Resonant Raman scattering by a localized mode in CsI

T. P. Martin

Max-Planck-Institut für Festkörperforschung, Stuttgart, Federal Republic of Germany

(Received 9 September 1974)

Resonant Raman scattering by a localized mode with a wave number of 110 cm^{-1} was observed in additively colored CsI. The defect center, presumably I_2^- or I_3^-, produced observable scattering up to sixth order. The broad resonance enhancement curve peaking in the visible could be defined by a discrete number of lines from Kr and Ar lasers. Peak resonant enhancement for first- and second-order processes occurred at frequencies separated by about ten phonon energies. In addition, the Raman intensity increased sharply with decreasing sample temperature. These unusual features can be explained by a nonradiative loss process in the intermediate electronic state.

I. INTRODUCTION

Secondary radiation from a resonantly excited solid has recently received much attention. Sometimes this secondary radiation has been called resonant Raman scattering, sometimes hot luminescence. Although there seems to be good cause to distinguish between these processes, the distinction has been made in different ways.[1-5] We do not wish to enter into this controversy and will, in fact, use the terminology of both Raman scattering and luminescence to describe our experimental results.

In this paper we will study the resonant Raman scattering from localized modes of an intrinsic defect in CsI. First-order Raman scattering is not allowed in perfect crystals of CsI, since each ion is at a center of inversion. Defects destroy both the inversion symmetry and the translational symmetry, resulting in a continuous first-order Raman spectrum superimposed on a continuous relatively unperturbed second-order spectrum. If the defect has associated Raman-active localized modes, these too should be observable as discrete Raman lines.

Resonant Raman scattering has now been studied in some detail in a number of intrinsic semiconductors. These studies include very-high-order scattering by discrete optical modes[6-9] and, more recently, second-order scattering by a two-phonon continuum.[10] The phenomenon of resonant defect-induced Raman scattering[11-16] is also of interest but has received considerably less attention.

II. EXPERIMENT AND RESULTS

The CsI crystals used in this experiment were grown from the melt using the Bridgeman method. Coloration was achieved by growing the crystal in an ampoule containing 200 Torr of HI vapor. The Raman measurements were made using a Jarrel-Ash double monochromator, Ar and Kr lasers, and photon-counting detection. The low-temperature measurements were made in a Leybold exchange-gas helium-evaporation cryostat. Transmission measurements were made in the visible, ir, and uv, using a Cary spectrometer. Since x-ray measurements of CsI need very long exposure times, the orientation of the crystals was determined by stress-induced birefringence.[17]

Figure 1 shows the Raman spectrum of additively colored CsI. These particular data were taken using a sample cooled to 150 °K and the 5145-Å line of an Ar laser. The spectrum consists of a series of five equally spaced lines and a relatively weak continuum peaking at a frequency (here "frequency" is measured in units of wave number) somewhat less than 100 cm^{-1}. This continuous spectrum is primarily due to the second-order Raman scattering expected in pure CsI.[18] The series of discrete lines also appears on the anti-Stokes side of the laser line, indicating that the process is not ordinary luminescence. Since the maximum phonon frequency in pure CsI is 80 cm^{-1}, the scattering must involve a localized mode with a frequency well above the density-of-states continuum of the pure crystal. The presence of higher-order Raman scattering, up to sixth order, indicates that we are observing resonant Raman scattering.

The frequency, width, and relative intensity of the discrete Raman lines measured at 300 and 150 °K are listed in Table I. Notice that, within the accuracy of the experiment, all lines are multiples of 111 cm^{-1}, indicating that the mode is highly harmonic. The widths of the lines are directly proportional to the order of the process, the fifth-order line being five times broader than the first-order line. This is further evidence that we are seeing a multiple-phonon process.

In addition to the first-order scattering by localized modes, there exists a weaker impurity-induced first-order continuous spectrum superimposed on the second-order continuum.[19] This effect is shown in Fig. 2. In the lower set of curves the Raman spectra of pure and colored CsI are
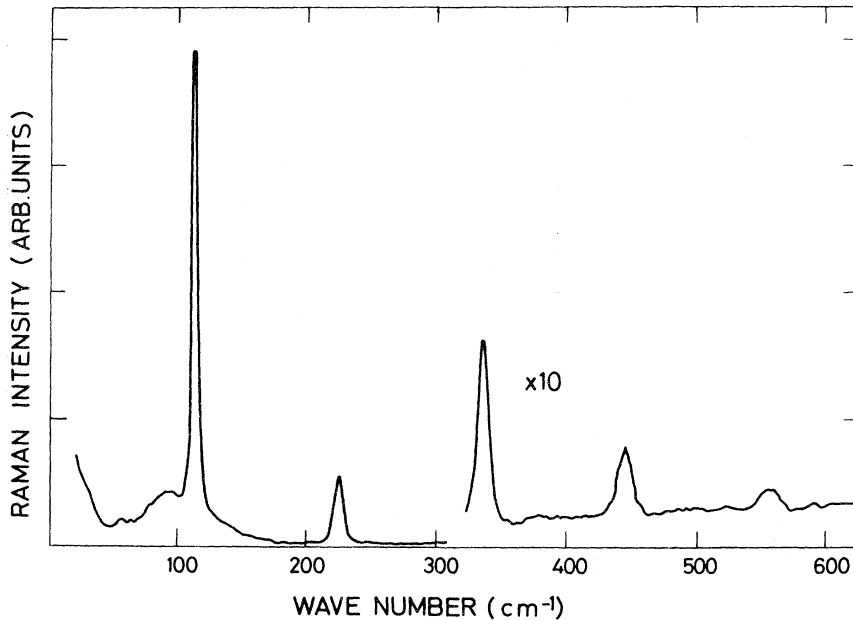
FIG. 1. Raman-scattering spectrum of additively colored CsI measured at 150 °K with the 5145-Å Ar line. The weak continuum spectrum peaking at 100 cm^{-1} is a combination of second-order and defect-induced first-order scattering. The five equally spaced lines are due to first- through fifth-order Raman scattering from a localized mode.

shown. These spectra can be seen to differ significantly in the frequency region of the one-phonon density of states. The structure in this additional scattering measured at 150 °K is compared in Fig. 2 with the density of states determined at room temperature.[20]

In order to demonstrate the suspected resonant nature of the Raman scattering, spectra were obtained using all available lines from Kr and Ar lasers. Figure 3 shows that the first-order Raman line at 111 cm^{-1} has a maximum intensity for laser wave numbers of about 17500 cm^{-1}, falling off by a factor of 10 for a wave number of 21839 cm^{-1}. The resonant-enhancement curve is broad enough that its general shape can be defined by the small number of laser frequencies.

Normalization of the Raman intensities for different laser lines can be obtained rather simply in this sample, since the second-order continuous spectrum is strong but not resonant. By dividing the intensity of the resonant scattering by the intensity of the second-order continuum, it is possible to correct not only for variations of laser power, spectrometer and photomultiplier response, and optical alignment, but also for absorption in the sample.

Notice in Fig. 3 that the intensity of second-order scattering at 222 cm^{-1} resonates more sharply than the first-order scattering. Moreover, the maximum is shifted to higher frequency.

The temperature dependence of the resonant enhancement is also shown in Fig. 3. This is perhaps the most surprising result obtained in this study. Even though the thermal occupation number $n(\omega) + 1$ drops by a factor of 2 in going from 300 to 90 °K, the Raman intensity increases by a factor of 4. In addition, there is a shift of the enhancement curves to higher frequency with decreasing temperature.

The Raman spectra in Figs. 1 and 2 were taken

TABLE I. Multiple-order Raman scattering in additively colored CsI.

	Position		width[a]		Intensity	
Order	300 °K (cm^{-1})	150 °K (cm^{-1})	300 °K (cm^{-1})	150 °K (cm^{-1})	300 °K (arb. units)	150 °K (arb. units)
1	111 ± 1	111 ± 1	3.5	2	25.0	70.0
2	222	224 ± 1	7	4	6.0	15.0
3	333	335 ± 1	12	6	1.7	4.3
4	···	445 ± 1	···	9	···	1.3
5	···	556 ± 2	···	10	···	0.8
6	···	666 ± 3	···	···	···	···

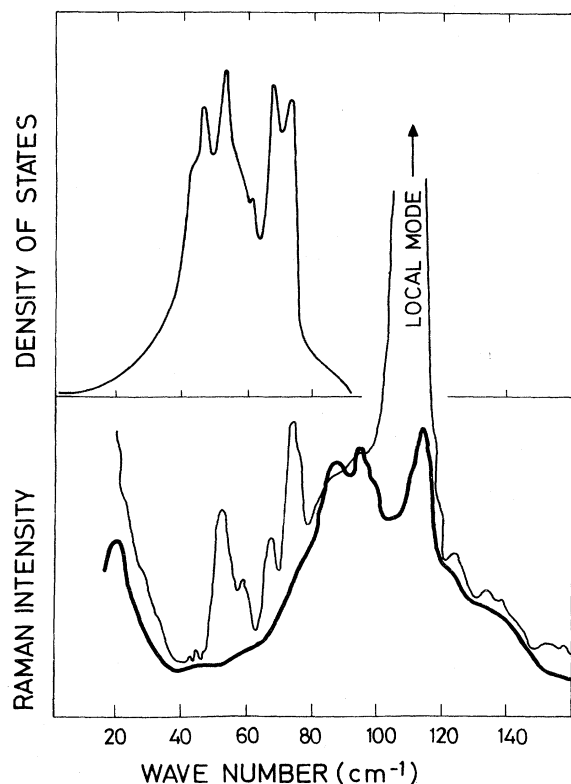[a]Corrected for instrumental width of 3 cm^{-1}.

FIG. 2. Raman-scattering spectrum of pure (heavy line, bottom) and additively colored (light line, bottom) CsI measured at 150°K. The density of states determined from room-temperature neutron measurements (Ref. 20) is shown at top.

indicating that a thermal quenching process is important.

III. DISCUSSION

Probably only one type of color center in the crystal has a localized mode at 110 cm^{-1}. However, the broad structureless absorption curve indicates that the sample contains many different types of color center which contribute not only to the absorption but also to the ordinary luminescence. Since these two important measurements cannot be used to help define the properties of the color center with the local mode, a complete quantitative analysis of the data is not possible. Therefore, this discussion must be limited to a qualitative explanation of several unusual experimental observations.

(i) The Raman intensity increases with decreasing sample temperature. (ii) The peaks of the resonant-enhancement curves for first- and second-order processes are separated by up to ten
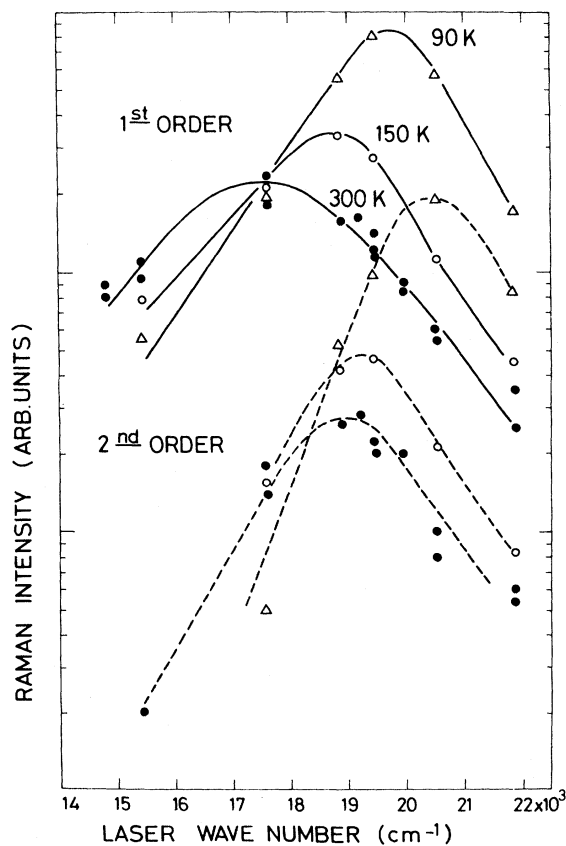
with no polarizer in the scattered beam. A presentation of the complete data for all independent scattering geometries is not warranted here, since the symmetry of the defect has not been established. Certainly, the defect symmetry is lower than the cubic symmetry of the lattice. Since the defect must assume several different orientations within the lattice, it is useful to measure the depolarization ratio as is done for molecules in a gas or liquid. This depolarization ratio was found to be $\frac{1}{3}$ for Raman scattering from the localized mode.

The absorption (Fig. 4) of the colored crystal was found to be weak, relatively structureless, and independent of temperature between 300 and 4°K. We attribute this disappointing result to a large number of distinctly different color centers in the crystal.

Ordinary luminescence excited with a 21839-cm^{-1} Ar line was measured at several temperatures (Fig. 4). The shape of the spectrum was independent of temperature between 300 and 150°K. However, the intensity of this luminescence was found to increase strongly with decreasing temperature,

FIG. 3. Laser frequency dependence of the integrated Raman scattering of the first-order line at 110 cm^{-1} (solid line) and of the second-order line at 220 cm^{-1} (dashed line). Measurements were made at 300°K (●), 150°K (○), and 90°K (△).
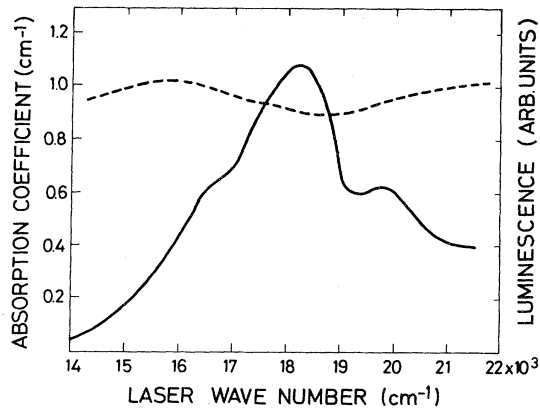
FIG. 4. Absorption coefficient (broken line) and ordinary luminescence (solid line) of additively colored CsI at 150 °K.

phonon energies. (iii) The absorption curve is temperature independent with the nearest peak separated by 30 phonon energies from the peak of the resonant-enhancement curve.

In discussing these experimental results, we could use a model based on the theory of either Raman scattering or hot luminescence. For a qualitative explanation of the data, the descriptive terminology of luminescence is particularly appropriate.

For a defect with a localized mode the configuration-coordinate description of luminescence is both valid and convenient. The essential points of this description are shown in Fig. 5. The energy of the electron-phonon system characterizing the center is considered to be a function of the local-mode amplitude Q. In the harmonic approximation the total energy can be represented by two parabolas, one for the ground electronic state and one for the excited electronic state. The parabolas will have the same curvature but will be displaced from one another in the Q direction if we assume an electron-phonon interaction only of lowest order. Most probably, absorption takes place by means of a vertical transition from the ground vibrational state of the ground electronic state to a high vibrational state of the excited electronic state. The system quickly loses its vibrational energy by the successive decay of localized phonons into plane-wave-like lattice phonons. Ordinarily luminescence then takes place from the ground vibrational state with the emission of a photon. Photons emitted before thermal equilibrium with the lattice phonons is achieved result in what is called hot luminescence. One can see that hot luminescence should consist of a series of lines displaced in frequency from the absorbed light by multiples n of the phonon energy. Qualitatively, the intensity of the luminescence

should be greatest for exciting frequencies near the absorption maximum. If appreciable hot luminescence is to be observed, clearly, the lifetime of the localized phonons must be relatively long.

If P_R is the probability per unit time for radiative decay resulting in hot luminescence and if P_A is the probability for anharmonic phonon decay to the next lower vibration state, then the intensity of the nth-order luminescence line is

$$I_n \sim \frac{P_R}{P_A+P_R}\left(\frac{P_A}{P_A+P_R}\right)^n . \tag{1}$$

Here we have neglected the order dependence of P_R, which manifests itself in the form of harmonic-oscillator overlap integrals. This assumption is valid for a qualitative discussion if the electron-phonon interaction is strong enough to displace the parabolas in Fig. 5 by many phonon energies.[21] According to Eq. (1) the ratio of the intensity of the second-order line to that of the first-order line, written in terms of lifetimes, should be $(\tau_A/\tau_R+1)^{-1}$. The measured values of this ratio as a function of laser wave number are shown in Fig. 6. Near resonance the ratio is larger than 0.1. Since a typical lifetime for radiative decay is 10^{-8} sec, our simple model predicts that the localized phonon should have a lifetime of 10^{-7} sec. This is an un-
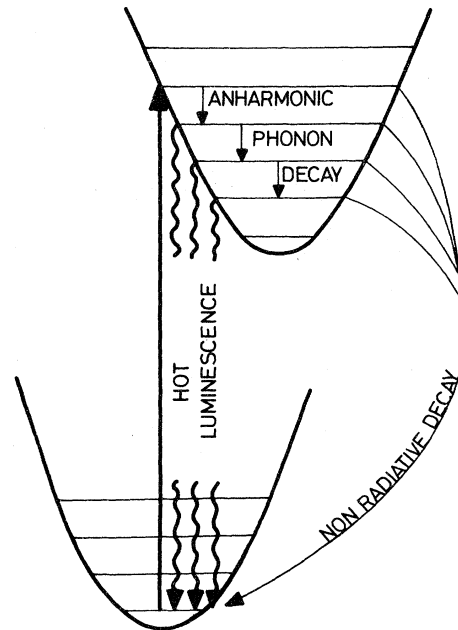

FIG. 5. Schematic representation of the energy of a color center as a function of local-mode coordinate. Typical transitions involved in absorption (heavy solid line), hot luminescence (wavy lines), anharmonic decay of the localized mode, and nonradiative decay from the excited electronic state to the ground state have been indicated.
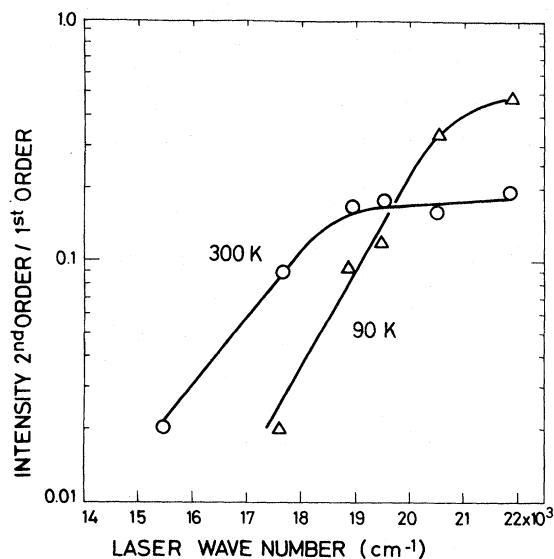
FIG. 6. Ratio of the integrated Raman intensity from the second-order line at 220 cm^{-1} to the intensity of the first-order line at 110 cm^{-1} in colored CsI as a function of laser wave number. Measurements were made for sample temperatures of 300°K (o) and 90°K (△).

reasonably long-lived phonon even for a localized mode. However, the model can be extended to explain the relative intensities of different-order lines by assuming a third nonradiative-loss mechanism with lifetime τ_{NR}. In this case the intensity of the nth-order line is

$$I_n \sim \left(\frac{\tau_R}{\tau_{NR}} + \frac{\tau_R}{\tau_A}\right)^{-1} \left(\frac{\tau_A}{\tau_{NR}} + 1\right)^{-n}. \tag{2}$$

Here we have made the assumption that τ_R is very much larger than τ_{NR} or τ_A. The large intensity ratio of second to first order can now be explained by the more plausible condition that τ_A/τ_{NR} is on the order of 10.

The simple configuration-coordinate model predicts that a great deal of structure should be present in the resonance-enhancement spectrum and in the absorption curves, since dipole transitions are allowed at regular frequency intervals of 110 cm^{-1}. From the previous discussion we know that the lifetimes of these states are long enough to make them well defined and distinct. However, no fine structure was observed in the experimental spectra. We believe that this is due to inhomogeneous broadening of the defect states. The electronic energy of defects with different surroundings could easily differ by one phonon energy. This small shift in the vertical position of the configuration-coordinate parabolas would not necessarily change the curvature or phonon energy. Therefore the hot-luminescence spectra would remain sharp.

We have seen that it is necessary to assume a nonradiative-decay process in order to explain the relative intensities of the hot-luminescence lines. The unusual properties of this luminescence can be explained if the lifetime for nonradiative decay, τ_{NR}, is dependent on both the excitation frequency and the temperature of the sample. If the rate of nonradiative decay from the excited state decreases with decreasing temperature, then the intensity of the secondary radiation should increase. In addition, the ratio of the intensities of the second- to first-order lines should increase since the second-order process is proportional to a higher power of τ_{NR}. Both of these effects were observed experimentally. Additional evidence exists which tends to support a temperature-dependent τ_{NR}. The intensity of ordinary luminescence also increases by more than a factor of 10 when the sample is cooled from 300 to 150 °K. However, as mentioned above, we cannot be certain that this ordinary luminescence arises entirely from the defects with the local mode. Other experimental observations can be explained if we assume that the rate of nonradiative decay increases or the rate of anharmonic decay decreases with decreasing vibrational energy. The shape of the resonance-enhancement curve (Fig. 3) is only partly determined by the harmonic-oscillator overlap integrals that define the absorption line shape. A strongly frequency-dependent lifetime will not only shift the peak of the first-order resonance enhancement from the peak absorption, but also from the peak of the second-order resonance-enhancement curve.

The first-order defect-induced continuous spectrum at frequencies below 80 cm^{-1} was observed to resonate in a manner similar to the discrete spectra of the localized modes. However, the continuous spectrum was always much weaker. The wave functions of the localized electronic states associated with the defect center have greater overlap with the localized phonon than with the more extended band modes. The resulting difference in the strength of the electron-phonon coupling is responsible for the experimental result.

We have not been able to identify the color center responsible for the resonant Raman scattering. There exists, however, indirect evidence which indicates that the center may be I_2^- or I_3^-. Raman scattering from a hole center, Cl_2^-, has been reported in potassium-chloride–potassium-borate glass.[22] The frequency of this Cl_2^- Raman line occurred at 256 cm^{-1}, just about half the frequency of a free neutral Cl_2 molecule. The frequency of the Raman line reported in the present paper is just about half the frequency of a free neutral I_2 molecule,[23] 214 cm^{-1}. In addition, I_3^- in water is known[24] to have a Raman line at 116 cm^{-1}, almost the same frequency reported in the present paper.

IV. CONCLUSIONS

Up to sixth order, Raman scattering by a localized mode was observed in additively colored CsI. The intensity of the Raman scattering was found to increase with decreasing sample temperature. The excitation frequency for maximum scattering was order dependent. In order to explain the relative intensities of different-order lines, a nonradiative-loss mechanism in the intermediate electronic state must be assumed. The unusual temperature dependence of the intensities can then be made plausible if the rate of nonradiative decay decreases with temperature. An increase in the rate of anharmonic decay with increasing vibrational energy can explain the large observed shift with order of the resonance-enhancement spectra.

ACKNOWLEDGMENTS

[1] K. K. Rebane, P. M. Saari, and T. H. Mauring, in *Luminescence of Crystals, Molecules and Solutions*, edited by F. Williams (Plenum, New York, 1973).

[2] M. V. Klein, Phys. Rev. B **8**, 919 (1973).

[3] Y. R. Shen, Phys. Rev. B **9**, 622 (1974).

[4] W. Holzer, W. F. Murphy, and H. J. Bernstein, J. Chem. Phys. **52**, 399 (1970).

[5] W. Kiefer and H. J. Bernstein, Mol. Phys. **23**, 835 (1972).

[6] R. C. C. Leite and S. P. S. Porto, Phys. Rev. Lett. **17**, 10 (1966).

[7] R. C. C. Leite, J. F. Scott, and T. C. Damen, Phys. Rev. Lett. **22**, 780 (1969).

[8] M. V. Klein and S. P. S. Porto, Phys. Rev. Lett. **22**, 782 (1969).

[9] P. Y. Yu, Y. R. Shen, and Y. Petroff, Phys. Rev. Lett. **30**, 283 (1973).

[10] B. A. Weinstein and M. Cardona, Phys. Rev. B **8**, 2795 (1973).

[11] P. Saari and K. Rebane, Solid State Commun. **7**, 887 (1969).

[12] J. M. Worlock and S. P. S. Porto, Phys. Rev. Lett. **15**, 697 (1955).

[13] C. J. Buchenauer, D. B. Fitchen, and S. B. Page, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer, New York, 1969).

[14] M. Zigone, R. Beserman, and M. Balkanski, in *Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971).

[15] M. P. O'Horo and W. B. White, Phys. Rev. B **7**, 3748 (1973).

[16] W. Kiefer, Appl. Spectrosc. **28**, 115 (1974).

[17] K. Maier, J. Cryst. Growth **6**, 111 (1969).

[18] B. S. Agrawal, R. D. Kirby, and J. R. Hardy (unpublished).

[19] M. Buchanan, W. Bauhofer, and T. P. Martin, Phys. Rev. B (to be published).

[20] W. Bührer and W. Hälg, Phys. Status Solidi B **46**, 679 (1971).

[21] P. R. Fenstermacher and R. H. Callender, Opt. Commun. **10**, 181 (1974).

[22] M. Hass and D. L. Griscom, J. Chem. Phys. **51**, 5185 (1969).

[23] P. F. Williams and D. L. Rousseau, Phys. Rev. Lett. **30**, 951 (1973).

[24] W. Kiefer and H. J. Bernstein, Chem. Phys. Lett. **16**, 5 (1972).