

Cl, Br, I, Sn, Zn, and P. In no case was there conclusive evidence of bulk conductivity. It is possible that the diffusion rates are significantly slower than those observed in II-VI compounds (e. g., CdS),¹⁶ but we have been equally unsuccessful in doping with Ge, P, and Zn during growth.

As discussed in connection with luminescence, both crystals show evidence of containing relatively shallow impurities. These impurities might be contained in some form of neutral complex and therefore unable to contribute carriers, or the crys-

tals might be self-compensating for both n - and p -type conductivity.

ACKNOWLEDGMENTS

We wish to thank R. L. Barns for obtaining the lattice constants quoted in Sec. II, and R. A. Laudise and A. G. Chynoweth for their interest in this work. In addition, we thank J. L. Shay and G. D. Boyd for several useful discussions, J. J. Wiegand for x-ray work, and Mrs. A. A. Pritchard and A. L. Albert for sample preparation.

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Temperature-Induced Wavelength Shift of Electron-Beam-Pumped Lasers from CdSe, CdS, and ZnO

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(Received 3 May 1971)

Experimental results on the temperature dependence of the laser frequency and threshold pump power are presented in the range from liquid helium to room temperature for electron-beam-pumped CdSe, CdS, and ZnO lasers. A linear shift of the laser frequency at high temperatures and a relatively slow linear increase of threshold with increasing temperature are found. A model is proposed that takes into account the reabsorption in the crystal below the lowest exciton energy. The results of this model are in quantitative agreement with the experimental data. The absorption coefficient at the laser frequency is determined in the three materials.

INTRODUCTION

Laser emission from II-VI semiconductors has been reported by several authors,^{1,2} even at elevated temperatures.^{3,4} In ZnO, CdS, and CdSe, Packard, Campbell, and Tait⁵ reported laser emission due to the phonon-assisted annihilation of free excitons (Ex-LO). Later, Benoit a la Guillaume and co-workers reported that at least three different processes could lead to laser action in CdS,⁶ the first being the Ex-LO process mentioned above; the

second, the exciton-exciton collision process; and the third, the exciton-electron collision process. However, these processes alone fail to explain the temperature behavior of the laser action observed at elevated temperatures.^{7,8}

Leheny *et al.*⁸ proposed that the temperature behavior of the laser action in CdS was strongly influenced by reabsorption in the crystal at higher temperatures. In this paper, we investigate the application of a similar model to electron-beam-pumped CdSe, CdS, and ZnO lasers. The model

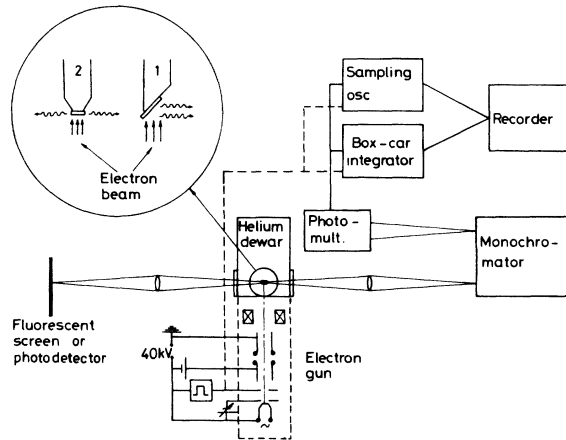


FIG. 1. Diagram of experimental setup.

is based on our experimental results on the spontaneous emission at higher temperatures and on absorption data taken from the literature. We compare the predictions of this model with our experimental results on the laser action in the three materials.

EXPERIMENTAL SETUP

A diagram of the experimental setup is shown in Fig. 1. The electron-beam energy was usually 40 keV, and current densities exceeding 10 A/cm^2 with a beam diameter of about 0.5 mm could be obtained. The beam was pulsed at a rate of 50 pulses per sec, with pulse lengths between 100 and 300 nsec.

The insert in Fig. 1 shows the two different sample geometries used; 1 is the geometry appropriate for spontaneous emission studies where the light emitted directly from the bombarded face was detected, and 2 is the laser geometry in which the light emitted from the cleaved face normal to the bombarded face was analyzed. The light emitted was either analyzed by a photomultiplier and monochromator or detected directly by a calibrated large-area silicon photodetector. At low excitation levels, the box-car integrator was used, whereas the sampling oscilloscope (0.33-nsec time window) was used at higher excitation levels where heating and other time-dependent effects could occur.

In all three materials, the samples were as-grown platelets, cleaved to form cavities with a typical length of 0.5 mm.

EXPERIMENTAL RESULTS

In CdSe and CdS, we have obtained laser emission in the whole temperature range from liquid helium up to room temperature, whereas in ZnO the highest temperature for lasing was 250 K.

Figure 2 shows the temperature variation of the peak positions of the spontaneous and stimulated

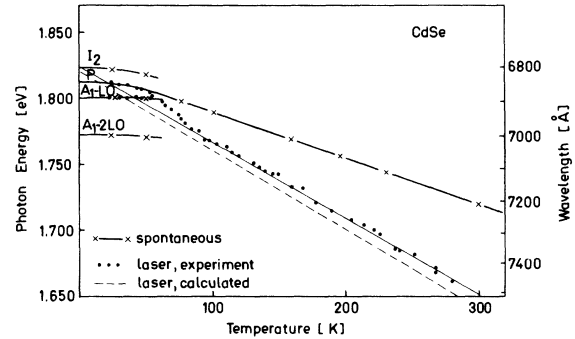


FIG. 2. Temperature dependence of peak energies of spontaneous and stimulated emission in CdSe.

emission lines from CdSe. At low temperatures, the spontaneous emission from the I_2 bound exciton line is dominant, while laser action takes place on the exciton-exciton collision line (P line) as well as on the Ex-LO line as reported earlier.⁹ With increasing temperature, the laser line shifts to longer wavelengths compared to the spontaneous lines. Above 80 K, the photon energy of the spontaneous as well as the stimulated emission shifts linearly with temperature. The spontaneous emission shifts with a rate of $3.50 \times 10^{-4} \text{ eV/K}$, while the rate of shift of the laser line is considerably larger and equals $5.73 \times 10^{-4} \text{ eV/K}$. Above liquid-nitrogen temperature, the spontaneous emission consists of a single line that broadens linearly with temperature as shown in Fig. 3. The spontaneous lines are symmetric on an energy scale and very close to a Gaussian line shape (Fig. 9). The position of this line at low temperatures together with its broad line shape and the fact that it can give rise to laser action at elevated temperatures make it probable that the relevant recombination mechanism is the exciton-exciton collision process.⁸

The temperature shifts of the spectra of CdS are very similar to those of CdSe (Fig. 4). In CdS, the laser peak shifts linearly with temperature from

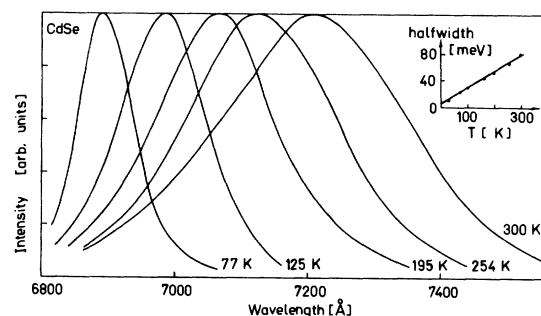


FIG. 3. Spectral shapes of the spontaneous emission from CdSe at various temperatures. Insert: the temperature dependence of the linewidth (FWHM).

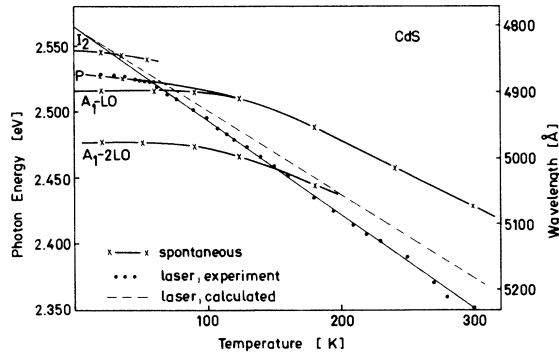


FIG. 4. Temperature dependence of peak energies of spontaneous and stimulated emission in CdS.

60 to 300 K with a rate of 7.14×10^{-4} eV/K. At low temperatures, the laser line is situated an exciton binding energy below the free exciton line, corresponding to the exciton-exciton collision line which we denote by the *P* line. In CdS, the spontaneous emission mainly consists of the first and second LO-phonon replicas of the free exciton line at intermediate temperatures (Fig. 5). Near liquid-nitrogen temperature, the *P* line is merged into the A_1 LO-phonon line which makes it difficult to determine which one persists at the higher temperatures. At 300 K, the spectrum consists of a single line with a half-width of 58 meV and a low-energy tail. This suggests lasing on the *P* line since the A_1 -LO line typically has a high-energy tail (Fig. 5).

For ZnO, the positions of the spontaneous and stimulated lines vs temperature are shown in Fig. 6. Here, the laser line shifts linearly with temperature above liquid-nitrogen temperature at a rate of 7.86×10^{-4} eV/K. In an earlier publication, this high-temperature laser action was proposed to be due to a process involving the collision of a free exciton and a bound electron.⁷ However, the great similarity between the behavior of the laser emission at high temperatures in the three materials investigated suggests a common origin of the tempera-

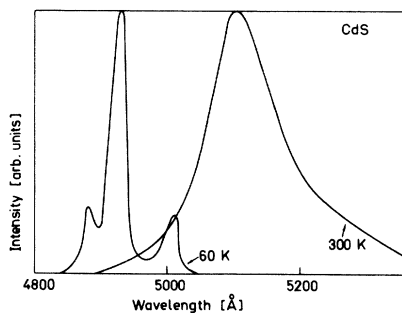


FIG. 5. Spectral shapes of spontaneous emission from CdS at different temperatures.

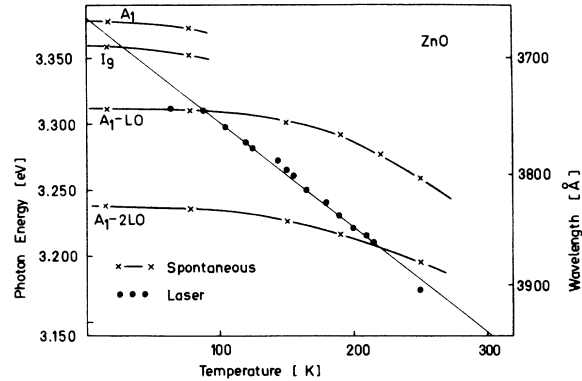


FIG. 6. Temperature dependence of peak energies of spontaneous and stimulated emission in ZnO.

ture shift of the laser lines in these materials.

The threshold for obtaining laser action varied considerably from sample to sample in all three materials, and also with the position of the electron beam on the sample. If we consider only the best samples, the threshold increased when going from CdSe to CdS and again from CdS to ZnO at all temperatures above liquid-nitrogen temperature. At low temperatures, the thresholds were low and comparable in the three materials. In Fig. 7, the temperature variation of the threshold current is shown. We observe that the threshold increases slowly and approximately linearly with temperature.

All the data listed so far concerning the spectral behavior of the laser emission, as well as the threshold for laser action, have been obtained by sampling the light pulse on its leading edge. This is done in order to avoid the influence of heating and other time effects during the pulse. Such other time effects, in fact, do occur. The spectral position of the laser line is strongly dependent on the delay between the onset of the pulse and the sampling time. The tuning of the laser wavelength with time cannot be explained simply by heating because it was almost an order of magnitude larger than the shift of the spontaneous lines, which gives the shift

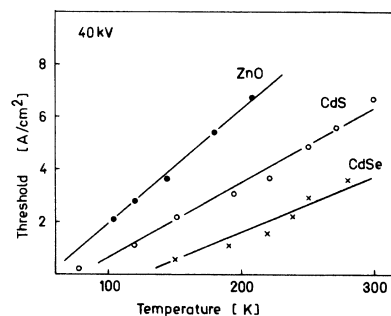


FIG. 7. Temperature dependence of threshold for laser action in CdSe, CdS, and ZnO.

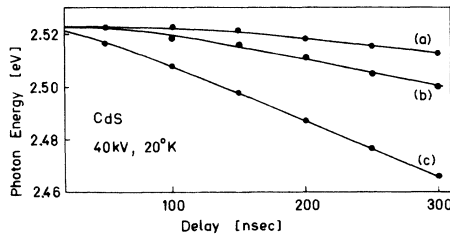


FIG. 8. Photon energy of the laser emission as a function of delay after the onset of the electron pulse at various excitation intensities J . (a): $J = 0.7 \text{ A/cm}^2$, (b): $J = 1.1 \text{ A/cm}^2$, (c): $J = 3.5 \text{ A/cm}^2$.

of the band gap due to heating directly. Figure 8 shows the tuning of the laser energy in CdS as a function of delay after the onset of the electron pulse at various electron currents. We observe that the tuning rate is strongly dependent on the excitation intensity and amounts to 0.2 meV/nsec at $J = 3.5 \text{ A/cm}^2$, which is in good agreement with values reported by Shewchun *et al.*¹⁰ However, we have not found any saturation in the tuning rate, in contrast to earlier reports for CdSe.¹¹

THEORY AND DISCUSSION

It is a common feature of the laser action at high temperatures in CdSe, CdS, and ZnO that the temperature dependence of the photon energy E_l of the laser emission can be expressed by

$$E_l = E_1 - \beta kT, \quad (1)$$

where β is a constant between 5 and 10 and E_1 is close to the lowest free-exciton energy A_1 in all three cases. k is Boltzmann's constant and T is the temperature. The actual values of β and E_1 are given in Table I.

Leheny *et al.*⁸ proposed that the shift of the laser line in CdS to the long-wave side of the spontaneous line is due to the influence of an edge absorption that is a rapidly varying function of energy and temperature. At high temperatures, this absorption edge is often described by the empirical Urbach's rule,¹²

TABLE I. Constants determining the linear shift of the laser energy $E_l = E_1 - \beta kT$. A_1 is the lowest free exciton energy.

Material	β	E_1 [eV]	A_1 [eV] ^a
CdSe	6.64	1.824	1.826
CdS	8.28	2.564	2.554
ZnO	9.11	3.380	3.377

^aJ. O. Dimmock, in *Proceedings of the International Conference on the II-VI Semiconducting Compounds, Providence 1967*, edited by D. G. Thomas (Benjamin, New York, 1968), p. 277.

$$\alpha(E, T) = \alpha_0 e^{-\sigma(E_0 - E)/kT}, \quad (2)$$

where σ is a constant of the order of unity at temperatures above a certain temperature T_0 which is typically 100 K. α_0 and E_0 are constants, E_0 usually being close to the lowest fundamental absorption peak, although on the high-energy side in the case of free exciton absorption.¹³ Urbach's rule has recently been demonstrated to fit the absorption edges of both CdSe¹⁴ and CdS,¹⁵ and the fitted parameters are shown in Table II.

We now calculate the influence of this absorption tail on the spectral shape of the net gain $G(E, T)$ defined by

$$G(E, T) = g(E, T) - \alpha(E, T), \quad (3)$$

where $g(E, T)$ is the gain resulting from the stimulated recombination process, and $\alpha(E, T)$ is the internal absorption due to other processes. We will use the case of CdSe as an example.

We assume that the spectral shape of the gain curve is the same as the shape of the corresponding spontaneous emission line, which is justified when the rate of stimulated emission is much greater than the rate of absorption from the inverse process, as is the case, for example, in the exciton-exciton collision process.⁶

In CdSe, we found that the spontaneous emission curve was very close to a Gaussian line shape as shown for room temperature in Fig. 9. Here, the spectrum is regarded as a gain curve with a maximum gain of 50 cm^{-1} , which is a reasonable value as the reflection losses alone correspond to cavity losses $\alpha_R \approx 30 \text{ cm}^{-1}$ with our sample dimensions. In the same diagram we insert the absorption edge as taken from Ref. 14, and the net gain is shown as the difference between the two.

We see that the steep rise of the absorption edge in connection with the slow fall of the gain curve results in a shift of the maximum net gain to lower energies with respect to the gain curve from the

TABLE II. Parameters concerning the absorption and the spontaneous and stimulated emission.

	Symbol	CdSe	CdS
Constants in Urbach's rule (literature)	σ	2.65 ^a	2.45 ^b
	α_0 [cm^{-1}]	8×10^9	1.5×10^9
	E_0 [eV]	1.875	2.572
Spontaneous emission (experimental)	E_2 [eV]	1.825	2.578
	γ	4.06	5.80
	Max: $E_m = E_2 - \gamma kT$	w_0 [meV]	3.6
Width: $w = w_0 + skT$	s	1.73	(1.73)
Laser parameters (calculated)	E_1 [eV]	1.820	2.565
	β	6.96	7.36
	α_l [cm^{-1}]	8	2

^aReference 14.

^bReference 15.

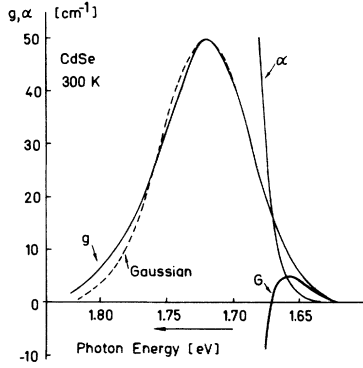


FIG. 9. Spectral shape of the net gain curve G at 300 K obtained by subtracting the absorption tail α from the spontaneous emission line interpreted as a gain curve g , normalized to 50 cm^{-1} .

recombination process alone. This shift will be an increasing function of temperature in the range from liquid-nitrogen temperature to room temperature because of the broadening of the gain curve and the shift of the absorption tail.

The laser energy at threshold and the threshold pump power are determined by the equations

$$\left. \frac{dG}{dE} \right|_{E=E_l} = 0, \quad (4)$$

$$G(E_l, T) = \alpha_R, \quad (5)$$

thus requiring the net gain to be maximum at the laser energy and equal to the wavelength- and temperature-independent cavity losses which are mainly due to reflection losses.

We express the gain curve by the Gaussian line

$$g(E, T) = A e^{-(E_m - E)^2 / w^2}. \quad (6)$$

E_m and w denote peak energy and linewidth, respectively, at temperature T , and the amplitude A depends on the pumping power P as the latter is proportional to the area under the gain curve, i. e.,

$$P = c A w, \quad (7)$$

where c is a constant.

Inserting (2) and (6) in (4) and (5) and calling the threshold pump power P_{th} , we get the equations

$$\begin{aligned} \frac{2P_{\text{th}}(E_m - E_l)}{c w^3} \exp\left(-\frac{(E_m - E_l)^2}{w^2}\right) \\ = \frac{\sigma}{kT} \alpha_0 \exp\left(-\frac{\sigma(E_0 - E_l)}{kT}\right), \end{aligned} \quad (8)$$

$$\frac{P_{\text{th}}}{c w} \exp\left(-\frac{(E_m - E_l)^2}{w^2}\right) = \alpha_0 \exp\left(-\frac{\sigma(E_0 - E_l)}{kT}\right) + \alpha_R. \quad (9)$$

Dividing (8) into (9), we find an equation that deter-

mines the laser energy once the gain curve and the absorption data are known,

$$\frac{w^2}{2(E_m - E_l)} = \frac{kT}{\sigma} \left[1 + \frac{\alpha_R}{\alpha_0} \exp\left(\frac{\sigma(E_0 - E_l)}{kT}\right) \right]. \quad (10)$$

In the general case, this equation can only be solved numerically. We have found experimentally, however, that at high temperatures the spontaneous maximum E_m as well as the linewidth w vary linearly with temperature. Thus, by putting $E_m = E_2 - \gamma kT$ and $w = w_0 + s kT$, we find the following solution at high temperatures where $|E_0 - E_l| \ll kT$ and $w_0/s \ll kT$:

$$E_l = E_1 - \beta kT, \quad (11)$$

with β and E_1 determined by

$$\beta = \frac{1}{\sigma} \ln \frac{\alpha_0}{\alpha_R} + \frac{1}{\sigma} \ln \left(\frac{\sigma s^2}{2(\beta - \gamma)} - 1 \right) \quad (12)$$

and

$$E_1 = E_2 - \frac{\sigma w_0 s}{1 + (\alpha_R/\alpha_0) e^{\sigma \beta}}. \quad (13)$$

Under the same assumptions, we note from Eq. (9) that the linear variation of E_m as well as E_l at higher temperatures implies that P_{th} is proportional to the width w . This means that apart from a possible decrease in the power-conversion efficiency which we have not taken into account so far, we only expect an increase in threshold with temperature that is sufficient to compensate for the linear increase in the linewidth of the gain curve. We expect the efficiency to be a weak function of temperature and therefore the threshold to increase slowly and almost linearly with temperature. This is in contrast to the calculated threshold for the Ex-LO process that rises exponentially with temperature above 100 K,¹⁶ and therefore makes this process very unlikely at high temperatures.

In their discussion of the temperature dependence of the laser action in CdS, Leheny *et al.*⁸ assumed a gain curve of Lorentzian shape and with a fixed half-width of 20 meV. Such a temperature-independent gain profile would not solve the above equations to give a linear solution for E_l and P_{th} . On the other hand, the exact line shape is of minor importance to the result, and we have assumed a Gaussian line shape because it gave the best fit to the measured line shape in CdSe. The linear increase with temperature of the linewidth is to be expected from the interaction of excitons that are Boltzmann distributed at temperature T .⁶ A preliminary calculation of the line shape due to an exciton-exciton collision process gave a broad line shape with exponential tails and a half-width of 2.5 kT, i. e., similar to what we have observed.

The parameters in Urbach's rule are known from the literature for CdSe and CdS (see Table II), and

using the values for E_2 , γ , w_0 , and s from our experiments, we can find β by iteration from (12) and E_1 from (13). The values are listed in Table II and the calculated shifts of the laser line with temperature are shown in Figs. 2 and 4 for CdSe and CdS, respectively. The agreement with experiment is good, especially considering that no adjustable parameters have been used in the calculation.

For CdS, we had no experimental values for w_0 and s , and we have, therefore, tentatively used the values from CdSe. We note that the condition $|E_1 - E_0| \ll kT$ is not easily fulfilled in the case of CdSe. On the other hand, the value for E_0 , as defined by the convergence point of the absorption curves at different temperatures in a semilogarithmic plot, is not well determined.

The linear solution for E_l implies that the absorption coefficient α_l at the laser frequency is nearly constant at higher temperatures as $|E_0 - E_l| \ll kT$.

Values for α_l are given for CdSe and CdS in Table II. We notice that at the laser frequency, the absorption losses are small compared to the reflection losses ($\alpha_R = 30 \text{ cm}^{-1}$) at all temperatures.

In the case of ZnO, no experimental absorption data exist to justify the application of Urbach's rule to the absorption tail. However, from a comparison of the temperature behavior of the laser effect in ZnO with the behavior in CdS and CdSe, we suggest that Urbach's rule is also valid in ZnO. From the absorption data by Dietz, Hopfield, and Thomas,¹⁷ we estimate $\sigma \approx 1.80$, although these data only cover absorption coefficients in the range from 10 to 200 cm^{-1} . If we assume that the laser energy vs temperature, as determined experimentally, represents a curve of constant bulk absorption, we can put $E_0 = E_1 = 3.380 \text{ eV}$, and hence $\alpha_0 = 2 \times 10^7 \text{ cm}^{-1}$ can be determined from an extrapolation of the above absorption data. With these values for σ , E_0 , and α_0 we find the absorption coefficient at the laser frequency to be $\alpha_l \approx 1.5 \text{ cm}^{-1}$, that is, even lower than in CdS. These high transparencies of semi-

conductor lasers have been reported earlier by Holonyak *et al.*¹⁸ who observed laser action in samples where the cavity length was many times the width of the active volume.

As to the threshold variation with temperature, we note that for CdSe the linewidth increased by a factor of 2 while going from 150 to 300 K. In the same temperature interval, we have observed a decrease in power-conversion efficiency by a factor of 3, from which we should expect an increase in threshold by a factor of 6. Experimentally, we found the threshold for CdSe to increase by a factor of about 7 when heating from 150 to 300 K (Fig. 7) in reasonable agreement with the theory.

CONCLUSION

We have demonstrated that the laser effects in CdSe, CdS, and ZnO have very similar temperature dependences at high temperatures: a strong linear shift of the laser frequency and a slow linear rise of the threshold with increasing temperature. Furthermore, we have shown that a relatively broad gain curve with a linewidth increasing linearly with temperature, combined with the absorption tail described by Urbach's rule, is able to explain the observed behavior at higher temperatures in a quantitative way. Such a gain curve is expected from the exciton-exciton interaction process, which in addition has been identified as a laser transition at low temperatures where the reabsorption is negligible. From the linear shift of the laser frequency with temperature above liquid-nitrogen temperature, the absorption coefficients at the laser frequency has been determined in the three materials.

ACKNOWLEDGMENTS

The author is indebted to Professor N. I. Meyer for initiating and supporting this work. Thanks are also due to Dr. T. Skettrup for many helpful discussions and suggestions.

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