of the applied field. Intensities are arbitrary. Peaks B and C are the perpendicular and parallel components of the soft mode.
- Intrinsic (zero field) spectrum. The sharp features A and D appear in both the induced and intrinsic spectra (J. M. WORLOCK and P. A. FLEURY, Phys. Rev. Lett. 19, 1176 (1967)).

crystals has been given by DVORAK [17]. Dvorak obtained an estimate of the scattering efficiency by relating it to the quadratic electro-optic constant (which he attributed primarily to the large electric field induced displacements of the atoms associated with the soft mode phonons) and to other experimental parameters. His calculations indicated that a field of the order of 10^3 V/cm would be sufficient to induce an observable first order scattering by the soft mode phonons in BaTiO_3 .

Electric field induced first order R scattering by IR active R inactive optical phonons has been observed in the paraelectric crystals KTaO_3 [2] and SrTiO_3 [3, 4] which have the cubic perovskite (BaTiO_3) structure. The results are particularly striking in the case of the soft (or ferroelectric) TO phonons in SrTiO_3 where an appreciable field induced scattering is observed at low temperature at fields as low as 200 V/cm (Fig. 2). Using an AC modulation technique to discriminate against the intrinsic second order spectra, WORLOCK and FLEURY [4, 18] were able to observe field induced scattering from all the TO phonon modes in SrTiO_3 including the F_{2u} 'silent' mode. They did not observe field induced scattering from the LO phonon modes. In KTaO_3 they were only able to observe the field induced scattering by two TO phonon modes in addition to the soft phonon mode. The frequencies of the phonons which they obtain in the field induced Raman scattering experiments are in excellent agreement with the values derived from neutron scattering.

Finally we consider the case of electric field induced R scattering with the electric field applied at optical frequencies [19]. When the frequency of the applied electric field is much higher than the frequencies of the optical phonons (i.e., $\omega_a > \omega_j$), \mathbf{d}_E will be relatively small and can be neglected. In this situation, the expression for $\alpha_{jE}^{(1,1)}$ (Equation (4.2)) becomes

$$\alpha_{jE}^{(1,1)} = \left(\frac{\partial a_j}{\partial E_a} \right)_{d_E} \mathbf{E}_a \mathbf{u}_j + \left(\frac{\partial b_j}{\partial E_a} \right)_{d_E} \mathbf{E}_a \mathbf{E}_j. \quad (4.5)$$

Only the first term occurs in the case of field induced scattering by TO phonons (since $E_j = 0$), whereas both terms occur in the case of field induced scattering by LO phonons with non-zero \mathbf{e}_j^* and by polaritons. When the electric field of the incident EM radiation in R scattering experiments serves as the applied field, e.g., $\omega_a = \omega_0$, the field induced R scattering involves processes in which two photons (ω_0, \mathbf{k}_0) are absorbed, a third photon (ω_s, \mathbf{k}_s) is emitted and an optical phonon (ω_j, \mathbf{q}_j) is created or annihilated. The requirements of energy and momentum conservation are given by $\omega_s = 2\omega_0 \mp \omega_j$ and $\mathbf{k}_s = 2\mathbf{k}_0 \mp \mathbf{q}_j$. Since second harmonic generation does not occur for centrosymmetric crystals (in the electric dipole approximation) the field induced R scattering bands should be the only structure that appears in the vicinity of $2\omega_0$. The effects should of course also be observable in crystals which lack a center of symmetry. For such crystals a second harmonic line should also appear in the spectra. However, the intensity of the second harmonic line will generally be weakened by phase mismatching [20].

Appendix

The macroscopic field associated with the j th (optical) mode of infinite wavelength can be written

$$E_\alpha(j) = -\frac{4\pi}{v_a} \sum_{\beta\gamma} S_{\alpha\beta} \hat{k}_\alpha \hat{k}_\beta \sum_{\kappa\delta} M_{\gamma,\delta}(\kappa) \frac{e_\delta(\kappa|j)}{(M_\kappa)^{1/2}} Q(j) \quad (A.1)$$

where v_a is the volume of a primitive unit cell, \mathbf{k} is a unit vector in the direction of the phonon wave vector, $M_{\gamma,\delta}(\kappa)$ is the dipole moment effective charge of the κ th ion in a primitive unit cell, M_κ is the mass of the κ th kind of ion, $\mathbf{e}(\kappa|j)$ is the vector displacement of the ion κ in the j th mode, and is normalized according to $\sum_\kappa \mathbf{e}(\kappa|j) \cdot \mathbf{e}(\kappa|j') = \delta_{jj'}$, $Q(j)$ is the normal coordinate for the j th mode, and $S_{\alpha\beta}$ is the $\alpha\beta$ element of the matrix inverse to

$$S_{\alpha\beta}^{-1} = \delta_{\alpha\beta} + 4\pi \sum_\lambda \hat{k}_\alpha \hat{k}_\lambda \alpha_{\lambda\beta}, \quad (\text{A.2})$$

where $\alpha_{\lambda\beta} = (\epsilon_{0\lambda\beta} - \delta_{\lambda\alpha}) 4\pi$ and $\epsilon_{0\lambda\beta}$ is the dielectric tensor at optical frequencies. The dipole moment per unit cell due to the atomic displacements in the mode j is given by

$$M_\alpha(j) = \sum_{\kappa\beta} M_{\alpha,\beta}(\kappa) \frac{e_\beta(\kappa|j)}{(M_\kappa)^{1/2}} Q(j), \quad (\text{A.3})$$

which can be written schematically in the form

$$M_\alpha(j) = \sum_\beta e_{\alpha\beta}^*(j) u_\beta(j). \quad (\text{A.4})$$

The effective charge tensor of the mode j , $e_{\alpha\beta}^*(j)$, and the displacement amplitude $u(j)$ are the equivalent harmonic oscillator quantities for the j th optical mode.

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