Theory of stimulated hyper-Raman scattering in noncentrosymmetric crystals

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Based upon the density-matrix formalisms of nonlinear optical susceptibility, stimulated hyper-Raman scattering has been studied in noncentrosymmetric crystals. While applied to ferroelectrics, the characteristic behavior of hyper-Raman gain constant as a function of both the soft-optical-phonon-mode frequency and crystal temperature is found to be in very good agreement with the qualitative behavior of hyper-Raman intensity spectra observed experimentally in $KTa_{1-x}Nb_xO_3$ at both low and high niobium concentrations.

Hyper-Raman spectroscopy is a modulation technique in which the pump laser not only excites the Raman process but also modulates the system under study. It covers a broader range of symmetry types than any other existing infrared method[1] and provides novel spectroscopic information.[2] The phenomena of stimulated hyper-Raman scattering (SHRS) can be regarded as active nonlinear optical phenomena[3] arising because of the fifth-order optical susceptibility $\chi^{(5)}$ at frequencies $\omega_{HR}=2\omega_p\pm\omega_v$, with ω_p and ω_v being the pump laser and optical-phonon frequencies, respectively. A number of oxidic ferroelectrics possess large nonlinear optical and electro-optical coefficients and are regarded as potential candidate materials for optical device applications.[4] $KTa_{1-x}Nb_xO_3$ (KTN) is such a compound and has drawn the attention of a large number of workers, because by varying x from 0 to 1, the properties can be adjusted between the two extremes of $KTaO_3$ and $KNbO_3$.[5] Kugel *et al.*[5] have studied experimentally the ferroelectric soft-optical-phonon mode in KTN for $0.008\leq x\leq 0.21$ and measured the hyper-Raman intensity I_{HR} as a function of ω_v. In an attempt to establish a correlation between the HR spectra and the response function of a damped harmonic oscillator, these authors found that the fitting was reasonably satisfactory only for crystals with low niobium concentrations ($x\leq 0.02$). At higher concentrations ($x\geq 0.05$), such correlation fails. This remarkable discrepancy between the damped harmonic-oscillator model and the observed HR intensity spectra provided the present authors with the necessary stimulation to undertake the development of an independent model that could explain the occurrence of SHRS in KTN crystals with both low and high Nb concentrations.

In the present communication, we report the study of SHRS in noncentrosymmetric (NCS) crystals, based upon the density-matrix formalisms of the complex optical susceptibility[6] arising due to finite permanent dipole moments, in the absence of any external field. Since this is one of the basic features of ferroelectrics, the present model is applied to $KTa_{1-x}Nb_xO_3$ and very good agreement with experimental observations has been achieved.

We follow a semiclassical approach, with electrons being treated quantum mechanically while the photons and phonons are regarded as classical waves.[6,7] The optical-phonon-mode equation under one-dimensional configuration is

$$\frac{\partial^2 u}{\partial t^2}+\omega_0^2 u+\Gamma\frac{\partial u}{\partial t}=N\langle f\rangle/d \ . \tag{1}$$

Here, u ($=u\exp[i(k_v x-\omega_v t)]$) represents the relative displacement of nuclear positions within the crystal lattice. ω_0 is the optical-phonon frequency when the wave vector $\mathbf{k}_v=0$, Γ takes into account the phenomenological damping, while N and d are the number of unit cells per unit volume and mass density, respectively. $\langle f\rangle$ is the generalized force experienced by the nuclei due to the pump laser and is defined as[8]

$$\langle f\rangle=\langle f^{(1)}\rangle E+\langle f^{(2)}\rangle E_0 E+\langle f^{(3)}\rangle E_0^2 E+\cdots \ . \tag{2}$$

Neglecting the interactions of ions with the electromagnetic pump, the interaction Hamiltonian can be given by

$$H_{\rm int}=H_{e\text{-}v}+H_{e\text{-}r} \ , \tag{3a}$$

with

$$H_{e\text{-}r}=-\mu E_0\exp(-i\omega_p t) \tag{3b}$$

for spatially uniform pump field and

$$H_{e\text{-}v}=-uf\exp[i(k_v x-\omega_v t)] \ . \tag{3c}$$

For transitions between the ground state $|g\rangle$ and excited state $|n\rangle$ in the NCS crystals, we define μ and f matrices as

$$\mu=\begin{bmatrix}\mu_{gg} & \mu_{gn}\\ \mu_{ng} & \mu_{nn}\end{bmatrix} \text{ and } f=\begin{bmatrix}f_{gg} & f_{gn}\\ f_{ng} & f_{nn}\end{bmatrix} ,$$

with all the matrix elements being finite. The ensemble averages of μ and f of any order j can be obtained as

$$\langle\mu^{(j)}\rangle=\mathrm{Tr}(\mu\rho^{(j)}) \tag{4a}$$

and

$$\langle f^{(j)}\rangle=\mathrm{Tr}(f\rho^{(j)}) \ , \tag{4b}$$

respectively. $\rho^{(j)}$ is the density matrix of order j with $j=1,2,3,\ldots$. For $j=1$ and 2, one gets the second- and

third-order optical susceptibilities, respectively, and discussed elsewhere.[6-8] SHRS in NCS crystals can be studied only when $j=3$. A straightforward perturbation technique under rotating wave approximation yields the density-matrix elements of various orders. Consequently, for $j=3$, we obtain

$$\langle f^{(3)}\rangle E_0^2 E_{\rm HR}^* = \frac{|\mu_{ng}|^2(f_{nn}-f_{gg})(\mu_{nn}-\mu_{gg})E_0^2E_{\rm HR}^*}{\hbar^3\Omega_p\Omega_s(\omega_v-i\Gamma)} \tag{4c}$$

and

$$\langle \mu^{(3)}\rangle = \frac{|\mu_{ng}|^2(f_{nn}-f_{gg})(\mu_{nn}-\mu_{gg})E_0^2u^*}{\hbar^3\Omega_p\Omega_s\Omega_{\rm HR}} . \tag{4d}$$

$E_{\rm HR}\exp[-i(2\omega_p-\omega_v)t]$ represents the electric field associated with the Stokes component of the hyper-Raman mode. Also, $\Omega_p=\omega_p-\omega_{ng}-i\Gamma$, $\Omega_s=\omega_p-\omega_v-\omega_{ng}-i\Gamma$, and $\Omega_{\rm HR}=2\omega_p-\omega_v-\omega_{ng}-i\Gamma$.

In order to study SHRS at frequency $\omega_{\rm HR}=2\omega_p-\omega_v$, we consider that $\langle f^{(3)}\rangle E_0^2E$ in Eq. (2) is the only appropriate force component that should replace $\langle f\rangle$ in Eq. (1). This yields u^* in terms of the pump field and the crystal parameters and Eq. (4d) leads to

$$\chi^{(5)}(\omega_{\rm HR}) = \frac{N^2|\mu_{ng}|^4(f_{nn}-f_{gg})^2(\mu_{nn}-\mu_{gg})^2}{\epsilon_0 d\hbar^6|\Omega_p|^2|\Omega_s|^2D_p^2\Omega_{\rm HR}(\omega_v+i\Gamma)} , \tag{5}$$

with $D_p^2=\omega_0^2-\omega_v^2+i\Gamma\omega_v$. Here, we have used the general expressions for the induced polarization

$$P=N\langle\mu\rangle=\epsilon_0(\chi^{(1)}+\chi^{(2)}E+\chi^{(3)}EE+\chi^{(4)}EEE+\chi^5EEEE+\cdots)E$$

and equated the terms with identical electric field dependences. We define $\chi^{(5)}(\omega_{\rm HR})$ as the stimulated hyper-Raman susceptibility $\chi_{\rm HR}$. ϵ_0 is the permittivity of free space.

In general, on parity considerations, $\chi^{(5)}$ is finite for crystals exhibiting inversion symmetry, while Eq. (5) suggests that $\chi^{(5)}$ responsible for SHRS is finite only for systems possessing permanent dipole moments (viz., μ_{gg}, $\mu_{nn}\neq 0$) arising because of parity indefiniteness in NCS crystals. The other components of $\chi^{(5)}$, such as $\chi^{(5)}(\omega_p\pm 2\omega_v)$, are finite in centrosymmetric systems and account for processes such as second-order stimulated Raman and Brillouin scattering phenomena due to optical- and acoustic-phonon modes, respectively.

In the present communication, we have analyzed the propagation characteristics of the hyper-Raman mode in the mixed ferroelectric KTN crystal $KTa_{1-x}Nb_xO_3$. The reason for the choice of this particular crystal lies not only in its recognized importance in optical device applications but also in the fact that soft-optical-phonon-mode propagation has been studied extensively in it over a wide range of system parameters like x and T, the crystal temperature.

It is well known that the intensity associated with a scattered wave can be studied in terms of the gain constant.[8] For SHRS, we define the gain constant as

$$g_{\rm HR}=-(k_v/2\epsilon_1)\chi^{(5)}_{{\rm HR}i}|E|^4 , \tag{6}$$

$\chi^{(5)}_{{\rm HR}i}$ being the imaginary part of $\chi^{(5)}_{\rm HR}$. ϵ_1 is the effective dielectric constant of the crystal. Using Eqs. (5) and (6), we get

$$g_{\rm HR}=\frac{A}{\epsilon_l}\frac{\Gamma\omega_0^2}{[(\omega_v^2-\omega_0^2)^2+\Gamma^2\omega_v^2](\omega_v^2+\Gamma^2)} , \tag{7}$$

where

$$A=\frac{k_v}{2\epsilon_0 d\hbar^6\Omega_{\rm HR}}\times\left[\frac{N|\mu_{ng}|^2(f_{nn}-f_{gg})(\mu_{nn}-\mu_{gg})|E|^2}{|\Omega_p||\Omega_s|}\right]^2 .$$

$g_{\rm HR}$, given by Eq. (7) with ϵ_1 and ω_0 as constants, can be used to study SHRS in any NCS crystal. It also reveals that the stimulated hyper-Raman gain constant for the Stokes component should have a near Lorentzian shape, with its peak value around the soft-optical-phonon frequency ω_0.

While applying Eq. (7) to ferroelectrics, we treat both ϵ_1 and ω_0 as functions of the crystal and Curie temperatures T and T_c, respectively, such that[9]

$$\epsilon_1=\epsilon_{10}+B(T-T_c)^{-\gamma} \tag{8}$$

and

$$1/\omega_0^2=1/\omega_1^2+A'/(T-T_c) , \tag{9}$$

respectively. ϵ_{10} is the lattice dielectric constant at infinite temperature, B is a constant that depends upon the composition of the mixed crystal. T_c varies as $(x-x_c)^{1/2}$, with x_c being the critical concentration ($=0.008$) for $KTa_{1-x}Nb_xO_3$.[10] In Eq. (8), $\gamma=1$ or 2 under classical and quantum limits, respectively. For $KTa_{1-x}Nb_xO_3$, $1/\omega_1^2=0.37\times10^{-4}$ cm^2, $A'=0.0263$ K cm^2. Equation (9) is accurately satisfied for the crystal temperature range $300<T<1300$ K.

We now consider the two cases of $KTa_{1-x}Nb_xO_3$ with low and high Nb concentration x, in view of the fact that Eqs. (8) and (9) have limits of applicability depending upon T. First, we will discuss SHRS at low niobium concentrations. We choose a typical example of KTN crystal with $x=0.012$ and numerical estimates are made at $T=40$ and 80 K with $\gamma=2$. In this regime, we have used the values of ω_0 and Γ obtained by Kugel *et al.*,[5] who studied the dependence of HR intensity on soft phonon frequency for $T=40$ to 204 K. The other physical constants are $T_c=21$ K (Ref. 5), $\epsilon_{10}=60$, and $B=46\,000$ K^2 (Ref. 9). The SHRS gain $g_{\rm HR}$ against soft phonon frequency ω_v has been plotted in Fig. 1. It reveals that at a given T ($>T_c$), $g_{\rm HR}$ is large when ω_v is very low ($\omega_v^2\ll\Gamma^2$). With the increase in ω_v, $g_{\rm HR}$ decreases and attains a minimum value when $\omega_v\sim\Gamma$. A further rise in ω_v causes the rise in $g_{\rm HR}$ until it attains a peak value at $\omega_v^2\sim\omega_0^2-\Gamma^2$. For $\omega_v^2>\omega_0^2-\Gamma^2$, $g_{\rm HR}$ decreases in almost a Lorentzian manner. The same feature of $g_{\rm HR}$ with respect to ω_v is retained even if the crystal temperature is raised from 40 to 80 K. Of course, the increase in $T-T_c$ reduces the gain constant appreciably and the sharpness of

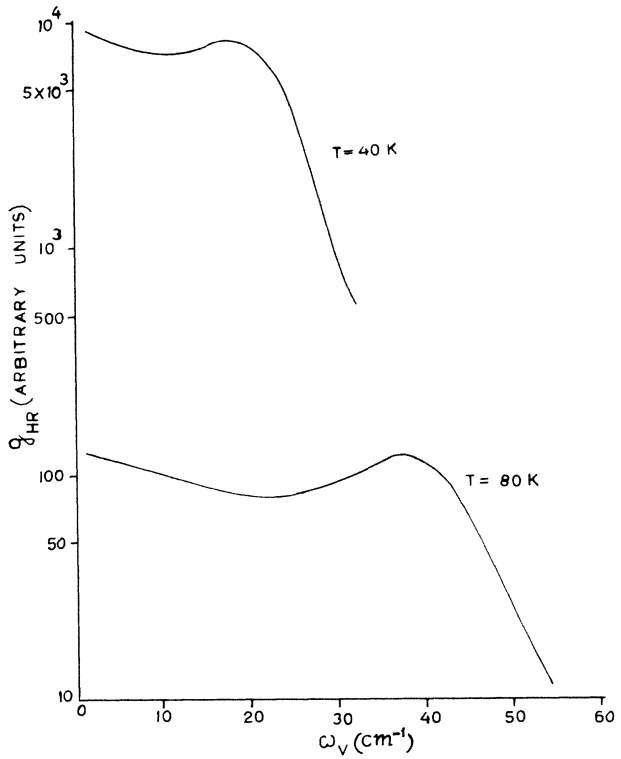

FIG. 1. Variation of stimulated hyper-Raman gain constant g_{HR} with soft-optical-phonon frequency ω_v in $KTa_{1-x}Nb_xO_3$ with $x=0.012$. At $T=40$ K, $\omega_0=22$ cm^{-1}, and $\Gamma=12$ cm^{-1}, at $T=80$ K, $\omega_0=41$ cm^{-1}, and $\Gamma=16$ cm^{-1}.

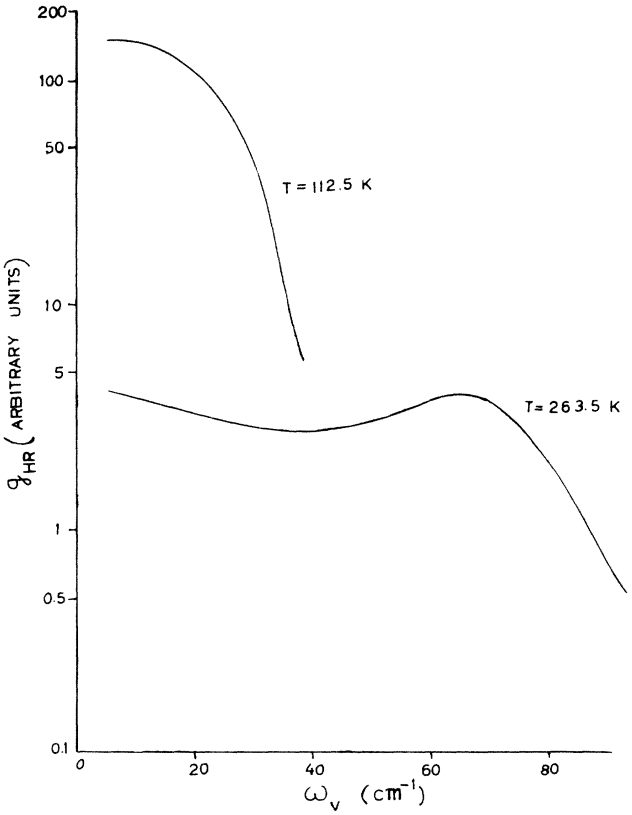

FIG. 2. Dependence of g_{HR} on ω_v in $KTa_{1-x}Nb_xO_3$ with $x=0.09$. At $T=112.5$ K, $\omega_0=27.58$ cm^{-1}, and $\Gamma=34$ cm^{-1}, at $T=263.5$ K, $\omega_0=72.34$ cm^{-1}, and $\Gamma=30$ cm^{-1}.

the peaks is also diminished. The qualitative behavior of g_{HR} depicted here is in very good agreement with the experimentally observed spectra of hyper-Raman intensity for $\omega_v > \Gamma$ by Kugel *et al.*[5] However, the disagreement with experimental observations[5] at $\omega_v < \Gamma$ suggests a lower value of Γ than that which is obtained by using the damped harmonic-oscillator model.

Next, we will discuss SHRS at high niobium concentration. Figure 2 demonstrates the behavior of g_{HR} with variation in ω_v at $T=112.5$ and 263.5 K for $x=0.09$. The Curie temperature T_c for this crystal is 93 K. The soft-optical-phonon-mode frequency ω_0 is obtained by using Eq. (9). The figure indicates that at $T=112.5$ K, the hyper-Raman gain constant decreases almost exponentially with a rise in ω_v. Quite interestingly, the same expression for g_{HR} yields a different type of analytical behavior at $T=263.5$ K which is very similar to that exhibited by the KTN crystal with low Nb concentration. The peak value of g_{HR} in the near Lorentzian regime is found to be at $\omega_v^2 \sim \omega_0^2 - \Gamma^2$. It is also clear from Fig. 2 that g_{HR} and, consequently, the hyper-Raman intensity I_{HR} decreases with an increase of $T-T_c$. The variation of g_{HR} at both 112.5 and 263.5 K can be compared with the spectra of I_{HR} observed experimentally[5] (Fig. 7 of Ref. 5 contains an error in the frequency scale and one should read 80 for 60).

We have further performed the g_{HR} estimations for the very-high-frequency transverse-optical-phonon mode at $\omega_0 \sim 540$ cm^1 ($\sim \omega_v \gg \Gamma$). Under this regime, Eq. (7) should be replaced by

$$g_{HR} = \frac{A}{\epsilon_l} \frac{\Gamma \omega_0^2}{\omega_v^2[(\omega_v^2-\omega_0^2)^2+\Gamma^2\omega_v^2]} . \tag{10}$$

From Eq. (10) it is clear that the hyper-Raman gain constant can be obtained as a nearly pure Lorentzian with the peak at $\omega_v \sim \omega_0$. Moreover, since the rise in Nb concentration x raises the Curie temperature T_c resulting in a fall in $T-T_c$, Eq. (9) yields a lower value of ω_0 at higher concentrations. Consequently, the peaks of g_{HR} will be shifted towards lesser and lesser values of the optical-phonon frequency. The above discussion is in complete agreement with the I_{HR} spectra obtained by Kugel *et al.* (Ref. 5, Fig. 9, where one should read 580 for 560 on the ω_v scale).

In conclusion, one may note that the density-matrix formalisms of nonlinear optical susceptibility can be successfully employed in the study of stimulated hyper-Raman scattering processes in noncentrosymmetric crystals including the ferroelectrics. It appears to be worth mentioning that the present treatment of SHRS can be easily extended to the study of hyper-Brillouin scattering phenomena in NCS crystals simply by replacing Eq. (1) by the acoustic-phonon-mode equation

$$\frac{\partial^2 u}{\partial t^2} + \left[\frac{C_a}{d}\right] \frac{\partial^2 u}{\partial x^2} + \Gamma \frac{\partial u}{\partial t} = N\langle f \rangle / d ,$$

with C_a being the linear elastic modulus of the crystal and $\omega_0=0$ at $k_v=0$.

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