SPECTROSCOPIC STUDIES OF LASER MATERIALS AND APPLICATION OF LASERS TO DEFENCE PROBLEMS

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Many important properties of the laser materials like the location of the electronic energy levels, the influence of the electric crystal field on them and the influence of concentration and life times of the levels can be obtained by the spectroscopic methods. A review of the recent techniques to find these properties with special reference to the rare earth materials is given in this paper. A few important applications of the lasers to defence problems are also given.

Spectroscopic studies enable us to obtain many important properties for laser action such as location of the energy levels, the influence of the electric crystal field on them, their width due to various causes, the influence of concentration, the magnetic properties of the states and life times of the levels.

The necessary prerequisite for laser action is the existence of a number of states whose mean life times are relatively long so that it must be possible to pile up a considerable amount of energy in the excited levels. Long life time of a level and the sharpness of the spectrum lines usually go together and so the best materials for lasers are crystals with sharp lines and low pressure gases. Since the rare earth crystals have sharp-lined fluorescence and absorption spectra, they are ideal for laser action.

For the ground states of the crystal ions, paramagnetic resonance methods give much valuable information. For the excited states however, only spectroscopic methods give the required information. Since most of the powerful solid-state lasers are obtained from the rare earths (14 elements from Lanthanum to Luticium in the periodic table), they would be dealt with here in detail.

It is a common practice to dilute the salt with an optically and magnetically inert material since the rare earth ions, if they are close to each other, produce undesirable line broadening. For this purpose, $LaCl_3$ and YCl_3 have been found very useful, the former is better for the lighter and the latter for the heavier rare earths because of the compatibility of the ion radii. Without undue distortion of the crystal lattice, a rare earth ion can take the place of La^{3+} or Y^{3+} respectively.

The knowledge of the energy level scheme is the first prerequisite for any maser application. The levels of the rare earths can be obtained directly from the absorption and fluorescence spectra and somewhat indirectly from the emission spectra of the free ions.

GENERAL FEATURES OF THE SPECTRA OF RARE EARTHS

A sharp line fluorescence spectrum is obtained containing, in some cases, several hundred sharp lines from the ultraviolet to the near infrared region by illuminating the crystal by an intense light source. When the coupling between the electronic level and the

crystal lattice is large, the excitation energy is dissipated before fluorescence can take place. This is the case for most hydrated   salts except for the central rare earths from Sm to Dy. In other lattices, all other rare earths fluoresce strongly but not from all levels. The anhydrous chlorides and bromides, the garnets and the oxides are among the crystals that show general fluorescence [1—12]. Fig. 1 illustrates the fluorescence spectra of the different rare earths at low temperatures.

In complicated fluorescence spectra, single levels can be excited by monochromatic illumination and this greatly helps in the analysis of such spectra. The fluorescence spectra are very sensitive for small amounts of the impurities and great care must be taken to identify such impurity lines which occur in even the purest available materials.

The crystal absorption spectra, like the fluorescence spectra, consist of several hundred lines from the ultraviolet to the near infra-red region. The Zeeman effect is often important to establish the nature of the transitions giving rise to the absorption lines. At low enough temperature, the wave numbers of the absorption lines, directly represent the position of the excited energy levels. The electric crystal field produces a Stark effect which splits all levels into a maximum of $2J+1$ components for an even number of electrons and $J+\frac{1}{2}$ components for an odd number. The number and spacing of the components depend on the symmetry and intensity of the crystal field.

The emission spectra of the rare earth ions are extremely complicated since the large number of levels give rise to thousands of lines from the vacuum ultraviolet to the near infra-red region[13].   Accurate   wavelength measurements are of the greatest importance as the possibility for finding spurious regularities is proportional to $(\triangle v^2)$ where $\triangle v$ is the uncertainty in the frequency measurements.
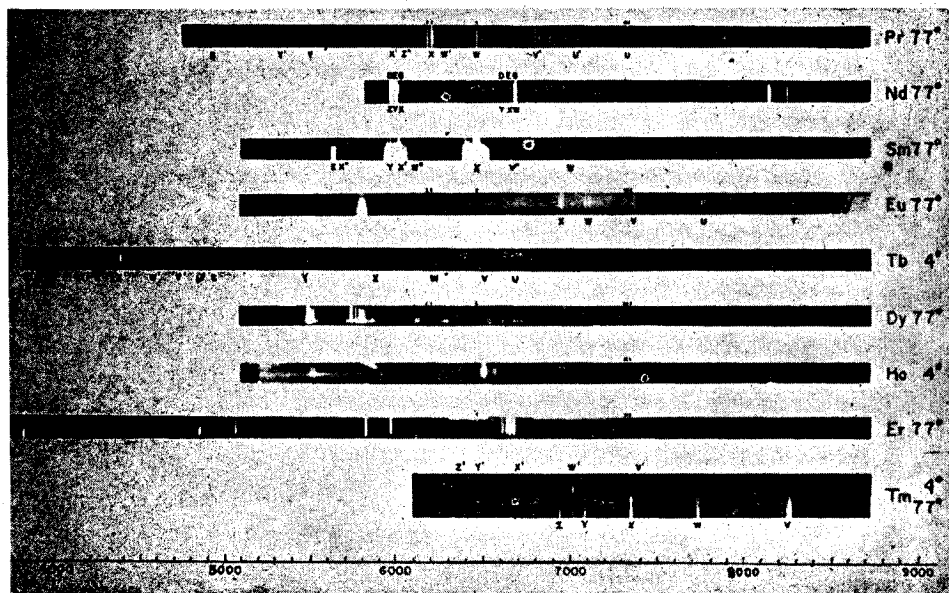

Fig. 1—*Flourescence spectra of the rare earth crystals at liquid air and liquid helium temperature*

For the crystal spectra, the task of obtaining the energy level system from the observed wavelengths of the absorption and fluorescence lines is, in general, direct and simple. For the free-ion emission spectra, this is a more elaborate and difficult problem. A satisfactory analysis of these complicated spectra would be virtually impossible without a thorough theoretical study of the structure of the energy levels. Such a study is based on the general theory of atomic structure as, for instance, set forth in the book by Condon and Shortley[14] and systematized for the rare earth cases by Racah[15].

EXPERIMENTAL TECHNIQUE TO OBTAIN THE SPECTRA

Single crystals are grown by the melt technique incorporating the desired concentration of the rare earth in a suitable host lattice. For example a small quantity of $NdCl_3$ is introduced into a large quantity of $LaCl_3$ so that the percentage of neodymium atoms is very small.

To get the fluorescence spectra, light from a high pressure mercury arc like $AH6$-lamp or xenon flash is condensed by means of a lens on the crystal. The scattered fluorescence radiation is condensed on the slit of the spectrograph. As sharp-lined spectrum is obtained only at low temperatures, the crystal is immersed in liquid air or liquid helium contained in a transparent dewar vessel. It is often advantageous to excite a particular level at a time and this is done with the help of a monochromator.

At the Johns Hopkins University, this was accomplished by using, for the illumination of the crystal, the output of a grating monochromator (Fig. 2) with the strong continuous light source (usually a high pressure mercury arc)[16].   Under favourable conditions, with a fairly narrow slit, the half-width of this beam was about $2A$ and this gave enough light to photograph in most cases the fluorescence spectrum in a matter of minutes.   In Fig. 2, M stands for mirror, S for slits, G for gratings, L for lens and P for Plate holder. The relatively high monochromacity of the exciting beam makes it possible to excite selectively and specified level and to even differentiate between the individual Stark components.

The electronic absorption spectra are obtained by sending a powerful beam of continuous light from a tungsten lamp or a high pressure mercury arc through the crystal kept at the temperature of liquid air or liquid helium and condensing the transmitted light on
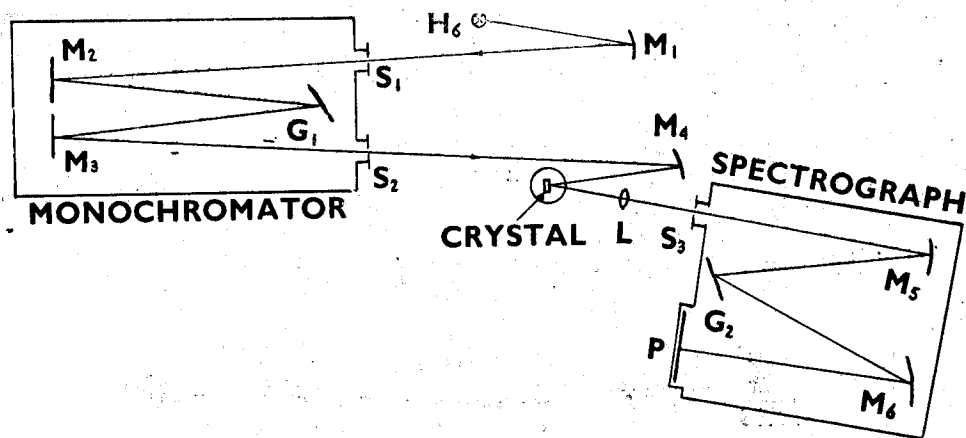

Fig. 2—*Experimental arrangement for the monochromatic excitation of fluorescence levels*

the slit of the spectrograph. For the study of the Zeeman effect, which helps to identify the levels, the dewar vessel, with the crystal inside, is placed between the pole pieces of an electromagnet and a field of about 30,000 gauss is applied on it. Since the Zeeman levels have separations of only a few wave numbers, the spectra are recorded with high dispersion spectrographs.

The free-ion spectra are obtained from a controlled spark in a rare gas atmosphere at reduced pressure [17]. The rare earth is taken in the form of small cylindrical metal rods which are inserted in a lavite holder with the gap of a few mm between them. The lavite holder with the metal electrodes is held in position in a discharge chamber evacuated and filled with helium at 20 mm pressure. Two stupakoff connectors on either side of the lavite holder provide the electrical leads to the outside through the discharge chamber as shown in Fig. 3.

The neutral and singly ionized spectra are produced by a d.c. arc discharge. The spectrum of doubly or triply ionized metal is readily excited by means of R-L-C circuit in which the discharge of a capacitor bank across the electrodes of pure metal produces a high current spark. It is not possible to obtain the spectrum of one stage of ionization free of that of the neighbouring stages but in each case it is possible to find conditions which will bring out a particular stage at its maximum intensity. It is found that for Neodymium, the hot spark is 600 amp in which the triply ionsed spectrum lines have the maximum intensity, the mild spark is 200 amp in which most of the doubly ionised spectrum lines have the maximum intensity and the low energy spark is 20 amp in which the intensity of the doubly ionised spectrum lines is much reduced and the intensity of neutral and singly ionised spectrum lines is increased. Lines of different ionization stages can be separated by comparing the relative intensities in different excitations as shown in Fig. 4.

DETERMINATION OF ENERGY LEVELS FROM SPECTRA

For any laser application, it is essential to know first the energy levels. The levels of the rare earths which are being used as laser materials can be obtained directly from the fluorescence and absorption spectra of the crystals or from the emission spectra of the free metallic ions.

While the empirical analysis of the observational data gives directly the set of energy levels, the comparison with calculated levels is necessary for their interpretation [18, 19]. The interpretation furnishes the labels such as $^4I_{15/2}$ which implies definite values for the
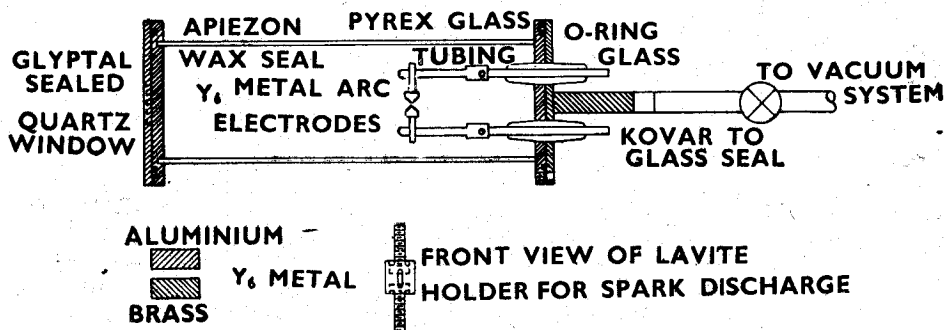

Fig. 3—*Spark bottle with the electrode assembly to get the emission spectra of the ionized rare earth elements.*
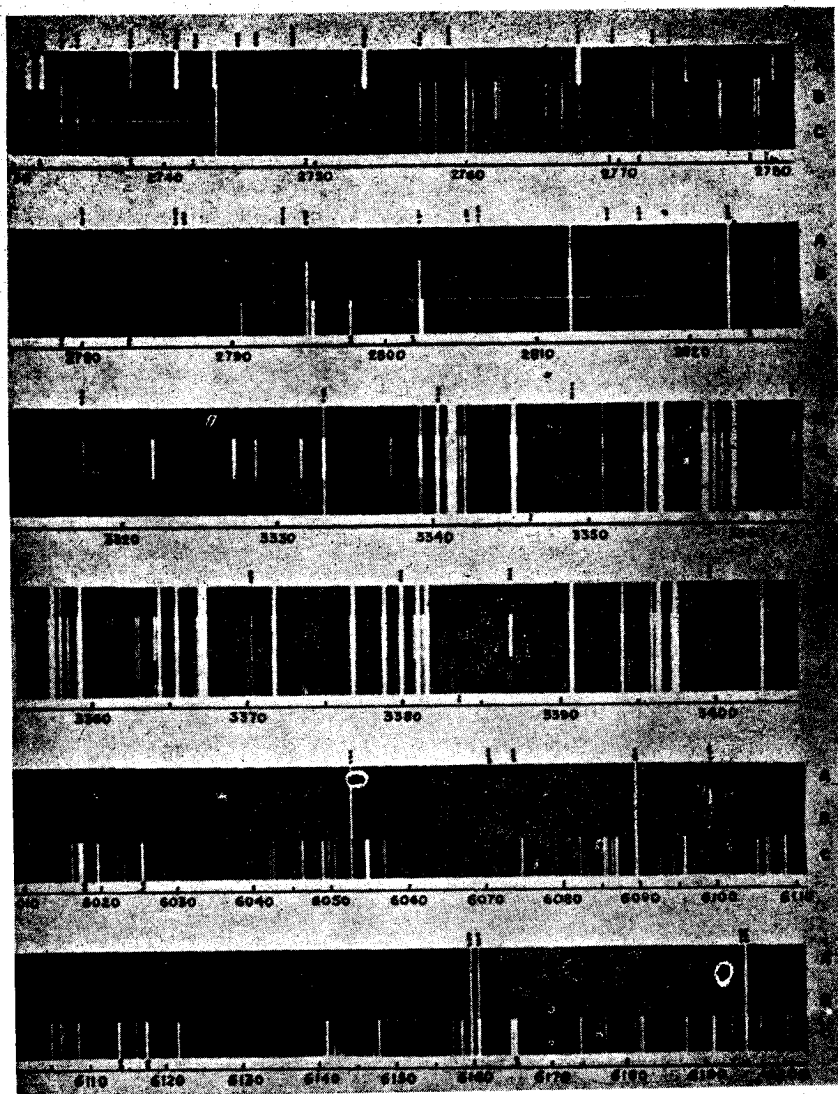
Fig. 4—*The praseodynium spectrum with different degrees of exitation. A, hot* ꟼ*spark; B, mild spark; C, d.c. arc.*
(Lines marked by four and three dots above the spectra belong to Pr. IV and Pr III respectively; those with
two dots below, to Pr II or I). see ref. 17.

quantum numbers S, L and J (in the example $S = 3/2$, $L = 6$ and $J = 15/2$). The scheme given in Fig. 5 is for the lower levels of each of the trivalent rare earth ion and is obtained from the results of the crystal spectra at the Johns Hopkins University.

Fig. 6 illustrates how the levels are established for a crystal of Y_2O_3 containing 1 per cent erbium. From theoretical considerations and previous experience, we expect to find a group (called the A group) of excited levels at about 10,000 cm^{-1} above the ground state which would correspond to the single free ion $^4I_{11/2}$ level. As the number of electrons for Er^{3+} is odd, we expect to find the Stark-split level to consist of $J + \frac{1}{2} = 6$ components. The ground state $^4I_{15/2}$ will be split into 8, but if the crystal is cold enough only the lowest of these will be occupied. Absorption transitions occur between this lowest level and any
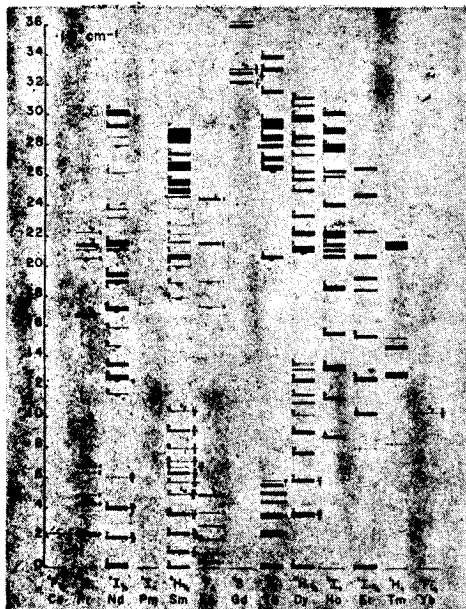
Fig. 5—*The lower energy levels of the $4f^n$ configuration for the triply ionised r are earths as obtained from crystal absorption and fluorescence spectra.*

Fig. 6—*Absorption and fluorescence spectra of 1%*
$$Er^{3+} \text{ in } Y_2 b_2$$

Left—Absorption from Z group to A group
$$\left({}^4I_{\frac{15}{2}} \gg {}^4I_{\frac{11}{2}} \right)$$

Right—Fluorescence from P group to A group
$$\left({}^2P_{\frac{3}{2}} \gg {}^4I_{\frac{11}{2}} \right)$$

see ref 13.

higher level unless forbidden by selection rules. All six appear in the left hand spectrum of Fig. 6. Fluorescence from the lowest Stark component of $^2P_{\frac{3}{2}}$ (P group) shown on the right confirms all six levels. Very low levels such as the higher Stark components of the ground state for which the absorption spectrum is not in the accessible region, must be confirmed by additional fluorescing levels. The levels can also be obtained from the absorption spectrum. Zeeman effects in the optical region help to identify the nature of the level *i.e.*, finding the quantum numbers of the states provided the lines are sharp enough to resolve the Zeeman components.

All sharp crystal lines in absorption or emission of the lanthanides are due to transitions between levels of the $4f^n$ configuration influenced by the crystalline field. In the emission spectra of the metallic ions, the free-ion analogs of the crystal lines do not appear as they are forbidden by selection rules. It is, therefore, possible to obtain the $4f^n$ configuration only through allowed transitions among which the most prominent ones are $4f^n$ — $4f^{n-1} 5d$. In turn, the $4f^{n-1} 5d$ levels are connected by allowed transitions to the $4f^{n-1} .6p$ configuration which, in turn, is connected to the $4f^{n-1} 6s$ levels. From an analysis of these four basic configurations, which furnish the strongest lines of the spectrum, the levels of $4f^n$ can be established. Since most of the lines of the triply ionised spectrum lie in the vacuum ultraviolet, only a few elements have been studied so far.

DETERMINATION OF THE LIFE TIMES OF THE LEVELS

When once the energy levels of the elements are established, we have to find out which levels are suitable for laser action. A very important criterion for laser action is that the mean life time of the upper energy level should be more than that of the lower level to which the photons terminate constituting the laser beam [20]. This means that, at any instant, more atoms should stay in the upper energy state than in the lower state so that more atoms can be stimulated to emit as coherent radiation.

The life times of the energy levels can be accurately determined by spectroscopic techniques [21,22]. The material is taken in microcrystalline form, sealed into narrow pyrex or quartz tubes with a filling of helium gas. The helium was necessary to maintain heat conduction even at the temperature of liquid air or liquid helium. Powdered samples are better than single crystals because they give stronger fluorescence due to the many internal reflections of the exciting radiation. The experimental set-up is shown in Fig. 7.

The circuit parameters are chosen so as to give the spark a duration of about half a microsecond. The intensity of the fluorescence is measured as function of the time and, if a straight line results when the logarithm of the intensity is plotted as function of the time, the mean life is determined from the slope of the line.

The measurements are made as follows. The on-time interval of the electronic switch that is the interval during which the signal is transmitted through the amplifier to the recorder, is chosen so as to give sufficient time resolution and enough deflection on the recorder for accurate measurement. The on-time setting is left unchanged for the duration of a run and a succession of delay times set, allowing the recorder to trace out the intensity reading at each delay time for as long as required to obtain a good average through the noise. The delay times are changed from the longest time chosen to the shortest and then repeated in reverse order.

The emission decay can be represented by an exponential formula $I = I_0 e^{-t/\tau}$ where τ is the mean lifetime of the state. The fact that the lifetime actually determined for the excited states from the decay of the fluorescence is often considerably shorter than the natural lifetime of the states must be attributed to depletion of the excited levels through radiationless interactions with the crystal lattice. If only the fluorescence radiation exists, we would have the natural lifetime τ_0. When only interaction with the crystal lattice depletes the state, we have a relaxation time τ_r. The actual decay time is determined by
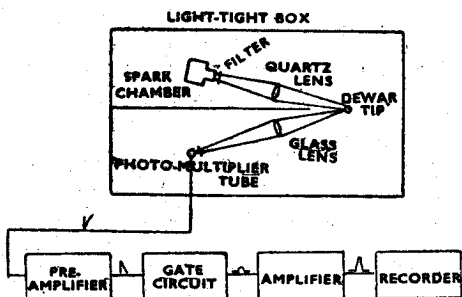
$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_r}$$

At very low temperatures, interactions with the crystal lattice are negligible and all the energy is dissipated as fluorescence radiation. Therefore, measurements made at very low temperatures give approximately the natural lifetime τ_0 of the level.

Fig. 7—*Schematic diagram of the experimental arrangement to determine the life time of the energy levels.* (*see reference 21*).

APPLICATION OF LASERS TO DEFENCE

After choosing a particular material and suitable energy levels for laser action, one can construct a laser using the experimental techniques described by Maiman [23], Javan[24] etc. By interposing suitable dielectric coated mirrors in the path of the laser beam, we can suppress the unwanted frequencies and obtain only a single laser frequency with the maximum transmittance.

Since the laser radiations have the advantageous preperties of high degree of monochromacity, coherence, directionality and power density, they are being used for many applications in science and technology. Only a few important applications to defence problems would be described in this article.

Ranging

The determination of the position of a distant object *i.e.*, ranging, can be accurately done with the help of a laser beam since it consists of short pulses of great intensity combined with high directivity. If we measure the time for the pulse to reach the target and return, we can estimate the distance of the target. The scientists of Hughes Aircraft Company have built a practical portable optical ranging device which they named as 'Colidar'. Successful ranging was reported at more than 30,000 m. in daylight and 112,000 m. at night with a distance accuracy of 15 ft. The advantages of the laser pulses over the microwave beam of the radar are greater power density and that the dimensions of the antenna or radiator required for the same gain is decreased by a factor or ten thousand.

Lasers are being used in satellite borne systems, capable of detecting and identifying ground targets, mopping the surface of the moon and for the guidance and communication systems of missiles and satellites.

On the battlefield, the laser can be used to fire non-deadly spears of laser light which gives target distance data for pinpoint shelling of the enemy. For field use, it can be mounted on a rifle stock, the power supply being carried in belt or back-packs. Thus, an infantry man can determine the trajectory to direct mortar and cannon fire by aiming the ranger as he would his carbine. In aircraft, a nose–mounted ranger could provide distance measurements needed for firing folding–fin type rockets.

The new ranger using the optical laser can also be used for surveying and mopping over water, chasms or other inaccessible points. Its use can be extended to underwater radar and communication problems for the Navy taking advantage of the transmission "window" that exists in sea water in the blue green light portion of the spectrum.

Determination of energy densities of high temperature gas discharges and shock waves

Another important application of the gas laser is to find the electron densities of high temperature gas discharges [25]. A He–Ne laser is used as a simple interferometer in which the optical cavity of the laser corresponds to the reference arm of more conventional interferometers. The method depends on that interference occurs if the radiation from He–Ne laser is reflected back into the laser by an external mirror. Since the laser produces simultaneously both visible light at 6328A° and infra-red at $3 \cdot 39\mu$, alignment of the optical system can be easily made since the laser beam is visible. Further, because both are produced by electron transitions from the same excited state, any modulation in the infra-red radiation produces a complementary modulation of the red light. This effect makes possible the use of a simple red–sensitive photomultiplier as a detector of effects in the infra-red.

Fig. 8 illustrates the apparatus to measure the electron density of the gas discharge. The laser and the external mirror are mounted in large concrete blocks supported by shock absorbing mounts so that the system is free from high frequency floor vibrations.

Before using the apparatus on a plasma, it was checked by substituting an air cell for the gas discharge plasma and counting the number of modulation cycles (fringes) produced by a known change in air pressure. When the system is found alright, the gas discharge tube is interposed in the path of the laser beam as shown in Fig. 8.

The refractive index of the gas discharge can be obtained from

$$(n - 1)\ t = (\triangle m)\ \lambda$$

where m is the refractive index, t is the thickness of the discharge column, $\triangle m$ are the number of fringes shifted and λ is the wavelength of the laser radiation. We have $n = [1 - (\omega_p / \omega)^2\ ]^{\frac{1}{2}}$, where ω_p is the plasma frequency and ω is the frequency of the probing radiation. From the above relation ω_p can be calculated. Since the electron density n_e is connected to the plasma frequency by the relation

$$\omega_p = (4\ \pi/n_{e.}\ e^2/m_e\ ) = 5 \cdot 6 \times 10^4 \times n_e^{\frac{1}{2}}$$

we can calculate the electron density of the gas discharge.

The accuracy of the laser measurements depends on the number of fringes observed. It is easy to estimate to one quarter of a fringe. This new interferometric method of measuring electron density with a laser has considerable advantages over microwave and conventional interferometry since it combines simple experimental set up and high precision.

Communications

In the field of communications, the laser has much greater advantages than the conventional electronic oscillators. With the great band width available at optical frequencies, almost limitless number of communication channels could be maintained in this part of the spectrum. To illustrate this, a laser may operate at a frequency of 5×10^{14} c.p.s. or 500 million Mcs., a frequency which is 10 million times that used in television and 10,000 times that of the highest microwave frequency in use. A single laser can theoretically accommodate all the telephone and television channels required for the whole world.

The low signal-to-noise ratio of laser amplifiers makes them an extremely useful tool in radio astronomy and satellite communication systems since they can be used to receive weak signals which would be lost in the noise background of conventional microwave amplifiers.
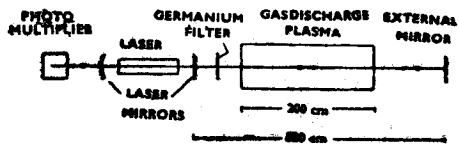

Fig. 8—*Schematic diagram of the experimental arrangement to determine the electron densities of high temperature gas discharges (see, reference 25).*

Suitable methods of modulation and demodulation of laser beams are being developed. Audio and vidio signals of good quality have already been transmitted over an infra-red laser channel 30 miles long. It is true that no light beam will penetrate through fog, rain or snow very well. Therefore, to be useful in earthbound communication systems, light

beams have to be enclosed in pipes. But the recent development of fibre optics might circumvent this difficulty also.

For space communications, laser would be ideally suitable. As laser communication can be effective through the exhaust of a rocket and through the ionised plasma sheath during re-entry of a space-vehicle, which is opaque to radio microwaves, it may be applied for communications between a space vehicle and earth during this phase of the operation.

ACKNOWLEDGEMENT

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