AVAILABLE LASER WAVELENGTHS FOR VISIBLE AND NEAR-INFRARED SPECTROSCOPY

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Abstract

Recent advances in semiconductor injection lasers and frequency-changing methods have significantly broadened the wavelengths spectrum in which laser energy can be generated. A review of available techniques in the visible and near-infrared is presented. At the present time, it appears possible to produce measurably intense coherent radiation at all wavelengths from 3245 Å to over 5 μ.

INTRODUCTION

Application of lasers to line spectroscopy has been severely restricted in the past because of the very low probability that any available laser wavelength will exactly match the wavelength of the particular spectroscopic line of interest. The widths of spectroscopic and conventional laser lines are generally less than a few tenths of an Angstrom, and very little wavelength tuning can be accomplished in conventional CW gas lasers or solid-state laser materials such as rubies or Nd^{+}-doped glasses.

This paper reviews several new developments which promise to remove these difficulties in the visible and near-infrared wavelength spectrum. The primary limitations appear to be the short pulse times available (30 to 300 nano-seconds) and the small total energy of the output (2×10^{-7} to 10^{-5} Joules) for methods which allow continuous tuning of the output wavelength. Methods for multiplying the number of discrete laser frequencies available are also discussed.

SEMICONDUCTOR INJECTION LASERS

In the last 3 years, there have been a whole host of semiconductor materials which, at liquid nitrogen temperatures and below, can be induced to efficiently emit coherent laser radiation. Without discussing the physical mechanisms involved, we simply state that, instead of the usual "pumping" with an external light source, these lasers are pumped most expediently either (a) with large reverse currents through standard p-n junctions, or (b) by electron-beam injection perpendicular to homogeneous semiconductor crystals. Figs. 1 and 2 present typical arrangements for the two schemes. IVEY (1966) presents a rather dated survey of semiconductor compounds exhibiting laser action.

Wavelength tuning in semiconductor lasers is accomplished by (a) choosing a semiconductor composition which is appropriate to the design wavelength, and (b) fine-tuning the wavelength by varying the temperature of the semiconductor. Some semiconductor injection

lasers will operate at room temperature with low efficiency (e.g. GaAs); conversion efficiencies (power out to power in) increase as the temperature is lowered, reaching typically 0.5 % at liquid nitrogen temperature ($77^{\circ}K$) and 2 % at liquid helium temperature for electron-beam pumping. Conversion efficiencies for current injection devices are much greater. GARFINKEL and ENGLER (1963) have produced 1.5 watts CW in a GaAs diode with an overall efficiency of 30 %, and LAX (1963) produced 100 watts pulsed output in GaAs.

Fig. 3 is a diagrammatic summary of the semiconductors which have been investigated for use as lasers. Compounds in which lasing action has been observed or is highly probably cover the spectrum from 3245 Å to 5.2 μ. Fig. 4 gives the observations of HURWITZ (1966 a) for the compound CdS_xSe_{1-x}, which covers the wavelength interval 4900 Å - 6900 Å. The data at $4.2^{\circ}K$ and $77^{\circ}K$ suggest the range of wavelength tuning achieveable with temperature changes: for this compound, the difference is about 15 Å, the wavelength increasing with temperature. Temperatures intermediate to these points should be achievable with proper heat sink arrangements, the use of liquid helium and small heating coils, or by thermoelectric cooling.

The main limitation to pulse length appears to be the rate at which the sample temperature rises during the pulse. HURWITZ (1966 b) and NICOL (1966) find that sample temperatures may rise as much as $80^{\circ}K$ during a 0.2 micro-second pulse, causing shifts of about 20 Å in the emitted wavelength over the duration of the pulse. GONDA, JUNKER, and LAMORTE (1965) have made a definitive study of the time-resolved spectral shifts of GaAs at $77^{\circ}K$, and find the line shift to be about 0.3 Å $(amp^2 - \mu s)^{-1}$. This sweeping may be advantageous in guranteeing coincidence between a particular spectral line and the laser line, but the effective pulse length may be reduced to a fraction of a nano-second if the spectral line is very sharp; a consequent reduction in total effective energy would result. Proper optics and clean spectroscopic techniques can do a great deal to overcome intensity problems, but it becomes progressively more difficult and more expensive as the

number of photons goes down. Experience with the Thomson scattering measurement at the University of Colorado suggests that useful data can be obtained with as few as 10^3 photons per pulse. Current injection lasers, being much more efficient in converting input power to radiation, should be less troublesome in this regard.

To give some feeling for the typical values which have been reported in the literature to date, we quote the results of HURWITZ (1966 c) for ZnS. Operating at 4.2°K (initial temperature) with 200 nano-second injection, 10 laser line groups were observed between 3245 Å and 3291 Å. Fig. 5 is the high-resolution spectrum of the line group at 3291 Å. Efficiency at liquid Helium temperature was 6.5 % (1.7 watts out) and 2 % at liquid Nitrogen temperature (0.6 watts out). The crystal size was 1 mm x 150 μ x 2 μ, and angular spread of the output beam (from the 1 mm side) was about 7°. ZnS is the newest and lowest-wavelength material investigated to date; no observations of laser action from the compound $Zn_xCd_{1-x}S$ have yet been reported, but no intrisic problem seems to exist.

Arrays of GaAs and other injection materials can be fabricated to give large total output powers. RCA Electronic Components and Devices, Div., Harrison, N.J. has announced the military availability of a 50 W output array of GaAs crystals (see Laser/Focus, January (1967), p.26).

OPTICAL PARAMETRIC OSCILLATION

Optical parametric oscillation allows the generation of a large band of wavelengths centered around a wavelength which is twice that of the incoming pump light. GIORDMAINE and MILLER (1965, 1966 a, 1966 b) have reported highly efficient (1 %) generation of coherent light output from a $LiNbO_3$ crystal pumped with 5300 Å radiation. The pump light was obtained by second harmonic generation using a Q-switched Nd^+ laser (1.06 μ).

The $LiNbO_3$ crystal is simply a Fabry-Perot cavity with two flat parallel faces which have dielectric coatings to form a resonance for the generated frequencies. BOYD and ASHKIN (1966) and GIORDMAINE and MILLER (1966 b) give relations for computing the change in cavity dimensions with temperature. This dimension change shifts the output frequency from ω_o to $\omega_o \pm \delta\omega$, where $\delta\omega$ is a calculable function of temperature. The fundamental frequency ω_o in the

Giordmaine-Miller experiment was 1.06 μ, twice the wavelength of the 5300 Å pump light and identical to the original Nd^+ output. Fig. 6 presents their experimental results, comiled from the three references listed.

The result essentially gurantees the ability to produce selected wavelengths of coherent light from 7300 Å to 1.93 μ at least. This simple conclusion ignores many subtle effects that do not, in reality, allow successful arbitrarily fine tuning by temperature alone; an electric field must also be applied to the crystal (see, e.g., BOYD and ASHKINS (1966) for additional details). These authors predict sharp line radiation of the order of 10mW (CW) should be possible using $LiNbO_3$ and the 5147 Å line of a commercially-available argon ion laser (see the following sections). The tunable wavelength region would be equivalent to that for the 5300 Å line of Nd^+.

FREQUENCY DOUBLING AND RAMAN SHIFTING

Nonlinear interaction between an intense laser source and a suitable crystal or liquid can lead to generation of second harmonics of the incoming laser light. This means that blue and green lines can be obtained from the red emission of conventional solid-state lasers (Nd^+, ruby, etc.) and weak ultraviolet around 2500 Å can possibly be obtained from the new argon ion lasers or by second-harmonic generation from second harmonics of red wavelengths. Since the intensity in the latter two cases would be proportional to the square of the input power, the intensities would be very low indeed.

WANG and RACETTE (1965) cite pertinent literature and experiments with a ruby at 6943 Å. The beam is passed through an ADP crystal+), is Q-switched to increase the instantaneous power to around 10^7 watts, and the second harmonic at 3472 Å is observed. At low powers, the conversion efficiency is proportional to P^2 while at high powers the conversion is proportional to $P^{3/2}$. WANG and RACETTE present a

+) ADP = ammonium dihydrogen phosphate, evidently readily available in crystal form.

nice theory which agrees with their experimental result. The maximum efficiency was 10 % at 20 MW, giving 2 MW of 3472 Å power. BOYD et al. (1965) have observed second harmonic generation using a He-Ne CW laser. A conversion efficiency of 20 % was also reported by TERHUNE et al. (1963) with a ruby laser; they also observed 0.05 % of the input power as third harmonic (2313 Å) output.

YOSHIKAWA and MATSUMURA (1966) have reported an interesting variation of this experiment. The second harmonic of the ruby line (3472 Å) was passed through a benzene cell, producing coherent Raman scattering: the following output wavelengths were measured:

3360 Å - (anti-Stokes Ramon line)
3472 Å - (ruby second harmonic)
3590 Å - (Stokes line 1)
3730 Å - (Stokes line 2)

Additional anti-Stokes lines with $\lambda < 3360$ Å were probably present but were not detected with the photographic film used.

It would be a useful undertaking to perform a cross-check between the several available intense laser sources and various kinds of liquids, solids and gases which have been used as Raman scattering media. The experiment of YOSHIKAWA and MATSUMARA strongly suggests that, using second harmonic generation, a multitude of relatively strong lines in the range of 3000 Å - 5000 Å should be possible. Ruby and Nd^+ lasers are slightly tunable with temperature (about 0.065 Å/deg (25° to 80°C) and 0.045 Å/deg (180° to 0°C)), which means that the Raman shifted wavelengths could cover an interesting fraction of the blue-green region. Appendix II of BIRNBAUM (1964) gives a comprehensive list of Raman-active substances. A more exhaustive survey of Raman-active materials is given by ECKHARDT (1966).

ION INDUCTION LASERS

New CW gas lasers are presently appearing on the commercial market which use highly-ionized noble gases. No survey of this type of device has been attempted. The following specifications are indicative of the commercially-available powers:

Spectra-Physics Model 140 ($ 24,750)

Spectral width (doppler broadening) = 5×10^9 Hz
Beam Size - 1.6 mm dia
Divergence - 0.7 milliradians
Total Output - 2 watts CW maximum, all wavelengths
Wavelengths (selectable with prisim)

λ (Å)	Approximate Power (mW)
4879.86	900
5145.32	900
4965	60
4765	60
4579	25
5017	25
4727	15
4658	15

Note that these blue-green lines are the first in CW lasers to be commercially produced with high average powers. Use with crystals for optical parametric oscillation is a distinct possibility, and Raman shifting with low threshold materials should also be feasible; the power is somewhat low for second harmonic generation exept possibly by fine optical focussing.

A review of over 200 ion lines produced by 11 different gases (measured up to March, 1965) is given by BRIDGES and CHESTER (1965). Laser action of singly-ionized gases has been observed in Hg, Ar, Kr, Xe, C,N, O, I, and Cl. They also report unpublished work which indicates laser production in Zn, Cd, S, and P. The observed wavelength go from 2357 Å to 1.05 μ.

Ion lasers using singly-ionized gases tend to saturate in output power at very high currents. Near the saturation region, several gases begin to emit laser light from doubly-ionized species. PAANANEN (1966) has demonstrated ultraviolet laser action in Ne II, Kr III, and Ar III, at very high powers. The following results were obtained:

Ion	λ (Å)	Max. Power Measured (mW-CW)
Kr III	3507	300
Ar III	3511	~ 13 or greater
Ne II	3324 and 3378	30 (total both lines)

They anticipate achieving 1 W CW soon with Kr III.

Fig. 1: Schematic of Cavity Injection Laser

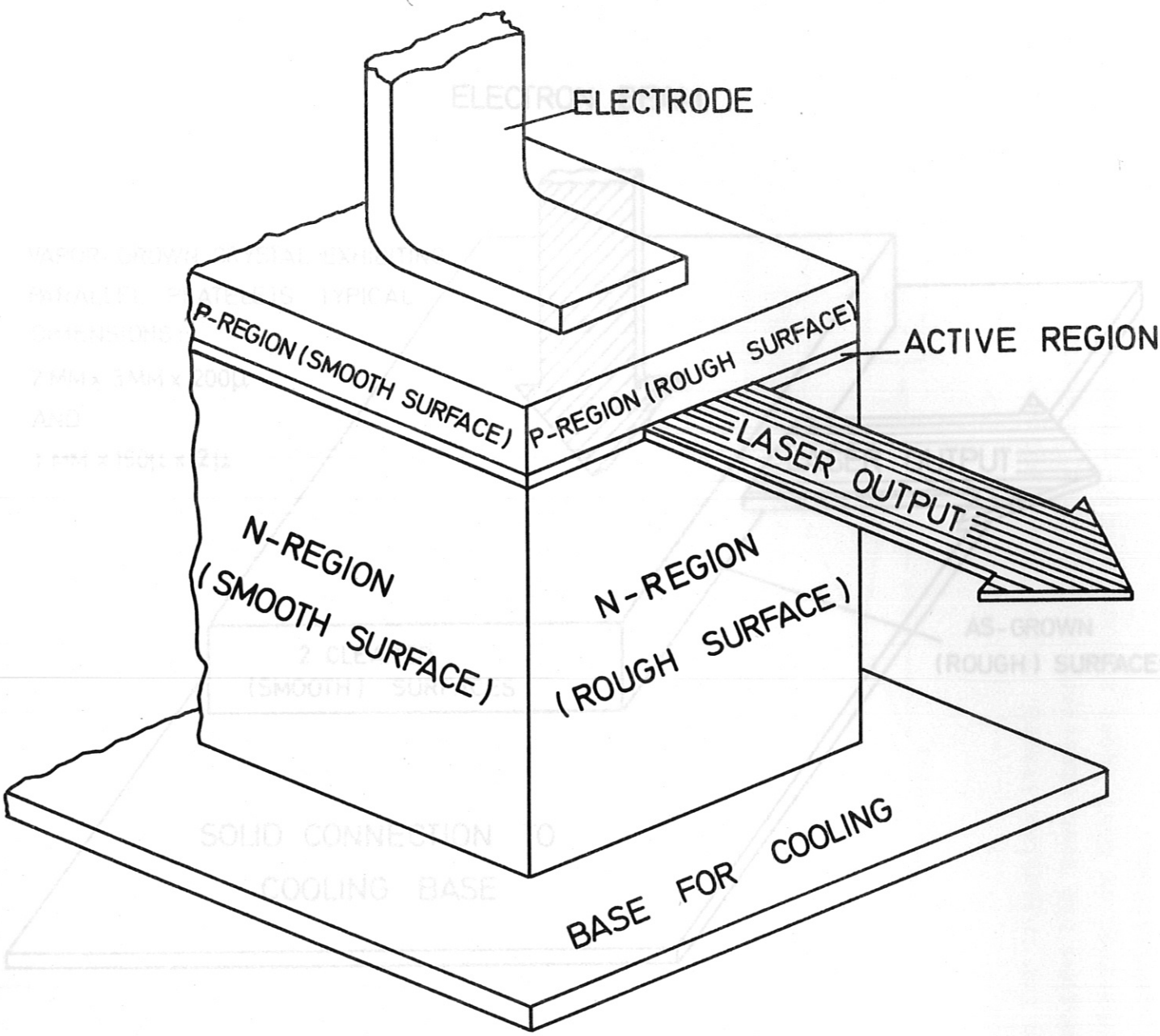

Fig. 1: Schematic of Current Injection Laser

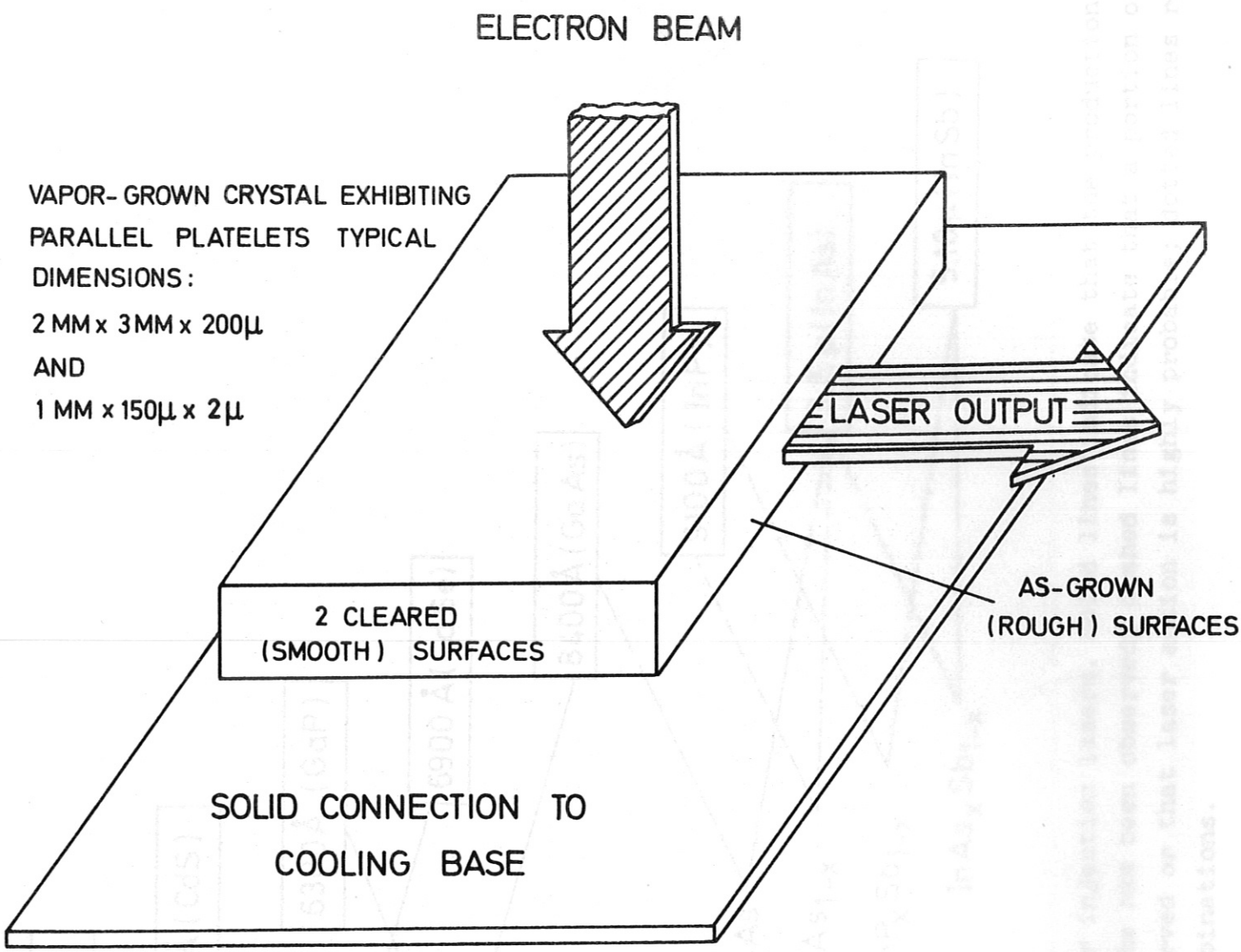

Fig. 2: Schematic of Electron-Beam Pumped Semiconductor

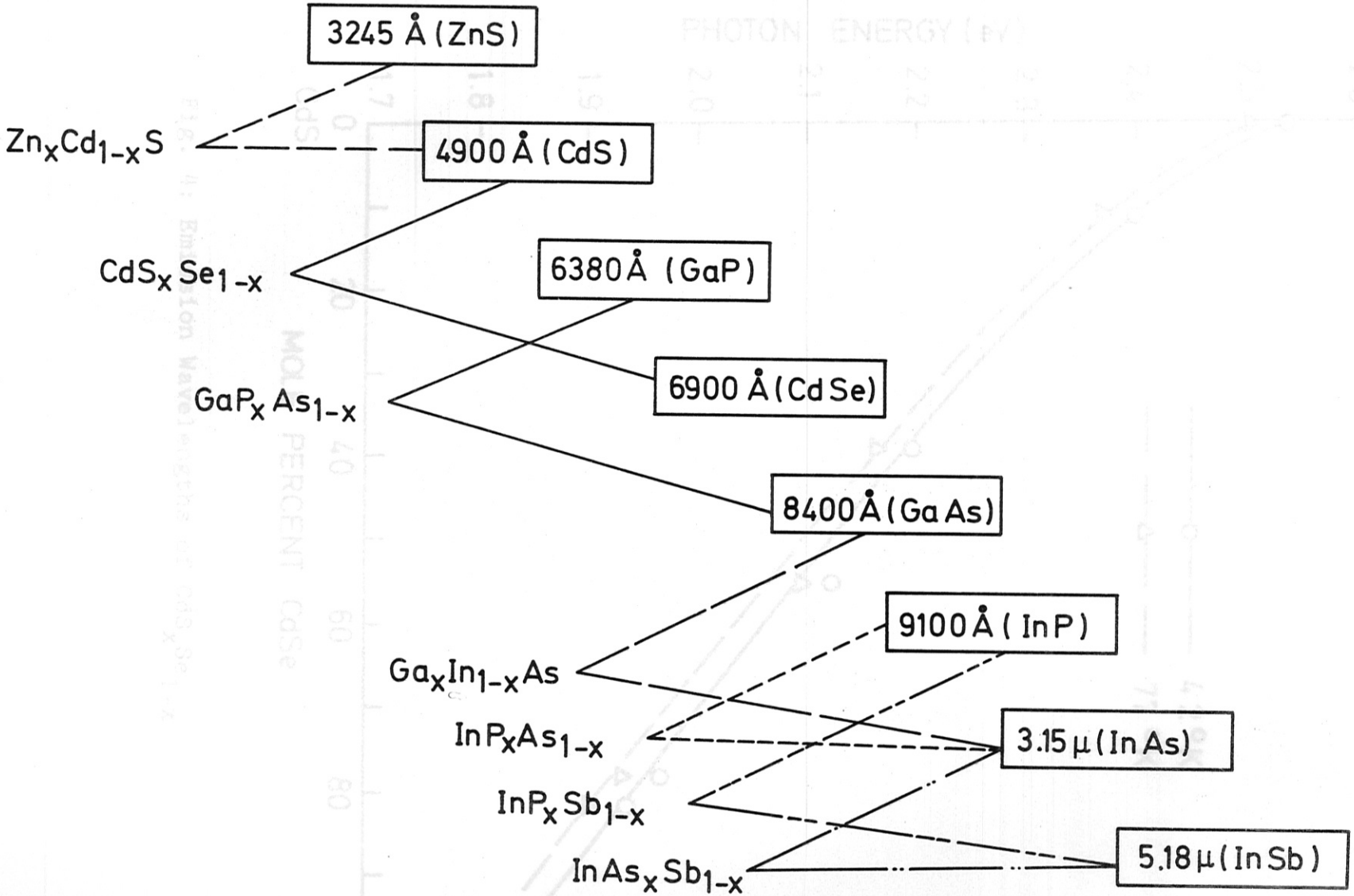

Fig. 3: Semiconductor compounds for injection lasers. Solid lines indicate that the production of all intermediate wavelengths has been observed; dashed lines indicate that a portion of the spectrum has been observed or that laser action is highly probable; dotted lines represent uninvestigated combinations.

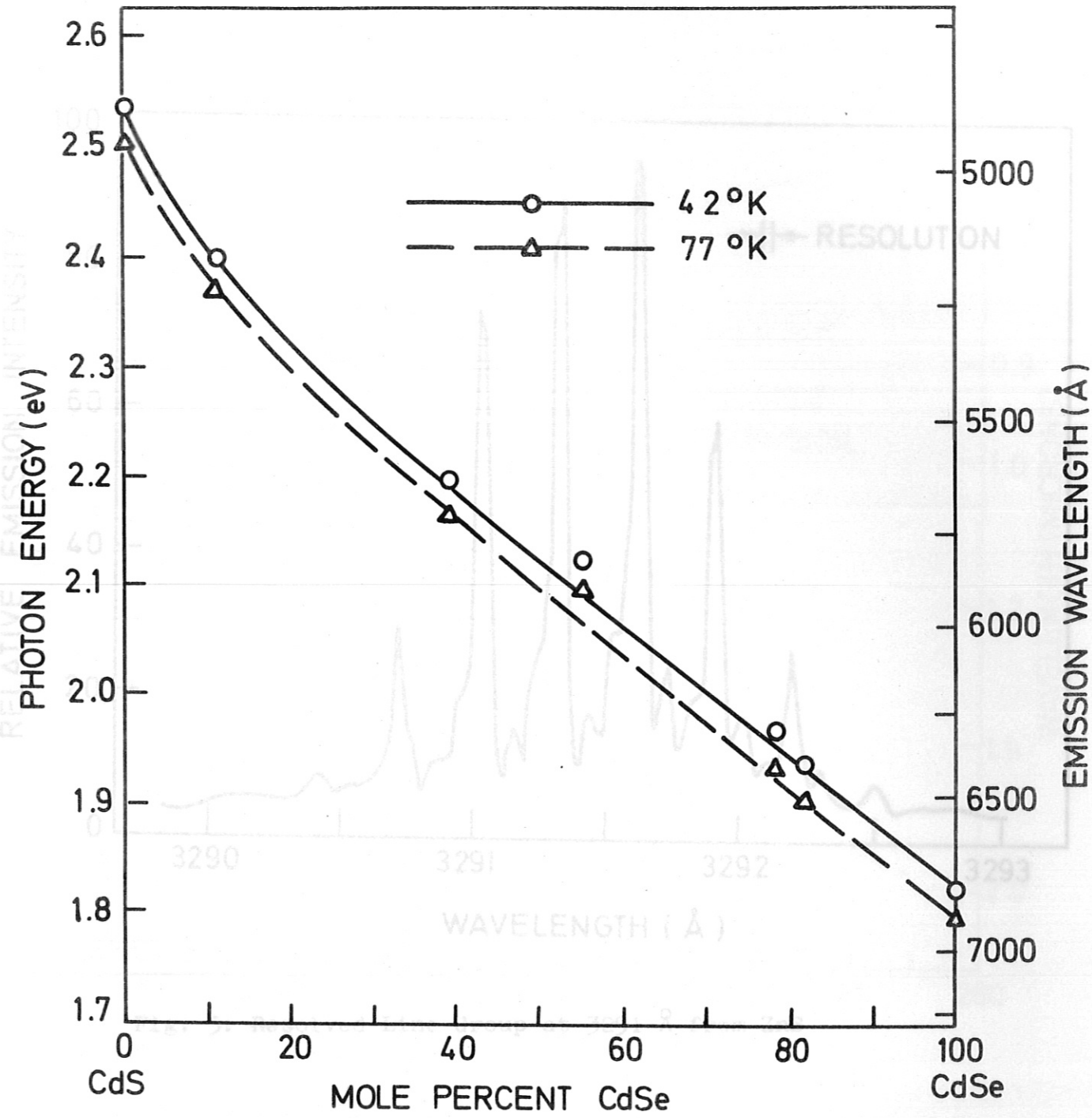

Fig. 4: Emission Wavelengths of CdS_xSe_{1-x}

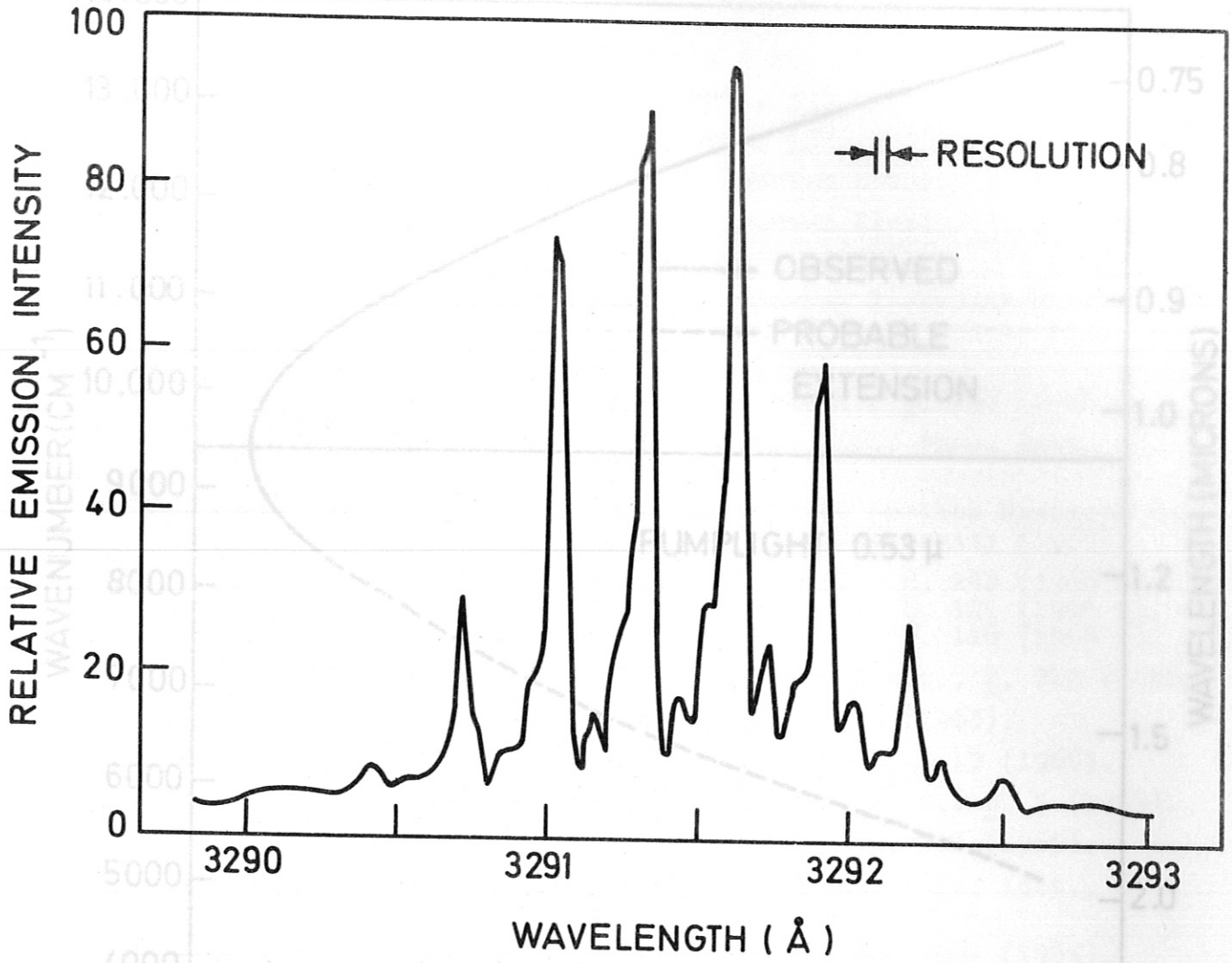

Fig. 5: Resolved Line Group at 3291 Å from ZnS

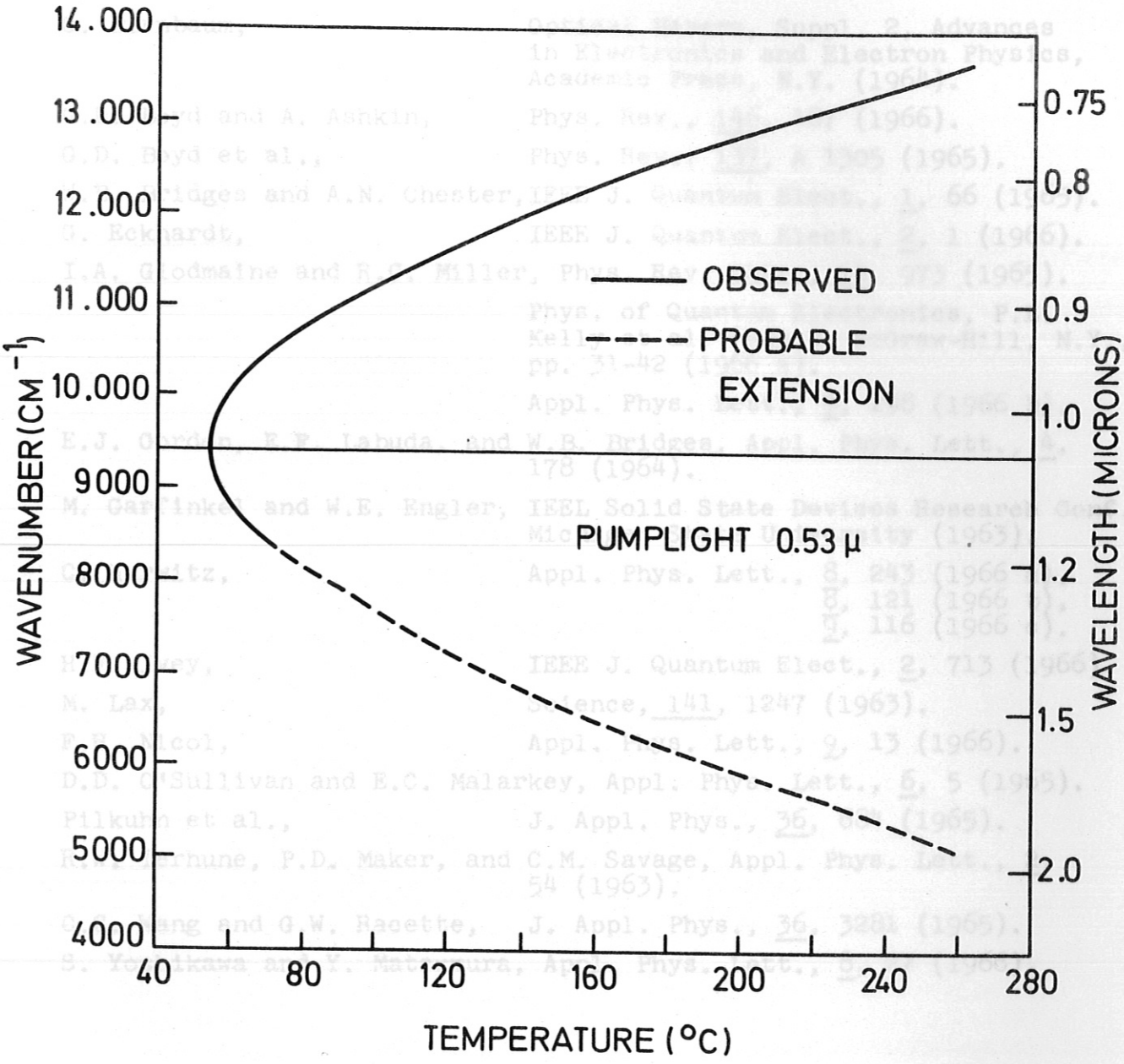

Fig. 6: Continuous Generation of Line Radiation between 0.73 μ and 1.93 μ using a Temperature-Tuned $LiNbO_3$ Optical Parametric Oscillator

BIBLIOGRAPHY

A.J. Alcock and S.A. Ramsden, Appl. Phys. Lett., 8, 187 (1966).

G. Birnbaum, Optical Masers, Suppl. 2, Advances in Electronics and Electron Physics, Academic Press, N.Y. (1964).

G.D. Boyd and A. Ashkin, Phys. Rev., 146, 187 (1966).

G.D. Boyd et al., Phys. Rev., 137, A 1305 (1965).

W.B. Bridges and A.N. Chester, IEEE J. Quantum Elect., 1, 66 (1965).

G. Eckhardt, IEEE J. Quantum Elect., 2, 1 (1966).

I.A. Giodmaine and R.C. Miller, Phys. Rev. Lett., 14, 973 (1965).

Phys. of Quantum Electronics, P.L. Kelly et al. (Eds.), McGraw-Hill, N.Y., pp. 31-42 (1966 a).

Appl. Phys. Lett., 9, 298 (1966 b).

E.J. Gordon, E.F. Labuda, and W.B. Bridges, Appl. Phys. Lett., 4, 178 (1964).

M. Garfinkel and W.E. Engler, IEEL Solid State Devices Research Conf., Michigan State University (1963).

C. Hurwitz, Appl. Phys. Lett., 8, 243 (1966 a), 8, 121 (1966 b), 9, 116 (1966 c).

H.F. Ivey, IEEE J. Quantum Elect., 2, 713 (1966).

M. Lax, Science, 141, 1247 (1963).

F.H. Nicol, Appl. Phys. Lett., 9, 13 (1966).

D.D. O'Sullivan and E.C. Malarkey, Appl. Phys. Lett., 6, 5 (1965).

Pilkuhn et al., J. Appl. Phys., 36, 684 (1965).

R.W. Terhune, P.D. Maker, and C.M. Savage, Appl. Phys. Lett., 2, 54 (1963).

C.C. Wang and G.W. Racette, J. Appl. Phys., 36, 3281 (1965).

S. Yoshikawa and Y. Matsumura, Appl. Phys. Lett., 8, 27 (1966).