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EXCITON DIFFUSION IN MOLECULAR
CRYSTALS OF NAPHTHALENE

by

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ABSTRACT

Exciton diffusion in naphthalene single crystals and in microcrystalline sublimed films is investigated experimentally. The naphthalene is purified by chemical methods and by zone refining. The impurity (probably anthracene) is reduced to about one part in 10^8 .

The excitons, both free and localized, are trapped by using anthracene impurities of known concentrations. The impurity concentration is varied over the range 5×10^{-3} - 10^{-8} mole/mole. The results indicate that the mean free path of free excitons is about 750 Å, and 60 Å for localized excitons. Only 40% of the total light absorbed by naphthalene appears as free excitons.

Theoretical predictions by Agranovich and Faigysh are in general agreement with these results. A considerable amount of additional detailed information could be derived from these results if the precise extinction coefficients were known.

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INTRODUCTION

This thesis is an experimental study of the diffusion of excitons in naphthalene crystals.

Simpson¹ reported some data on diffusion in microcrystalline films of anthracene while Borisov and Vishnevski² used thick (about 1 cm) crystals. In the first case surface and vacancy quenching complicates the data while in a thick crystal there is a considerable amount of reabsorption of the fluorescence radiation. Wolf³ also reported some data on methyl naphthalene crystals.

Unfortunately there are objections to the results obtained by the above workers. Furthermore this being a new field an effort should be made to test the procedures and analysis used at present. This thesis is an effort in this direction.

Ganguley⁴ and Bowen⁵ observed that when a small quantity of naphthacene (about one part in 10^5) is added to anthracene the fluorescence of the anthracene is suppressed and naphthacene fluorescence of high efficiency appears. The condition under which exciton trapping occurs is such that the impurity absorbs in the region of fluorescence of the matrix. This means that the fluorescence band of the matrix substance will overlap with the absorption band of the impurity. According to this anthracene could act as a detector of excitons generated in the naphthalene. Excitons can be generated in naphthalene in the 3100-2000A region.

Very little data is available concerning lifetimes, trapping, diffusion coefficients, temperature dependence, interaction with defects and the like. Considerable amount of detailed experimental studies will be needed before one can understand in a satisfactory manner energy transfer processes, photoconductivity, electronic spectra in molecular crystals. In fact there are only a few experimental studies in this field of research. Lipsett and Dekker⁶ (1952) pointed out that the lack of research is due to the lack of adequate apparatus. This is not the only reason high purity of the substances under investigation is also necessary. In our experimental work the naphthalene was purified to a high degree. We were able to reduce the impurities to less than one part in 10^7 . According to this we studied the effect of the added impurity (anthracene) over a wide range of concentrations. In this work the methods of Borisov and Vishnevski², and of Agranovich and Faidysh⁷ were considered. It was possible to estimate the mean free path of the free and localized excitons in the naphthalene crystals.

THEORETICAL CONSIDERATIONS

The theory of excitons in an atomic lattice was introduced by IA. I. Frenkel⁸ in 1931. According to Frenkel's ideas an exciton is a quasi-particle moving over the crystal lattice as excitation waves and transporting energy. The application of this theory to the ultra-violet spectra of molecular crystals was first made by Davydov⁹. The problem of energy transfer between pairs of randomly oriented molecules was treated quantum mechanically by Forster¹⁰. N. F. Mott¹¹ (1938) exciton model, consists of a positive hole and an electron in the crystal, bounded by a coulomb interaction.

When an atom or molecule is excited in a solid, the excitation will not, in general, remain localized at the original site of absorption. The transmission of the excitation takes place because of the translational symmetry of the crystal lattice, and the identity of the elementary cells of an ideal lattice. The transmission, from cell to cell, will occur by a resonant process and the excitation must diffuse through the crystal. The non-localized state of the excitation is called an exciton.

According to Frenkel's original theory, absorption of light by a molecular crystal can lead to an excited electronic state in which the excitation may move through the crystal. Excitons can be excited in a crystal lattice not only by light but by other methods, for example by the impact of particles (electrons, neutrons, α -particles, etc.)

In good insulators an exciton can be produced when the insulator is raised to the first excited state of its electronic system. The first electronic transition is called the first fundamental absorption band of the crystal. This region in good insulators is usually in the

ultraviolet¹. The non-conducting excited states, or exciton states in weakly bound solids (e.g. molecular crystals such as naphthalene, anthracene) correspond closely to the lowest excited states of the constituents atoms or molecules in the free state. In ionic and covalent crystals where the constituent particles are strongly bound, they arise from the removal of an electron from one atom to a neighbour. The exciton in this case may be regarded as a hole and electron, bound in their mutual coulomb field, travelling through out the crystal. This is actually the Mott view point¹¹. The exciton according to this picture can be treated, therefore, as a hydrogen-like quasi-atom. Experiments¹² with Cu_2O crystals at 1.3°K shows a series of narrow absorption lines near the absorption edge; these lines converge to a boundary whose frequency satisfies the serial dependence of the hydrogen like atom. Davydov⁹ has shown that in molecular crystals two types of excitons may be produced by the absorption of light. These are the free and the localised excitons. The free excitons coincide with the type we have already discussed. Their probability of being captured is greater than that of the localized ones. The localized exciton is a slowly propagating electron-oscillatory excitation of the crystal which is associated with local deformation of the lattice⁷. The localized exciton interacts strongly with the lattice vibrations thus increasing the probability of non-radiative transitions. For the sake of simple discussion let us limit our self to the assumption that only one type of excitons exist in a crystal lattice. In fact Agranovich and Faidysh mentioned in their paper (ref. 7) that "It seems that for a number of molecular crystals it is possible to neglect the diffusion

of "localised" excitons and consequently their participation in the transfer of energy from the base material to the impurity."

Since the excitons are neutral and can't conduct electricity their diffusion does not involve charge migration. Fig. 1 shows a diagram of exciton excitation in a crystal lattice and the location of the band in which the charge carriers are freed.

The life-times of excitons are relatively long in crystals which are not disturbed by imperfections of any type including impurity centers. The exciton can decay in several ways:

1. It can decay radiatively with emission of a quantum of fluorescence.
2. The exciton may undergo a non-radiative transition by interaction with lattice imperfections.
3. It may be captured at an impurity center.

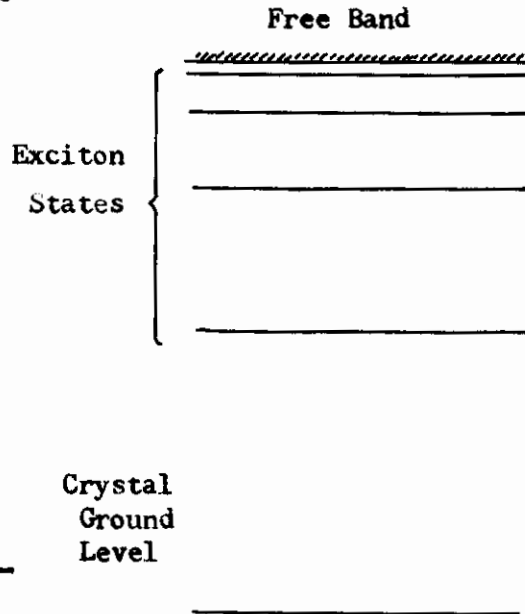


Fig. 1. Exciton Levels in a Crystal Lattice.

In the latter case if the impurity is itself luminescent the exciton capture may be followed by emission of fluorescence characteristic of the impurity.

The following are some observations that indicate the existence of excitons:-

1. The external photoelectric effect in alkali halides resulting from the ejection of electrons from F-centers by means of excitons.
2. Exciton migration has been shown to account quantitatively for the fluorescence quenching of aromatic hydrocarbons containing impurity¹³.
3. Sidman¹⁴ (1956) has presented evidence derived from the absorption and fluorescence spectra of anthracene which implies that excitons can be trapped at lattice imperfections.

The work of Gross¹² (1958), and Nikitine¹⁵ (1959) with Cu_2O ionic crystals can be considered as direct evidence of the existing of excitons in crystal lattices.

EXPERIMENTAL

1. Purification.

The naphthalene used in this work was originally Matheson Coleman and Bell and was recrystallized from alcohol. Purification steps were made as follows:-

a. Purification by chemical processes:

As a first step in purification the naphthalene was refluxed for 24 hours with an excess of sodium metal. The step was undertaken to remove the heterocyclic compounds containing sulfur, after Sponer and Nordhein¹⁶. The filtrate was allowed to cool slowly. The crystals were redissolved in 95% redistilled warm alcohol and filtered. The filtrate was left to cool again. The last recrystallization process was repeated four times, using fresh alcohol in every step.

b. Zone Refining:

Chemical methods of purification as explained by the foregoing steps are not sufficient for our purposes.

One method of purification, known as the zone refining method, depends on the "motion" of a narrow molten zone through a crystal. This method was used to purify naphthalene further in order to remove traces of anthracene since anthracene will be added in known quantities.

The basis of this method (see Fig. 2) is to move a tube containing the substance very slowly in a narrow hot region of a controlled temperature such that a narrow zone is just above the melting point of the substance contained in the tube. The success of the method depends on

the increase in solubility with increasing temperature. The impurities therefore dissolve in the melt (of the narrow zone) and move up the tube slowly. The speed with which the hot zone travelled was 2.5 mm/hr.

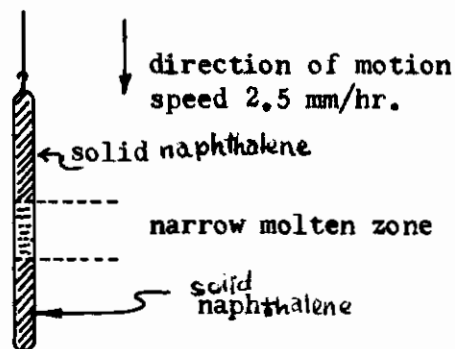


Fig. 2

The sample used for this experimental work were treated for about 200 hrs. or the equivalent of 5 passes. The impurity (anthracene) content was below 10^{-7} part per part of naphthalene. Special technique was followed in filling the tube with the naphthalene. The naphthalene sublimes easily when it is heated, therefore, only a small space should be left above it in the vacuum sealed tube.

2. Preparation of samples.

The samples of naphthalene with different amounts of impurity were prepared by two different methods:-

a. Preparation of thin films by sublimation:

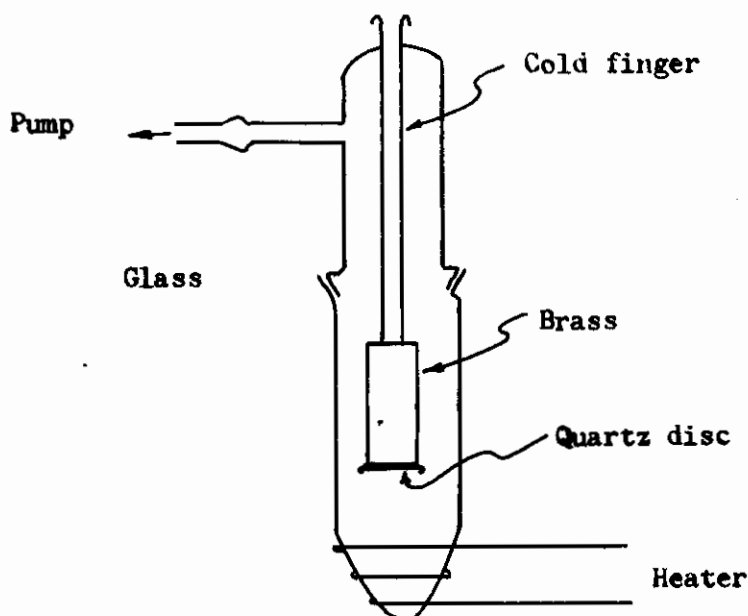


Fig. 3

In Fig. 3 , the apparatus used to sublime a thin layer ($\sim 5\mu$) of naphthalene with the added amount of impurity (anthracene) is shown.

After washing the apparatus extremely carefully a known amount of naphthalene is put at the bottom of the glass. Since the diameter of the quartz disc on which the film is sublimed is 2 cm, and the density of the naphthalene is about 1 gm/cc, only 2 mg of naphthalene is required to make a film of about 5μ thickness, providing that none of the naphthalene is lost during the pumping. To reduce evaporation of naphthalene during the pumping period, the lower part of the apparatus containing the naphthalene is dipped in liquid air after few minutes from the start of the pumping. In practice roughly double the amount of the substance is needed to produce the desirable thickness. When the pressure inside the apparatus is low enough, liquid air is introduced through the top opening of the cold finger. The liquid air reduces the temperature of the disc. The lower the temperature of the disc, the more compact is the resulting film. In our experiments it was necessary to add continuously liquid air for about one hour to produce good films. The piece of brass carrying the quartz disc was made of two parts. The two parts can be screwed inside each other such that the distance between the naphthalene powder and disc could be varied at will so as to give the best uniform film. Since one face of the disc is in full contact with the brass, the temperature of the disc is close to that of the brass, which is in contact with the cold finger. When the temperature of the disc is low enough (after one hour of cooling), the naphthalene is heated rapidly (from 80°K)

until it sublimates on the disc. The heater can supply a sudden pulse of energy. The naphthalene is collected by the cold disc in a very compact form.

If only a small amount of impurity (less than one part in 10^4 parts of naphthalene) is present, it can be carried uniformly by the naphthalene. It was noticed that when a larger amount of impurity is present, there is a non-uniform rate of sublimation of the anthracene. This was one of the bad features of this technique. The films obtained by this method were micro-crystalline in structure. The method has one advantage and that is the thickness of the films can be controlled and measured by direct weighing using a micro-balance.

b. Growing of thin single crystals:¹⁷

Thin single crystals of naphthalene are grown according to the following procedure : small amounts of naphthalene (3 mg) are dissolved in about 5 cc of normal hexane. The solution is then left over a surface of water, and when all the solvent evaporates, the naphthalene crystallizes in the form of single-crystals. More than one crystal usually appears on the surface of the water. The quality and size of the crystals depend on many factors, among which are, the area of the water surface, the concentration, and the amount of the impurity present. Normal hexane was found to be the most suitable solvent, since both the naphthalene and the anthracene are soluble in it to the required extent, and also since it is less dense than and is immiscible in water. Five hours, or more, were found to be necessary to ^{grow} a batch of crystals. This time depends on the rate of the

evaporation of the normal hexane. Faster rate of evaporation yields poorer crystals. This is why it is necessary to observe the environmental conditions carefully. Handling crystals requires skill and patience.

3. Apparatus and Experimental Procedure:

The samples under investigation were irradiated by the Hg lines 3020, 2970, 2890, 2800 and 2650 Å obtained from a Philips high pressure Hg lamp (type: 93110E) and a Carl Leiss double monochromator. The experimental set up is shown diagrammatically in Fig. 4. The naphthalene samples were enclosed between two quartz discs in order to reduce evaporation. The glass filter behind the sample was introduced to stop any of the exciting light which was not absorbed by the sample. The glass filter passes fractions of the naphthalene and anthracene fluorescence. The photomultiplier tube No. 6342 is sensitive in the visible but has very low sensitivity in the regions of the exciting bands.

The photocurrent was measured by a Keithley μ ammeter model 410. The high voltage power supply of the photomultiplier is a Hamner model N-401.

The exciting bands were chosen such that they are strongly absorbed by the naphthalene, but weakly absorbed by the anthracene. In every experiment two observations have to be made;

- a. the total fluorescence i.e. the fluorescence of the anthracene plus the fluorescence of the naphthalene which has not been trapped by the anthracene,
- b. the anthracene fluorescence separately. In the latter case the naphthalene fluorescence was absorbed completely by

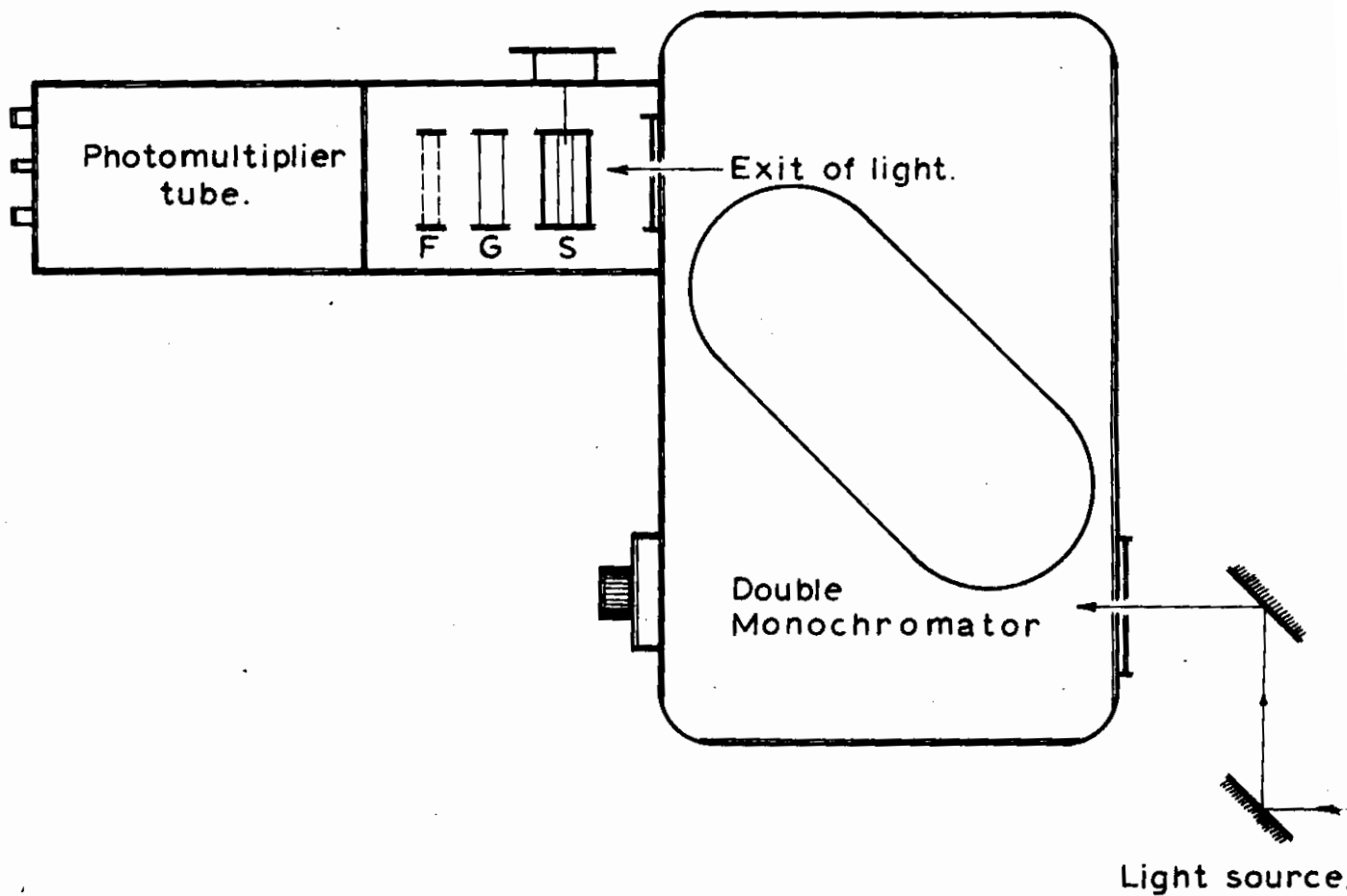


Fig.4. Experimental arrangement for irradiating sample 's' with light.

'G' & 'F' are the glass and anthracene fluorescence filters respectively.

suitable filter (Kodak No. 50). Correction factors for the measured quantities were determined and will be discussed in the following section.

4. Correction Factors:

a. Filters.

The transmission of the glass filter was determined. In the naphthalene fluorescence region (3150 - 3750 Å) the transmission varies from (25 - 85%). Exact percentage of the naphthalene fluorescence transmitted by the glass filter was found by considering the ratio of the areas under the curve obtained when the naphthalene fluorescence spectrum¹⁷ is multiplied by the transmission of the glass transmits 61.5% of the naphthalene fluorescence, its transmission in the anthracene region (3700-4800 Å) is constant and has a value of 90%.

The anthracene fluorescence filter (Kodak No. 50) has zero transmission at the naphthalene fluorescence region. Its transmission at the anthracene fluorescence region is only 2.64%. This value was obtained by using a pure anthracene film and observing the ratio of the photomultiplier current with and without the filter. These values are shown in Table I.

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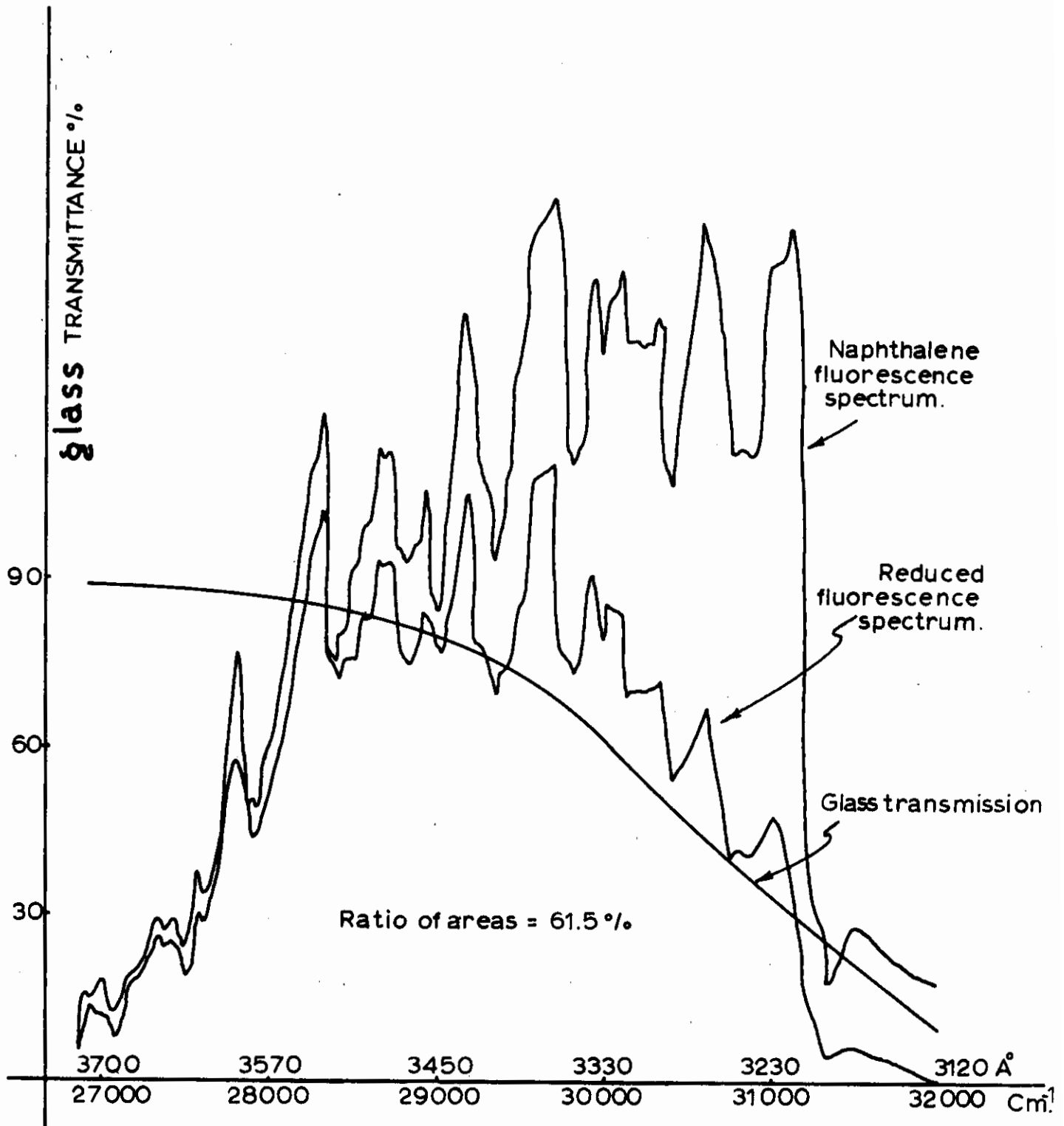


FIG. 5

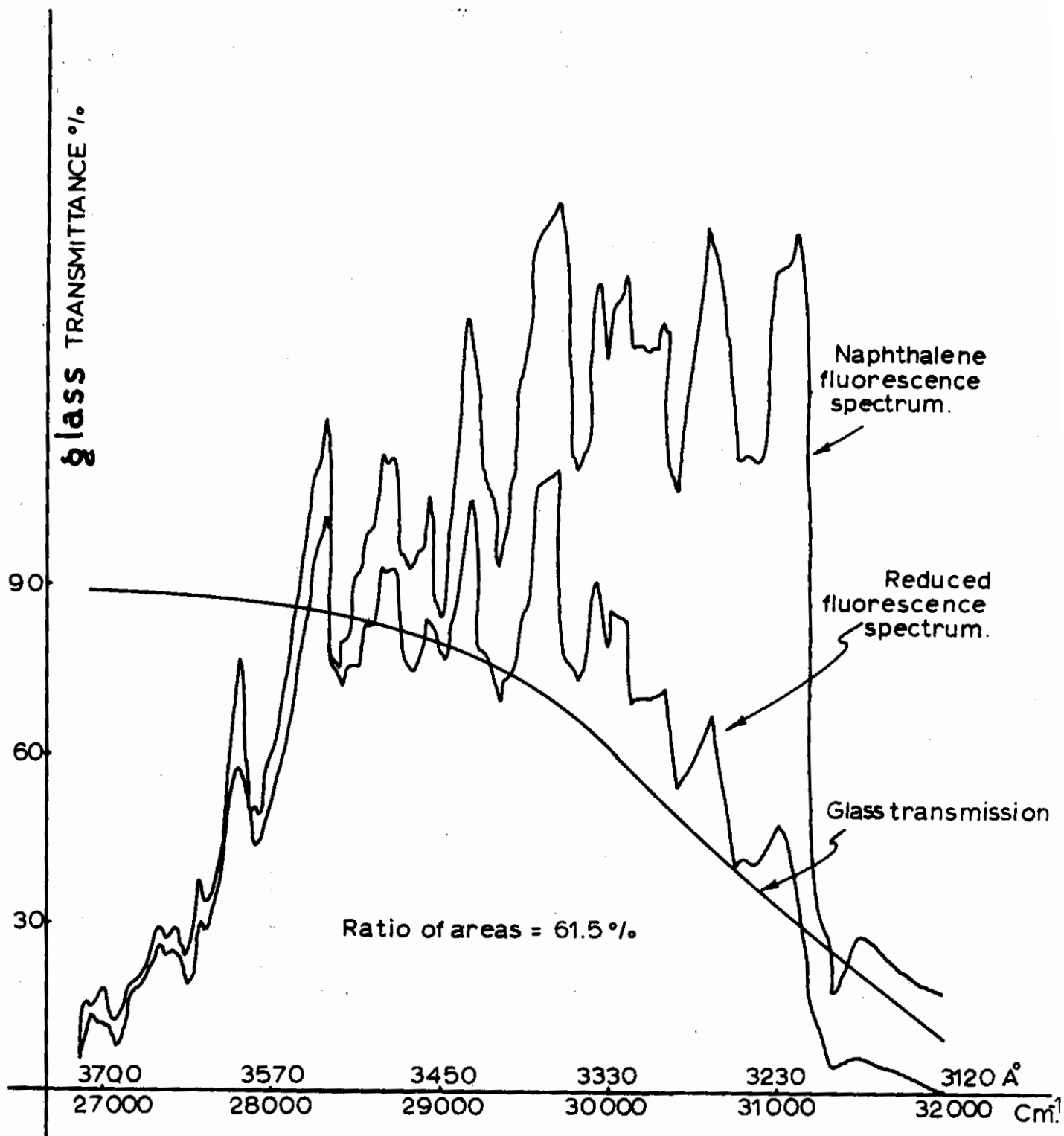


FIG. 5

TABLE I

Wavelength Å	Current x 10 ⁺⁸ amp. without filter	Current x 10 ⁺⁸ amp. with filter	Transmittance %
3020	420	11.30	2.69
2920	215	5.70	2.65
2890	52.4	1.35	2.57
2800	46.2	1.20	2.60
2650	48.2	1.25	2.70
			Av. 2.64

b) Determination of the relative intensities of the Hg lines:-

Consider the optical relation

$$I = I_0 e^{-\Sigma \ell} \quad \text{-----}(1)$$

If light of intensity I_0 falls on a specimen of thickness ℓ , the decrease in intensity ΔI (due to absorption by the specimen) is given by

$$\Delta I = -I_0 (e^{-\Sigma \ell} - 1) \quad \text{-----}(2)$$

If two different wavelengths λ_1 and λ_2 are considered having original intensities $I_0(\lambda_1)$ and $I_0(\lambda_2)$ respectively, the ratio of the light absorbed by the same specimen is

$$\frac{\Delta I(\lambda_1)}{\Delta I(\lambda_2)} = \frac{I_0(\lambda_1)}{I_0(\lambda_2)} \times \frac{(e^{-\Sigma_1 \ell} - 1)}{(e^{-\Sigma_2 \ell} - 1)} \quad \text{-----}(3)$$

But $\Delta I (\lambda_1)$ is proportional to the fluorescence intensity emitted by the specimen $F(\lambda_1)$ divided by the quantum yield of the substance, or

$$\Delta I (\lambda_1) \propto F (\lambda_1) / Q_1.$$

Since the current recorded (i) is proportional to the number of quanta received by the photomultiplier, hence,

$$\frac{\Delta I (\lambda_1)}{\Delta I (\lambda_2)} = \frac{F (\lambda_1) / Q_1}{F (\lambda_2) / Q_2} = \frac{i(\lambda_1)}{i(\lambda_2)} = \frac{F (\lambda_1)}{F (\lambda_2)}$$

since $\frac{Q_1}{Q_2}$ is one.⁺⁺

Therefore

$$\frac{I_o (\lambda_1)}{I_o (\lambda_2)} = \frac{i (\lambda_1)}{i (\lambda_2)} \times \frac{(e^{-\epsilon_2 \ell} - 1)}{(e^{-\epsilon_1 \ell} - 1)} \quad \text{-----(4)}$$

According to equation (4) the relative intensities of any two lines can be determined if both the absorption coefficient and the thickness ℓ are known.

If solutions are used instead of a solid specimen, formula (4) takes the form:

$$\frac{I_o (\lambda_1)}{I_o (\lambda_2)} = \frac{i (\lambda_1)}{i (\lambda_2)} \times \frac{(e^{-\epsilon_2 C_2 \ell} - 1)}{(e^{-\epsilon_1 C_1 \ell} - 1)} \quad \text{-----(5)}$$

where C stands for the concentrations in moles per liter, ϵ for the extinction coefficients, ℓ for the thickness of the cell.

++

The quantum yield of anthracene is independent of wavelength (see Weber, G. and Teale, W. Trans, Faraday Soc., No. 425, vol. 54, Part 5 (1958)).

In the experiment performed to determine the relative intensities of the Hg lines, a 5×10^{-3} mol/l solution of anthracene in cyclohexane was used. The cell thickness was 1 cm. The results are shown in Table II. The value of the extinction coefficients were deduced from reference 18.

TABLE II

λ Å	ϵ ($\frac{\text{cm mol}}{\text{liter}}$) ⁻¹	$i \times 10^{+8}$ amp.	Current ratio relative to $i(2650 \text{ Å})$	relative intensities relative to $I_0(2650 \text{ Å})$
3020	8.2×10^2	5400	8.18	8.26
2970	7.8×10^2	2600	3.94	3.98
2890	5.8×10^2	600	0.91	0.96
2800	6.2×10^2	500	0.76	0.79
2650	10^3	660	1	1

Two other independent methods for the determination of the relative intensities of the Hg lines were applied, and the results were in agreement with those in Table II. The second method was by using a thin film of anthracene and consequently measuring the currents recorded by the $\mu\mu$ ammeter, then taking the ratios in a similar fashion to what has been shown in Table II. The third method was a direct determination using a uv sensitive tube No. K1306. Correction has been made for the small variation in sensitivity from the sensitivity curve of the tube S-13. The relative intensities of the Hg lines in question relative to $I_0(2650 \text{ Å})$ are shown in Table III.

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Two other independent methods for the determination of the relative intensities of the Hg lines were applied, and the results were in agreement with those in Table II. The second method was by using a thin film of anthracene and consequently measuring the currents recorded by the μA ammeter, then taking the ratios in a similar fashion to what has been shown in Table II. The third method was a direct determination using a uv sensitive tube No. K1306. Correction has been made for the small variation in sensitivity from the sensitivity curve of the tube S-13. The relative intensities of the Hg lines in question relative to $I_0(2650 \text{ Å})$ are shown in Table III.

TABLE III

λ Å	Using Tube K1306	Using anthracene film
3020	8.87	8.76
2970	4.38	4.48
2890	1.01	1.09
2800	.870	.935
2650	1	1

c) Determination of the relative efficiency of the photomultiplier.

The sensitivity of the photomultiplier tube (6342) used in our experiments is not constant in the regions of the fluorescence of the anthracene and that of the naphthalene. The relative efficiency of the tube in both regions, therefore, has to be determined. Such a determination can be made easily with the aid of a second tube which is equally sensitive in the two regions. The tube (K 1306) has almost equal sensitivity, and therefore it can serve for this purpose. The correction for the variation in sensitivity of the (K 1306) tube was made from its sensitivity curve (S-13; RCA Handbook HB-3 vol. 3-4)

Let us suppose we use a solution of naphthalene and a solution of anthracene in some convenient solvent like normal hexane. When the solution is introduced in the place of the sample in Fig. 2, and we take two different sets of readings using both tubes in rapid succession

then we can say that the number of quanta (N) received by either tube are the same. N is also proportional to the corresponding current recorded and divided by the sensitivity of the tube, i.e.

$$N_n = \frac{in}{S_n} = \frac{in'}{S'n'} \quad \text{-----}(6)$$

Also

$$N_a = \frac{ia}{S_a} = \frac{ia'}{S_a'} \quad \text{-----}(7)$$

where i, S represent photomultiplier current and sensitivity, the prime referred to tube (K1306), and a, n denote anthracene, naphthalene respectively.

$$\frac{S_n}{S_a} = \left(\frac{in}{ia}\right) \left(\frac{ia'}{in'}\right) \left(\frac{S_n'}{S_a'}\right) \quad \text{-----}(8)$$

The relative efficiency can be determined. It has to be mentioned here that this determination is irrespective of any correction factors such as , glass filter, quantum efficiency, reabsorption, concentration dependence, geometrical factor, ...etc. To get $\frac{S_n'}{S_a'}$ we refer to the tube sensitivity (S-13), and we multiply it by the fluorescence spectrum¹⁹ of naphthalene and anthracene solutions in normal hexane. The ratio of the resultant area to the total area could then be determined which give the relative sensitivity in the anthracene and the naphthalene fluorescence regions, as shown in Fig. 6, and Fig. 7 respectively using results of Fig. 6 and Fig. 7 $\frac{S_n'}{S_a'}$ is equal to $\frac{.72}{.96}$.

Solutions with normal hexane were prepared and the experiment was repeated for a second time using other freshly prepared solutions. Data and results as calculated from equation (8) are given in Table IV. One exciting line could give us all the information for such a determi-

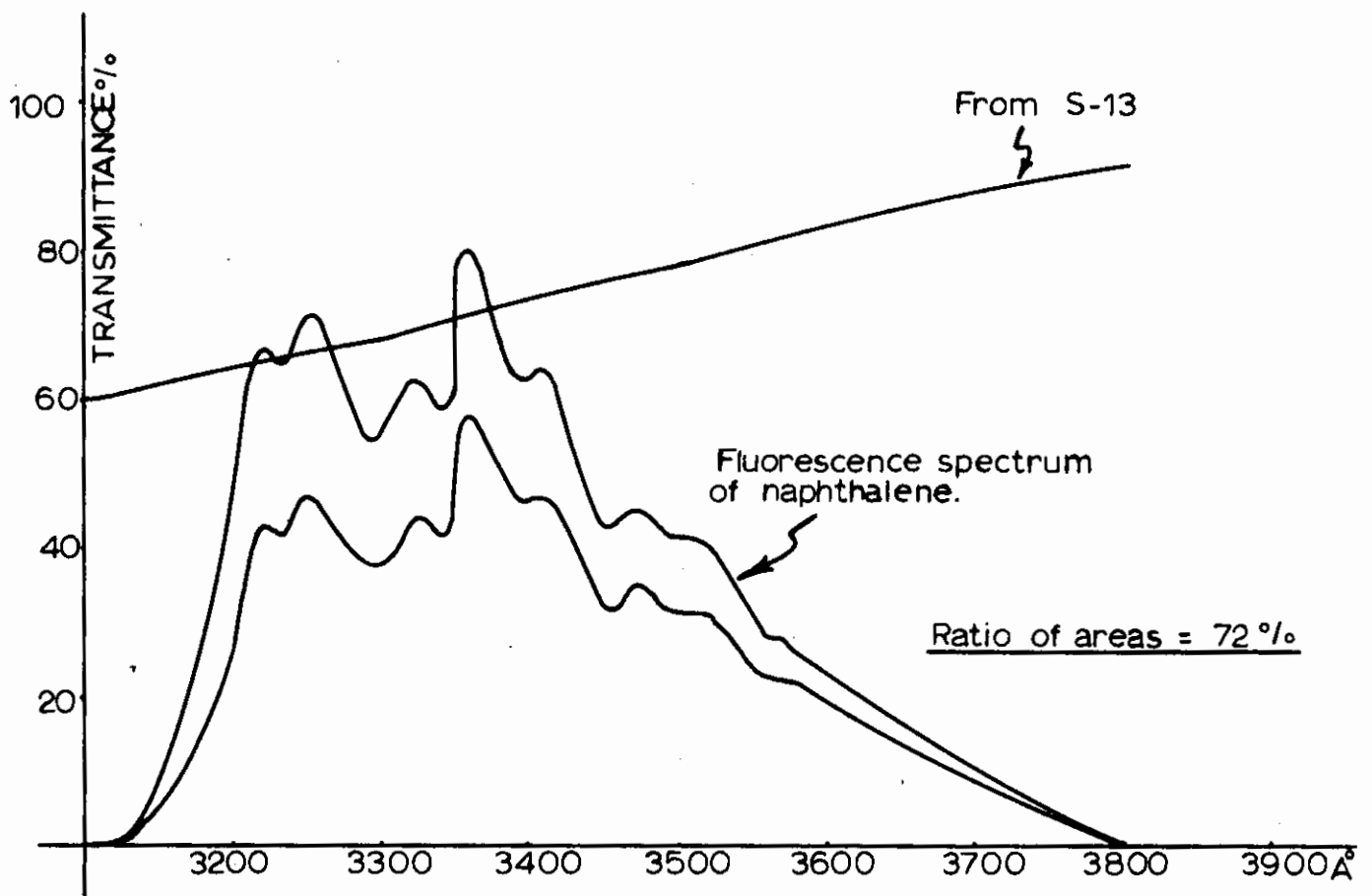
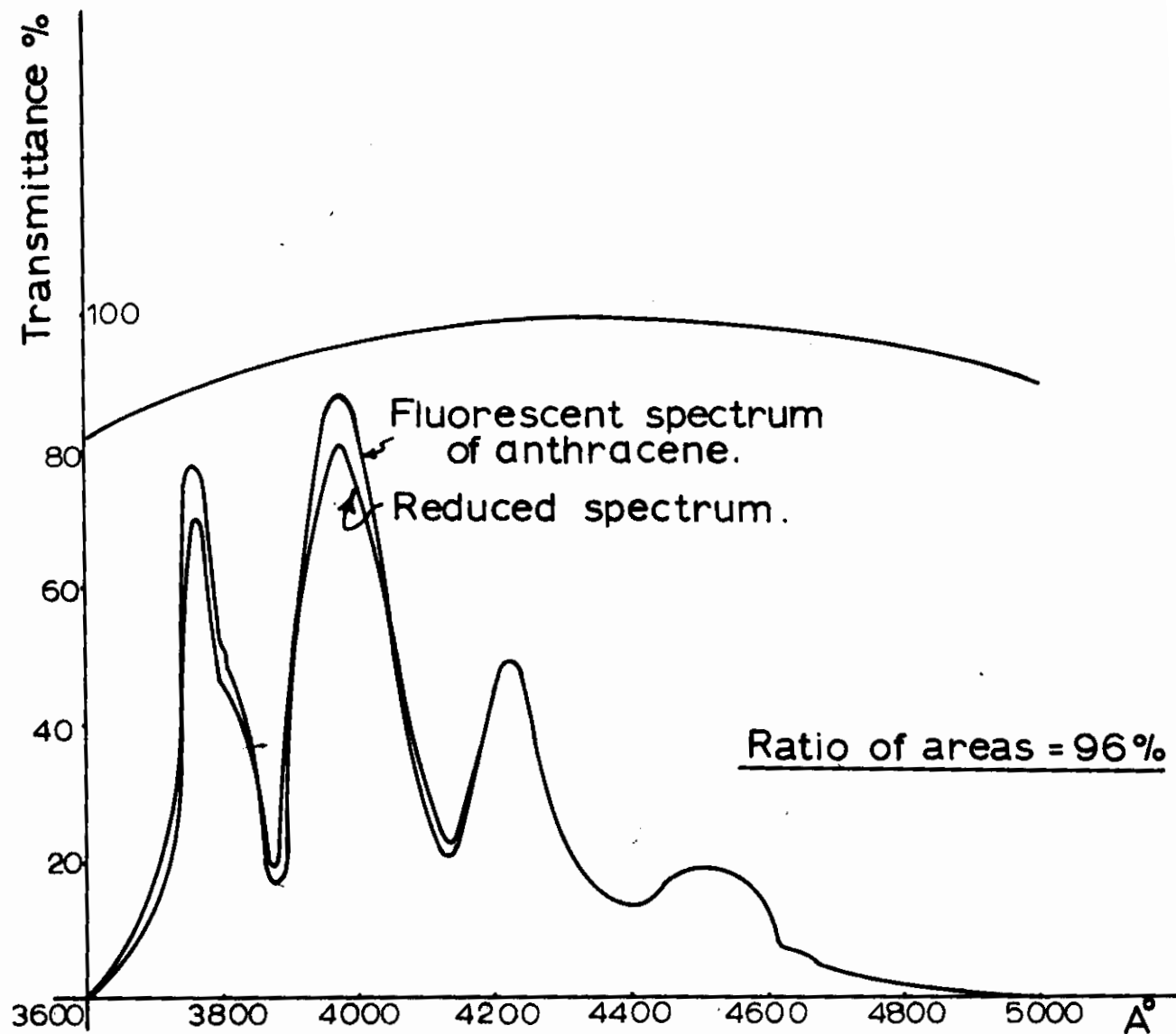


FIG. 6.

FIG. 7

nation, but to get rather a better check on our experimental results four different exciting lines were used. The lines are the 2970, 2890, 2000 and 2650 Å. The final result of the relative sensitivity is found by taking the average over all the eight observations.

TABLE IV

Tube 6342		Tube K 1306		Sn/Sa
$i_n \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$i_n^t \times 10^{+8}$ amp.	$i_a^t \times 10^{+8}$ amp.	
55.0	920	171	1956	0.51
15.4	200	46.0	416	0.52
13.3	170	39.0	336	0.51
15.4	200	43.0	416	0.52
73.0	443	143	558	0.48
21.5	81.2	43.8	97.3	0.44
19.6	60.0	37.5	73.2	0.48
18.5	84.0	40.5	114	0.46

$$\text{Average } \left(\frac{S_n}{S_a} \right) = 0.49$$

An attempt was made to determine the relative sensitivity of the photomultiplier using the quantum yields of naphthalene and anthracene. However, it was found that there seems to be total disagreement on the actual quantum yield of anthracene. The values range from 0.46^{19} to 0.17^{20} . Furthermore reabsorption of fluorescence is a serious difficulty. Hence this approach could not be used.

RESULTS

The major part of our experimental work was the study of the effect of the impurity concentration on the migration and transmission of the excitation energy from the base material (naphthalene) to the impurity (anthracene). Grown crystals and micro-crystalline sublimed films (see experimental) were examined. The glass filter behind the sample was kept in the same position during all the experimental measurements. The other filter (Kodak 50) was introduced whenever it was required to stop the naphthalene fluorescence from reaching the photomultiplier detector.

When the sample is irradiated by the exciting light its emission is composed of the naphthalene fluorescence and anthracene fluorescence.

Let i be the current detected in the presence of the glass filter only, and i_a when the second filter is introduced, then,

$$i = i_a' + i_n \quad \text{-----}(9)$$

where

$$i_a' = \frac{i_a}{F}$$

i_a' , i_n are the currents detected by the photomultiplier which are due to the anthracene and naphthalene fluorescence transmitted by the glass filter, and F is the transmission of the (Kodak No. 50) filter. Suppose now that the glass filter is removed, then i_a , i_n will have the values $\frac{i_a'}{G_a}$, $\frac{i_n}{G_n}$, where G_a , G_n are the glass transmission of the anthracene and the naphthalene fluorescence. Using equation (9) we see that

$$\frac{i_n}{G_n} = \left(i - \frac{i_a}{F} \right) \times \frac{1}{G_n}, \quad \text{-----}(10)$$

and

RESULTS

The major part of our experimental work was the study of the effect of the impurity concentration on the migration and transmission of the excitation energy from the base material (naphthalene) to the impurity (anthracene). Grown crystals and micro-crystalline sublimed films (see experimental) were examined. The glass filter behind the sample was kept in the same position during all the experimental measurements. The other filter (Kodak 50) was introduced whenever it was required to stop the naphthalene fluorescence from reaching the photomultiplier detector.

When the sample is irradiated by the exciting light its emission is composed of the naphthalene fluorescence and anthracene fluorescence.

Let (i) be the current detected in the presence of the glass filter only, and i_a when the second filter is introduced, then,

$$i = i_a' + i_n \quad \text{-----(9)}$$

where

$$i_a' = \frac{i_a}{F}$$

i_a' , i_n are the currents detected by the photomultiplier which are due to the anthracene and naphthalene fluorescence transmitted by the glass filter, and F is the transmission of the (Kodak No. 50) filter. Suppose now that the glass filter is removed, then i_a , i_n will have the values $\frac{i_a'}{G_a}$, $\frac{i_n}{G_n}$, where G_a , G_n are the glass transmission of the anthracene and the naphthalene fluorescence. Using equation (9) we see that

$$\frac{i_n}{G_n} = \left(i - \frac{i_a}{F}\right) \times \frac{1}{G_n} \quad \text{-----(10)}$$

and

$$\frac{i_a'}{G_a} = \frac{i_a}{F G_a} \quad \text{-----(11)}$$

From (10) and (11)

$$\frac{\left(\frac{i_a'}{G_a}\right)}{\left(\frac{i_n}{G_n}\right)} = \frac{i_a G_n}{F G_a \left(i - \frac{i_a}{F}\right)} \quad \text{-----(12)}$$

To get the ratio of the anthracene fluorescence to that of the naphthalene fluorescence $\left(\frac{J_a}{J_n}\right)$ we have to multiply equation (12) by $\frac{S_n}{S_a}$.

$$\therefore \frac{J_a}{J_n} = \frac{i_a G_n \frac{S_n}{S_a}}{F G_a \left(i - \frac{i_a}{F}\right)} \quad \text{-----(13)}$$

Substituting the values of the constants; G_n , G_a , $\frac{S_n}{S_a}$, and F which are; 0.615, 0.90, 0.49 and 2.64×10^{-2} respectively we get

$$\frac{J_a}{J_n} = \frac{12.7 i_a}{i - 37.9 i_a} \quad \text{-----(14)}$$

In Table V a complete set of the original data is given as well as $\frac{J_a}{J_n}$ as calculated from equation (14) for different concentrations of the impurity (C_p).

TABLE V. A complete set of the original data including the currents i , i_a and the percentage of J_a/J_n at different impurity concentrations (cp). The values are arranged in order as obtained for the exciting 3020, 2970,²⁸⁹⁰ 2810 and 2650 Å respectively at room temperature.

$$c_p = 0 \text{ mol./mol.}$$

Grown Crystals			Sublimed films		
$i \times 10^{+8}$ amp	$i_a \times 10^{+8}$ amp	100 J_a/J_n	$i \times 10^{+8}$ amp	$i_a \times 10^{+8}$ amp	100 J_a/J_n
1426	2.33	2.2	2225	2.78	1.7
655.1	1.10	2.3	1064	1.55	2.0
165.8	0.27	2.2	272.0	0.39	1.9
139.6	0.24	2.3	235.0	0.33	1.9
164.6	0.22	1.8	285.5	0.37	1.7
				Thickness \sim 6 μ	
1984	3.38	2.3	2491	4.18	2.3
773.0	1.35	2.4	1235	2.45	2.7
196.0	0.29	2.7	307.0	0.49	2.2
169.0	0.29	2.2	257.0	0.41	2.2
215.0	0.27	1.7	316.5	0.47	2.0
				Thickness \sim 5 μ	
1305	1.87	1.9	2391	3.28	1.8
605.4	0.90	2.0	1196	1.55	1.7
155.8	0.19	1.6	307.0	0.34	1.5
135.6	0.19	1.9	247.0	0.29	1.6
157.4	0.21	1.8	291.0	0.31	1.4
				Thickness \sim 5.5 μ Av. 1.9	

$c_p = 0 \text{ mol./mol. (cont'd)}$

Grown Crystals

$i \times 10^{+8} \text{ amp}$	$i_a \times 10^{+8}$	$100 J_a/J_n$
1985	1.93	1.3
934.0	1.05	1.5
242.0	0.29	1.6
217.0	0.29	1.8
267.0	0.27	1.3
1141	1.98	2.4
536.0	0.95	2.4
137.0	0.22	2.2
117.4	0.17	1.8
146.5	0.19	1.7
		Av = 2.0

$$c_p = 7.2 \times 10^{-8} \text{ mol./mol.}$$

Grown Crystals

Sublimed films

$i \times 10^{+8} \text{ amp}$	$i_a \times 10^{+8} \text{ amp.}$	$100J_a/J_n$	$i \times 10^{+8} \text{ amp.}$	$i_a \times 10^{+8} \text{ amp}$	$100J_a/J_n$
1241	3.48	4.0	2590	3.48	1.8
566.0	1.65	4.2	1245	1.45	1.5
142.0	0.37	3.7	307.0	0.29	1.2
122.0	0.34	4.0	252.0	0.24	1.4
146.5	0.32	3.0	296.0	0.27	1.2
			Thickness $\approx 3.8\mu$		av = 1.4
1491	4.08	3.9			
666.0	1.75	3.7			
167.0	0.39	3.2			
142.0	0.34	3.3			
176.0	0.42	3.3			
1541	3.68	3.3			
736.0	1.35	2.5			
181.0	0.30	3.0			
162.0	0.29	2.2			
200.0	0.37	2.5			
		av = 3.3			

$$c_p = 3.6 \times 10^{-7} \text{ mol/mol.}$$

Grown Crystal

Sublimed Film

$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp	$100J_a/J_n$	$i \times 10^{+8}$ amp	$i_a \times 10^{+8}$ amp	$100J_a/J_n$
1821	0.37	8.1	1936	5.06	3.7
852.0	4.65	8.7	1034	3.04	4.2
226.0	1.29	9.2	269.0	0.79	4.2
196.0	1.09	8.9	237.0	0.69	4.1
236.0	1.27	8.5	278.0	0.77	3.9
				Av =	4.0
				Thickness $\sim 3.4\mu$	
1440	9.48	11.1			
705.0	5.18	12.8			
187.0	1.39	13.1			
167.0	1.19	12.3			
196.0	1.27	10.8			
1642	9.88	9.8			
807	5.05	10.4			
213	1.34	10.4			
185	1.22	11.1			
217.5	1.32	9.9			
1391	8.68	10.3			
656.0	4.75	12.6			

$$c_p = 3.6 \times 10^{-7} \text{ mol./mol. (cont'd)}$$

Grown Crystal

$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$
172.0	1.24	12.5
157.0	1.11	12.2
191.5	1.17	10.1
1520	9.18	9.9
735.0	4.25	9.3
187.0	1.09	9.4
162.0	0.99	10.1
191.0	1.07	9.1
	Av. =	<u>10.4</u>

$$c_p = 7.2 \times 10^{-7} \text{ mol.}/\text{mol.}$$

Grown Crystals

Sublimed Films

$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$	$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$
1907	15.6	15.0	2099	6.00	4.2
905.6	7.25	14.6	975.0	3.13	3.6
247.8	1.95	14.2	249.6	0.79	4.6
211.6	1.69	14.5	212.5	0.67	4.5
250.5	2.02	14.7	256.4	0.78	4.4
			Thickness $\sim 5.3\mu$		
1583	12.81	14.7	1095	3.60	4.7
733.4	5.55	13.5	507.0	1.94	5.6
200.0	1.58	14.3	131.0	0.50	5.6
171.7	1.38	14.6	112.0	0.45	6.0
209.3	1.62	13.9	137.5	0.49	5.2
			Thickness $\sim 5.4\mu$		
1841	15.9	16.2	2992	8.38	4.0
865.0	7.05	14.9	1497	4.25	4.0
229.0	1.89	15.2	377.0	0.99	3.7
197.0	1.59	14.3	297.0	0.79	3.7
236.0	1.97	15.4	357.0	0.92	3.6
			Thickness $\sim 11\mu$		
1490	11.2	13.4	3090	7.08	3.2
696.0	5.35	13.7	1545	3.45	3.1
187.0	1.49	14.5	387.0	0.79	2.8
162.0	1.29	14.4	335.0	0.66	2.7
196.0	1.57	14.6	386.0	0.67	2.4
			Thickness $\sim 3.5\mu$		

$$c_p = 7.2 \times 10^{-7} \text{ mol./mol.}$$

Grown Crystals

Sublimed Films

$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$	$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$
1907	15.6	15.0	2089	6.00	4.1
905.6	7.25	14.6	975.0	3.13	3.6
247.8	1.95	14.2	249.6	0.79	4.6
211.6	1.69	14.5	212.5	0.67	4.5
250.5	2.02	14.7	256.4	0.78	4.4
			Thickness $\sim 5.3\mu$		
1583	12.81	14.7	1095	3.60	4.7
733.4	5.55	13.5	507.0	1.94	5.6
200.0	1.58	14.3	131.0	0.50	5.6
171.7	1.38	14.6	112.0	0.45	6.0
209.3	1.62	13.9	137.5	0.49	5.2
			Thickness $\sim 5.4\mu$		
1841	15.9	16.2	2992	8.38	4.0
865.0	7.05	14.9	1497	4.25	4.0
229.0	1.89	15.2	377.0	0.99	3.7
197.0	1.59	14.3	297.0	0.79	3.7
236.0	1.97	15.4	357.0	0.92	3.6
			Thickness $\sim 11\mu$		
1490	11.2	13.4	3090	7.08	3.2
696.0	5.35	13.7	1545	3.45	3.1
187.0	1.49	14.5	387.0	0.79	2.8
162.0	1.29	14.4	335.0	0.66	2.7
196.0	1.57	14.6	386.0	0.67	2.4
			Thickness $\sim 3.5\mu$		

$$c_p = 7.2 \times 10^{-7} \text{ mol./mol. (cont'd)}$$

Grown Crystals

$i \times 10^8$ amp	$i_a \times 10^8$ amp.	$100J_a/J_n$	$i \times 10^8$ amp.	$i_a \times 10^8$ amp.	$100J_a/J_n$
1590	12.9	14.8	1089	2.56	3.3
795.0	6.65	15.5	545.6	1.25	3.2
222.0	1.89	15.9	138.1	0.32	3.2
192.0	1.59	15.2	120.7	0.30	3.5
241.0	1.97	15.0	147.1	0.32	3.0
					av. 3.9
			Thickness = 3.0 μ		
2091	17.5	15.5			
947.0	7.95	15.6			
259.0	2.19	15.7			
223.0	1.89	15.9			
272.0	2.27	15.5			
		av. = 14.8			

$$c_p = 1.44 \times 10^{-6} \text{ mol.}/\text{mol.}$$

Grown Crystals

$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100 J_a/J_n$
4600	55.0	27.8
2350	25.0	22.8
640	7.0	23.7
550	6.0	23.7
690	6.6	24.0
		av. = 24.4

$$c_p = 2.4 \times 10^{-6} \text{ mol./mol.}$$

Grown Crystals

Sublimed Films

$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$	$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$
2100	24.5	26.6	5100	50.5	20.0
1000	12.0	28.0	2550	26.0	21.1
270.0	3.3	29.0	670.0	6.7	20.5
235.0	2.9	29.5	580.0	5.8	20.4
270.0	3.2	26.9	640.0	6.4	20.3
			Thickness $\sim 3.2\mu$		
3100	41.5	32.3	4700	28.4	9.9
1550	19.9	31.5	2500	16.0	10.7
420.0	5.4	31.9	660.0	4.2	10.7
350.0	4.6	33.2	560.0	3.7	11.2
410.0	5.2	30.9	620.0	3.9	10.5
			Thickness $\sim 5.4\mu$		
2940	38.5	33.0	7000	55.6	14.5
1450	18.8	32.3	3600	30.6	16.0
390.0	5.2	34.2	920	8.0	16.5
320.0	4.4	34.3	780	6.8	16.6
390.0	5.0	31.7	890.0	7.2	14.8
			Thickness $\sim 4.5\mu$		
3100	37.6	28.6	4600	35.6	13.9
1500	17.6	26.6	2300	18.6	14.8
400.0	4.8	28.0	620.0	4.8	14.0
350.0	4.1	26.5	530.0	4.1	13.9
400.0	4.8	28.0	610.0	4.7	13.9
		av. = 30.1			av. = 15.2

$$c_p = 7.2 \times 10^{-6} \text{ mol./mol.}$$

Grown Crystals

Sublimed Films

$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$	$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$
4200	63.8	45.5	5500	65.0	27.2
2000	29.8	43.4	2650	31.0	26.6
640	7.8	40.6	670.0	7.2	23.0
470	6.7	39.4	560.0	6.0	22.9
560	8.0	39.7	650.0	7.0	23.1
			Thickness $\sim 4.3\mu$		
4500	65.9	41.8	4800	46.8	19.6
2150	30.8	39.8	2220	20.3	17.8
570.0	8.1	39.1	540.0	4.9	17.6
500.0	7.2	40.3	470.0	4.0	16.0
590.0	8.3	38.3	540.0	4.8	17.0
			Thickness $\sim 6.0\mu$		
4400	68.8	48.8	4100	35.2	16.2
2100	32.8	46.6	2400	20.2	15.7
560.0	8.7	47.8	620.0	5.9	18.9
490.0	7.2	42.1	540.0	4.9	17.6
560.0	8.7	47.8	600.0	5.2	16.3
			Thickness $\sim 3.7\mu$		
4100	58.7	39.8			
1900	26.2	36.7			
500.0	7.1	39.0			
430.0	6.0	37.5			
510.0	7.1	37.4			
	av.	41.7			

$$c_p = 2.4 \times 10^{-5} \text{ mol./mol.}$$

Grown Crystals

Sublimed Films

Grown Crystals			Sublimed Films		
$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$	$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$
3800	63.1	56.8			
1850	28.6	47.4			
490.0	7.4	44.8			
430.0	6.4	43.5			
500	7.6	45.5			
4100	69.0	59.0	8500	104	28.9
2050	33.0	52.4	3800	44.0	26.2
550.0	8.5	47.4	950.0	11.0	26.3
470.0	7.5	51.1	790.0	8.5	23.1
550.0	8.5	47.4	940.0	11.0	26.8
			Thickness $\sim 6.4\mu$		
47.00	82.0	65.4	7500	109	40.9
2400	38.0	50.0	3800	56.2	42.8
630.0	10.0	50.6	1000	14.5	40.9
550.0	8.4	46.0	830.0	12.1	41.5
630.0	10.1	51.8	970.0	13.7	38.5
		av. = 50.6			av. = 33.6

$$c_p = 7.2 \times 10^{-5} \text{ mol./mol.}$$

Grown Crystals			Sublimed Crystals		
$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$	$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$
			7185	102.0	38.1
			3694	51.0	36.9
			947.0	13.6	40.4
			817.0	11.7	39.8
			955.0	13.7	39.9
			Thickness $\sim 2.5\mu$		
4980	80.3	52.6	7183	112.0	48.4
2450	40.3	55.4	3593	57.0	50.5
645.0	10.7	56.9	977.0	15.2	48.0
565.0	9.0	50.9	857.0	13.1	46.0
643.0	10.7	57.4	1035	16.1	48.0
		av. = 54.6			43.7
			Thickness $\sim 4.5\mu$		

$$c_p = 2.4 \times 10^{-4} \text{ mol./mol.}$$

Grown Crystals

Sublimed Film

$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$	$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$
5700	101.1	68.5	11000	180.0	54.5
2650	46.1	65.0	5300	84.2	50.6
710.0	11.9	57.9	1350	20.2	43.9
610.0	10.2	58.3	1100	17.2	48.6
710.0	12.2	62.6	1300	20.1	47.3
			Thickness $\sim 7.0\mu$		
5800	97.0	58.0	8200	98.8	28.1
2820	47.1	57.9	3900	45.8	26.8
760.0	12.7	57.8	930.0	11.0	27.2
650.0	10.9	58.3	800.0	9.0	24.8
750.0	12.5	57.5	910.0	10.8	27.3
			Thickness $\sim 5.6\mu$		
6000	107.0	69.9	5800	79.0	35.6
2950	53.0	71.5	2700	37.0	36.1
790.0	14.0	68.7	670.0	8.9	33.9
700.0	12.0	62.0	540.0	7.3	35.2
800.0	14.0	66.1	650.0	8.4	32.2
			Thickness $\sim 5.5\mu$		
5400	88.2	53.9	5082	75.2	42.7
2750	45.2	55.3	2640	38.3	40.8
730.0	12.0	55.2	686.0	9.8	39.3
640.0	10.4	53.6	570.0	8.4	42.4
730.0	12.0	55.2	714.0	10.4	41.2
		av. = 60.7			av. = 37.9
			Thickness $\sim 1\mu$		

$$c_p = 4.8 \times 10^{-4} \text{ mol./mol.}$$

Grown Crystal

$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$
8800	162.0	77.3
4300	75.0	65.4
1150	20.0	64.8
1000	17.5	66.1
1180	21.0	69.4
		av. = 68.6

$$c_p = 7.2 \times 10^{-4} \text{ mol/mol.}$$

Grown Crystals

Sublimed Films

$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$	$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$
4990	85.4	61.7	12000	192	51.6
2450	43.4	68.4	5800	93.0	51.9
659.0	11.3	62.1	1500	24.0	51.6
579.0	9.8	57.5	1250	20.4	54.2
658.0	11.6	67.4	1520	25.0	55.4
		av. = 63.4			av. = 53.0
					Thickness $\sim 3.7\mu$

$$c_p = 1.44 \times 10^{-3} \text{ mol.}/\text{mol.}$$

Grown Crystal

$i \times 10^{+8} \text{ amp.}$	$i_a \times 10^{+8} \text{ amp.}$	$100J_a/J_n$
8500	147.0	63.7
4000	69.0	63.2
1030	18.0	65.7
900.0	16.0	69.2
1050	18.5	67.3
		<hr style="width: 20%; margin: auto;"/> av. = 65.8

$$c_p = 2.4 \times 10^{-3} \text{ mol./mol.}$$

Grown Crystal			Sublimed Film		
$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$	$i \times 10^{+8}$ amp.	$i_a \times 10^{+6}$ amp.	$100J_a/J_n$
6100	114.0	81.3	4900	80.0	54.4
3100	55.0	68.8	2400	39.0	53.7
810.0	14.4	69.2	600.0	9.6	51.6
700.0	12.4	68.6	490.0	7.8	51.0
790.0	14.2	71.6	590	9.5	52.4
				Thickness $\sim 8\mu$	
6400	119.0	80.0	5300	91.0	62.4
3200	56.0	66.0	2700	46.0	61.1
840.0	15.0	69.6	690	11.9	63.2
710.0	12.5	67.2	570	9.6	59.1
8300.0	14.7	68.4	650	11.1	61.5
				Thickness $\sim 8.3\mu$	
6400	119.0	80.0	7800	114.0	41.6
3200	56.0	66.0	3900	55.0	38.5
820.0	14.6	69.5	970.0	13.8	39.0
700.0	12.6	71.9	780.0	11.2	40.0
820.0	15.0	75.7	920.0	13.0	38.6
		av. = 71.5			av. = 51.2
				Thickness $\sim 5\mu$	

$$c_p = 3.6 \times 10^{-3} \text{ mol./mol.}$$

Grown Crystal

$i \times 10^{+8}$ amp.	$i_a \times 10^{+8}$ amp.	$100J_a/J_n$
10700	200	81.4
5400	100	78.9
1400	27	91.0
1240	24	92.2
1450	28	91.4
		av. = 87.0

$$c_p = 4.8 \times 10^{-3} \text{ mol.}/\text{mol.}$$

Grown Crystal

Sublimed Film

$i \times 10^{+8} \text{ amp.}$	$i_a \times 10^{+8} \text{ amp.}$	$100J_a/J_n$	$i \times 10^{+8} \text{ amp.}$	$i_a \times 10^{+8} \text{ amp.}$	$100J_a/J_n$
8200	165.0	107.8	6000	111.0	78.6
4100	84.0	116.4	3300	59.0	70.1
1120	22.5	106.9	840.0	15.6	79.6
980	19.8	109.5	720.0	12.6	65.9
1120	22.6	108.9	850.0	16.1	85.3
		av. = 110			av. = 75.9
				Thickness $\sim 5\mu$	

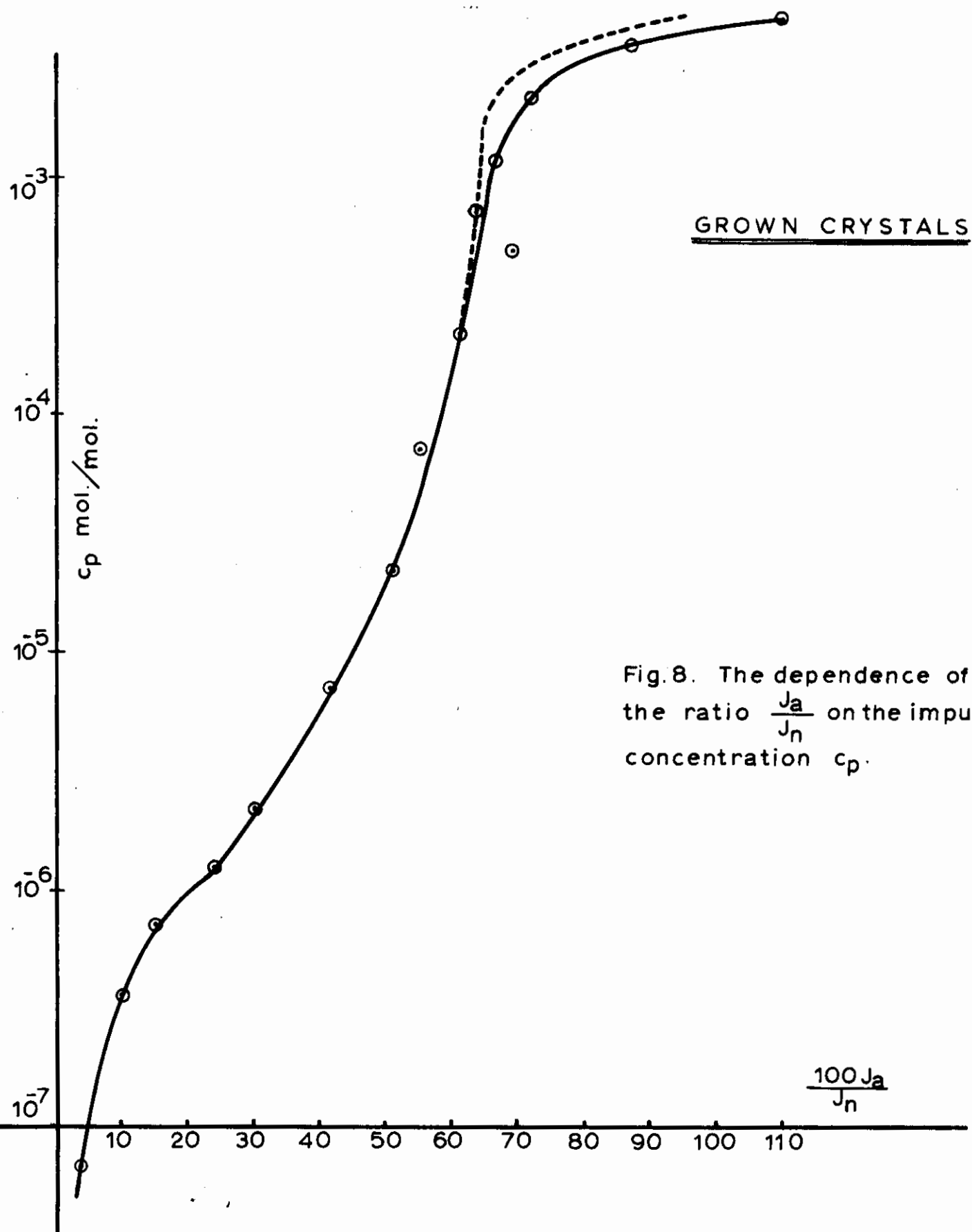
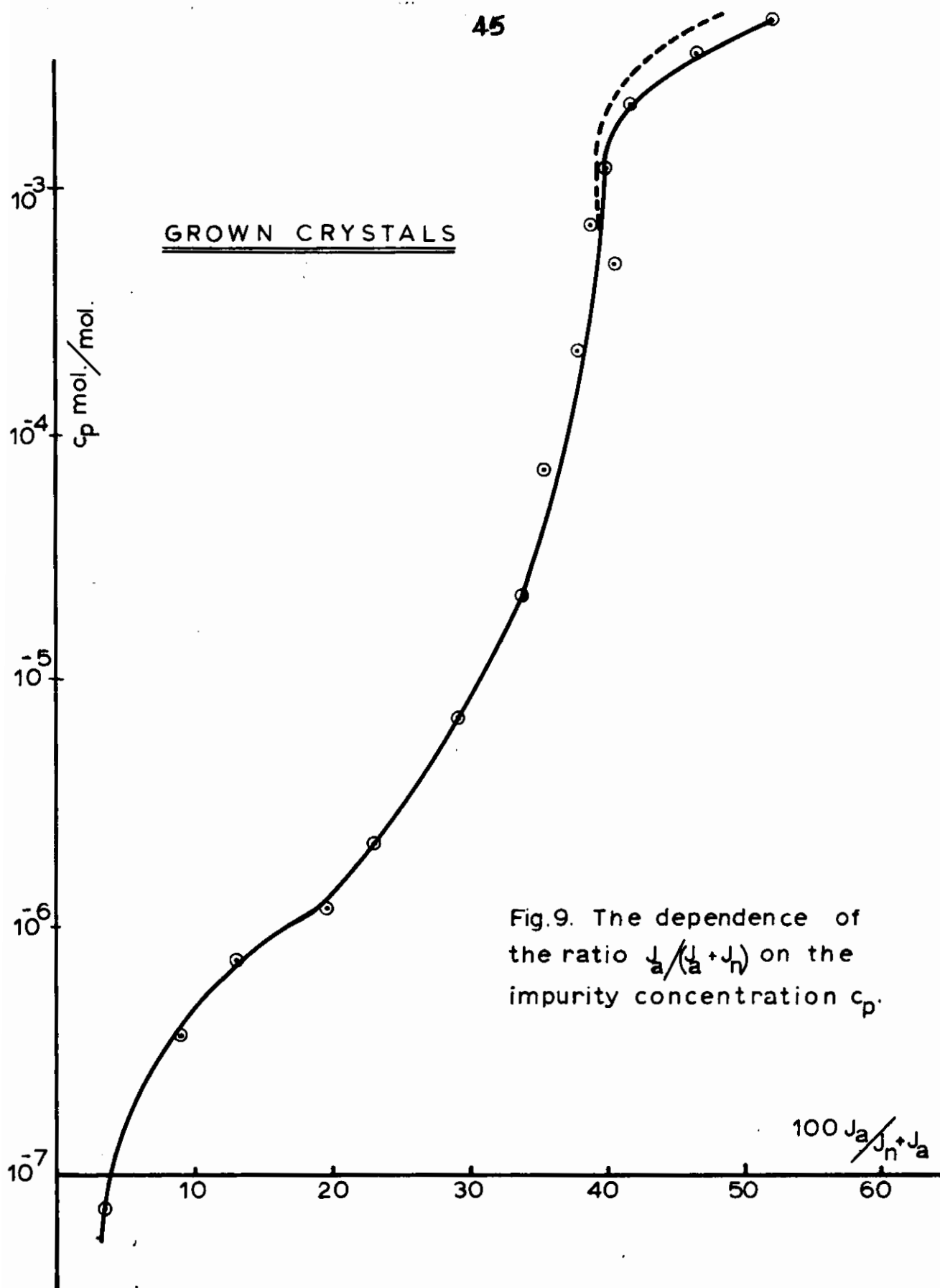


Fig.8. The dependence of the ratio $\frac{J_a}{J_n}$ on the impurity concentration c_p .



In Fig. 8 a plot of the concentration vs. the percentage of the average ratio $\frac{J_a}{J_n}$ is shown for the case of grown films. Fig. 9 shows a plot of the concentration vs $\frac{J_a}{J_a + J_n}$. For high concentrations it is probably important to correct the ratios $\frac{J_a}{J_n}$ for the fact that the anthracene might be excited directly by means of the exciting light. Wolf²¹ showed that the correction factor of the ratio $\frac{J_a}{J_n}$, call it (K) is related to the concentration (c_p) by the following relation:

$$c_p = 0.03 K$$

According to this the graphs shown in Fig. 8 and Fig. 9 were corrected and they are indicated by the dotted line.

Fig. 10 shows a similar graph plotted for the case of sublimed films.

Analysis of the data given in Table V shows that the first exciting line (3020 Å) yields a higher ratio (J_a/J_n). Compared with the rest this shows that there is a dependence on the wavelength of the exciting light. Fig. 11 shows that on the average the ratio J_a/J_n is smaller than the corresponding ones obtained when shorter wavelengths of the exciting light are used. To test this hypothesis in more detail experiments were performed using six different exciting wavelengths and different thicknesses of the sublimed films. The quantity of naphthalene used for growing the crystals was not the same. This was made in order to grow crystals of different thicknesses.

The thicknesses of the sublimed films were determined by means of a micro-balance. Crystals and sublimed films with no added impurity were examined only, so that no fluctuations in the ratio of $(\frac{J_a}{J_n})$ are produced which might due to different rate of sublimation of the impurity if added in larger quantities. The data are given in table VI.

Fig. 10 is a plot of the ratio $100 J_a/J_n$ vs concentration (c_p) in mole/mole for the sublimed films.

The graph shows :-

1. The ratios $100 J_a/J_n$ are smaller than the corresponding ratio for the grown crystal as in Fig. 8.
2. The points show considerable scattering with a large probable error as explained in page 66.
3. No plateau appears.

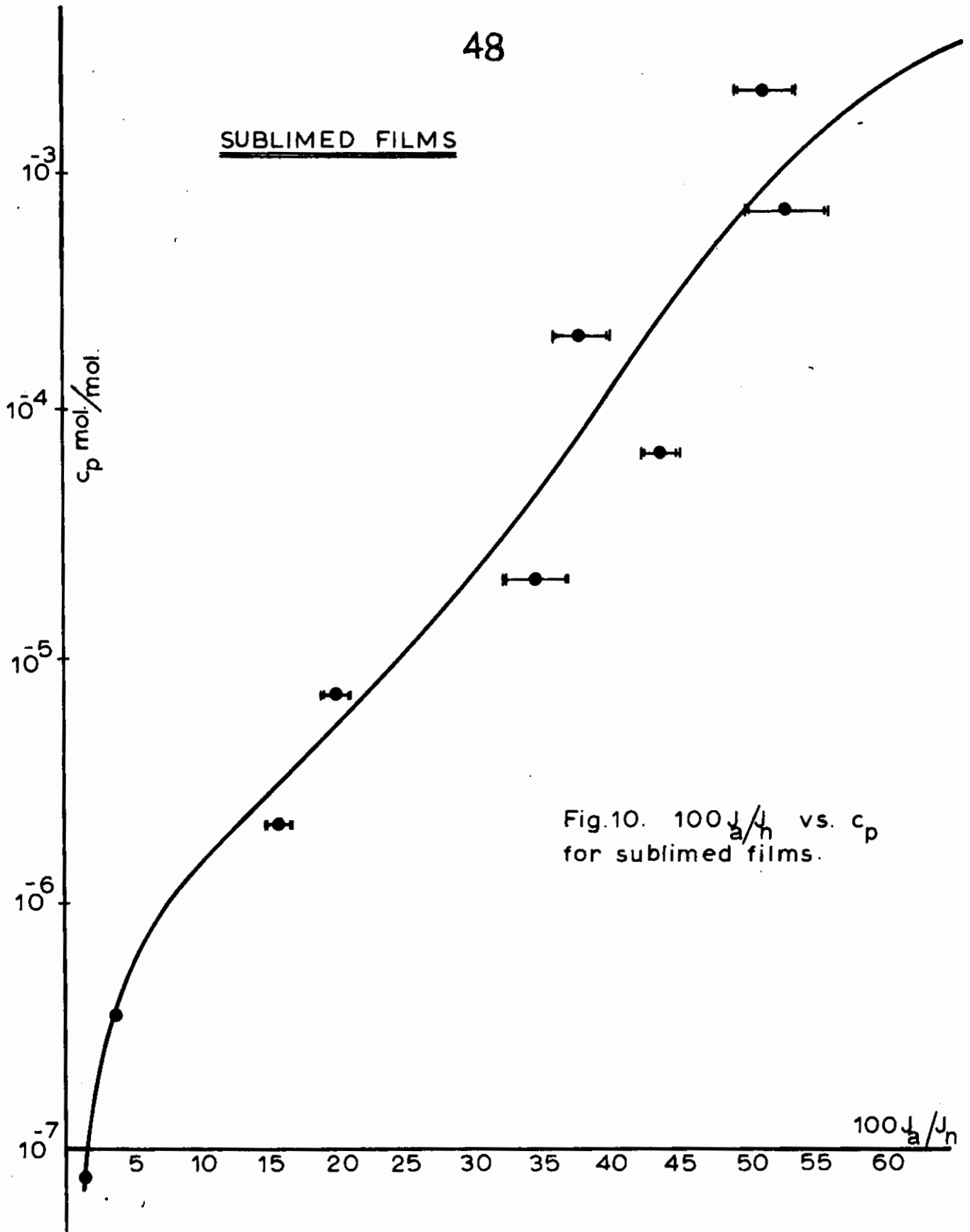
SUBLIMED FILMS

Fig.10. $100 J_a/J_n$ vs. c_p
for sublimed films.

Fig. 11 is a plot of $\frac{(J_a/J_n) \text{ at } \lambda = 2970 \text{ \AA}}{(J_a/J_n) \text{ at } \lambda = 3020 \text{ \AA}}$ at different concentrations (c_p) of the impurity. Since the extinction coefficient at $\lambda = 2970$ is higher than the corresponding one at $\lambda = 3020$, it is clear that the ratio J_a/J_n depends on the extinction coefficient of the exciting light.

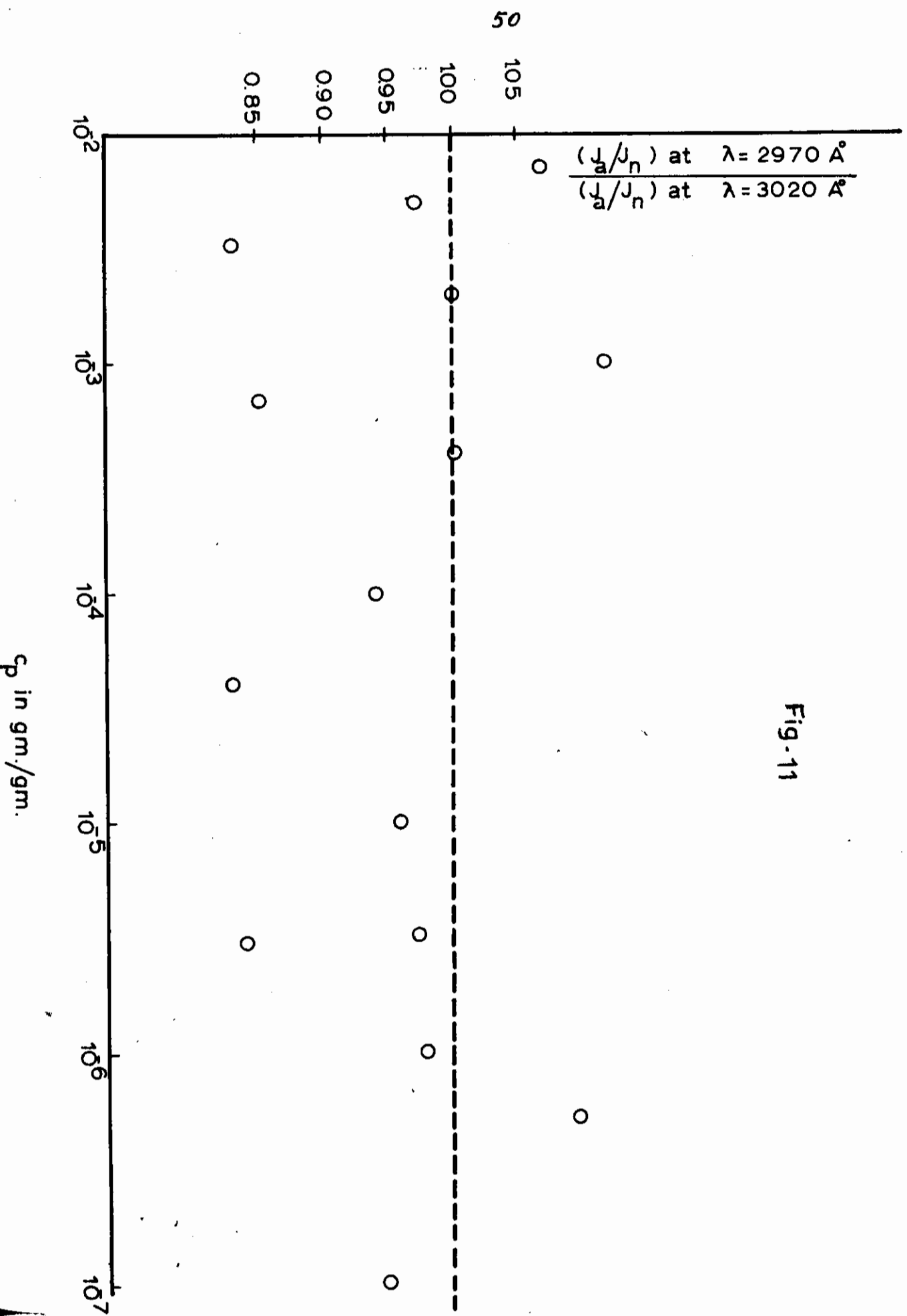


Fig. 11

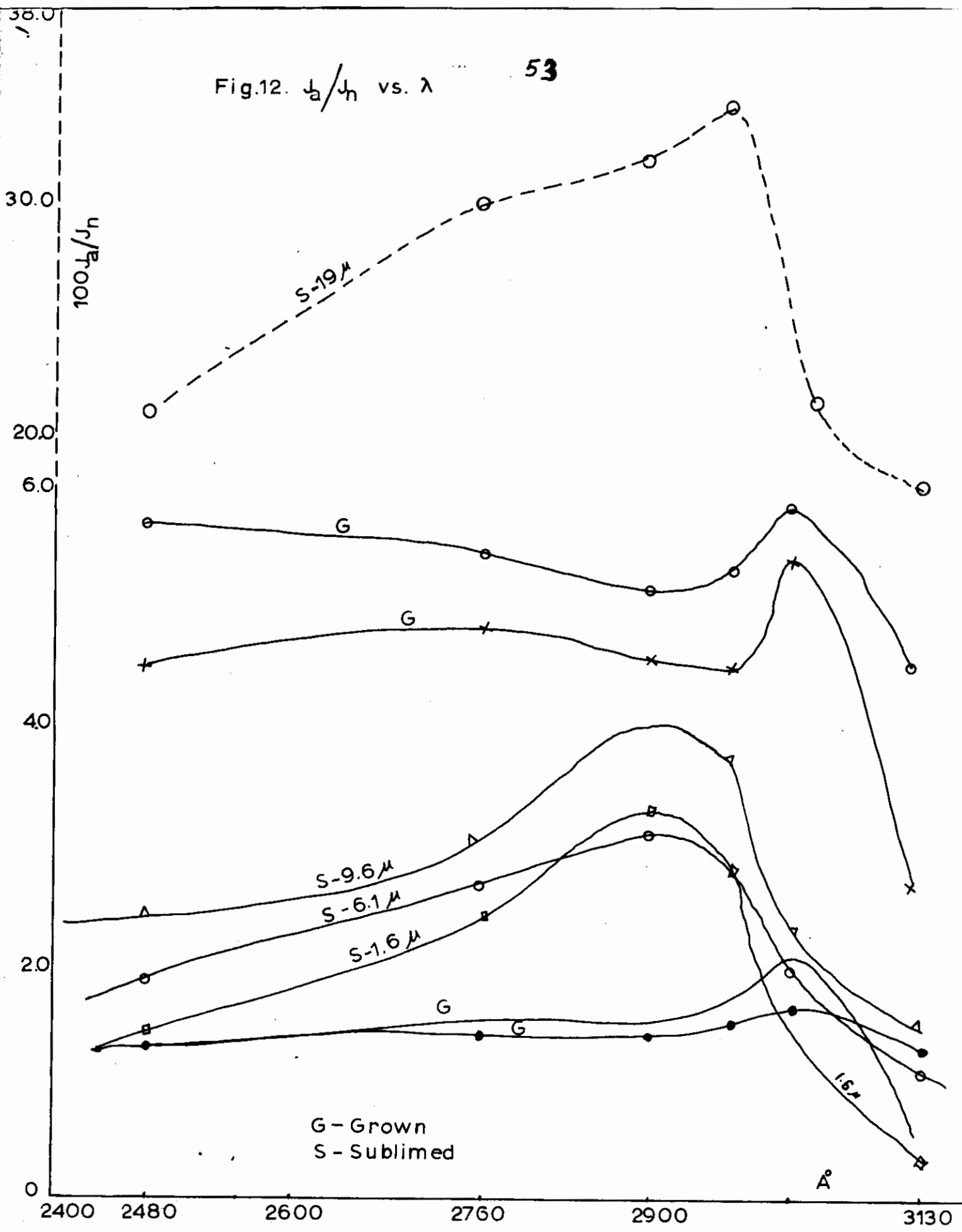
TABLE VI. A set of data for grown crystals and sublimed films with no added impurity at different wavelengths. The values of i , i_a are arranged in order for the exciting light of wavelengths 3130, 3020, 2970, 2900, 2760 and 2480 Å. (The glass filter was not used).

Grown Crystals			Sublimed Films		
$i \times 10^{+8}$ (amp)	$i_a \times 10^{+8}$ (amp)	$100 J_a / J_n$	$i \times 10^{+8}$ (amp)	$i_a \times 10^{+8}$ (amp)	$100 J_a / J_n$
13000	28.8	4.49	7000	49.3	18.0
3200	9.0	5.85	2150	17.3	21.6
1460	3.7	5.21	1200	12.9	34.0
370	0.9	4.97	310	3.2	30.0
420	1.1	5.40	280	2.8	23.0
110	0.3	5.65	58.5	0.5	
				Thickness 19 μ	
19500	25	2.50	7200	5.6	1.5
2900	7.6	5.40	1750	2.0	2.2
1420	3.1	4.42	800	1.5	3.7
360	0.8	4.50	200	0.4	4.0
380	0.9	4.83	205	0.3	2.9
90	0.2	4.51	44	.05	2.2
				Thickness 9.6 μ	
15000	11.3	1.44	11000	6.3	1.1
2950	3.2	2.10	2000	2.0	1.9
1460	1.3	1.71	900	1.3	2.8

Grown Crystals			Sublimed Films		
$i \times 10^{+8}$ (amp)	$i_a \times 10^{+8}$ (amp)	$100J_a/J_n$	$i \times 10^{+8}$ (amp)	$i_a \times 10^{+8}$ (amp)	$100J_a/J_n$
320	0.25	1.49	220	0.3	3.1
330	0.27	1.57	230	0.3	2.5
80	0.05	1.19	50	0.05	1.9
			Thickness 6.1μ		
14000	9.1	1.44	29000	4.0	0.26
2850	2.4	2.40	1550	1.2	1.48
1340	1.0	1.71	630	0.9	2.80
280	0.2	1.49	150	0.25	3.30
275	0.2	1.57	160	0.2	2.44
72	0.05	1.19	34	0.2	1.41
			Thickness 1.6μ		

Fig. 12 shows the dependence of the ratio of $\frac{J_a}{J_n}$ on the wavelengths of the exciting light for both the sublimed films and the grown crystals at different thicknesses. It can also easily be seen from the same set of graphs given in Fig. 12 that the ratios of $\frac{J_a}{J_n}$ depends on the thickness. Fig. 13 shows this dependence in more detail.

Fig.12. J_a/J_n vs. λ 53



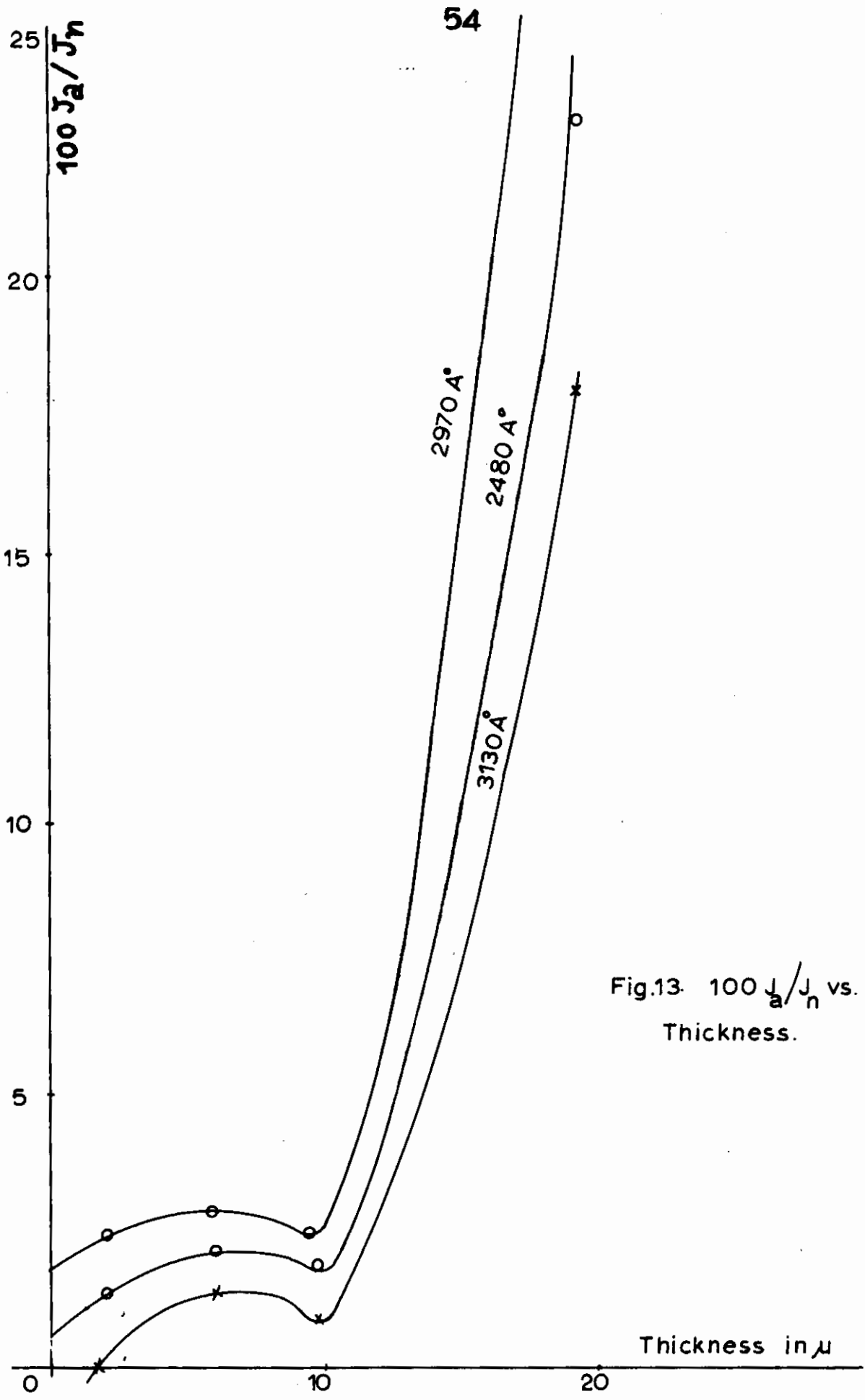


Fig.13. $100 J_a/J_n$ vs. Thickness.

Discussion of Results

The model adopted by Borisov and Vishnevski² is fairly simple. The excitons are assumed to diffuse throughout the crystal and to satisfy a diffusion equation. In the steady state

$$\frac{\partial n}{\partial t} = 0$$

where $n(x, t)$ is the exciton concentration as a function of time and as a function of only one dimension.

The diffusion equation

$$\frac{\partial n}{\partial t} = D \frac{d^2 n}{dx^2} + Ake^{-kx} - \frac{n}{\tau} = 0 \quad \text{-----(19)}$$

The second term refers to the generation of excitons, the term (n/τ) refers to the decay of the excitons by thermal quenching.

k = extinction coefficient for the crystal

τ = life time of the exciton

D = diffusion coefficient

A = constant with dimensions of $\frac{n}{\tau}$.

If one uses three different exciting light $\lambda_a, \lambda_b, \lambda_c$ and if a, b, c are the corresponding absorption coefficients. The solution² of the diffusion equation after applying the boundary conditions:

$$x = 0, \quad D \frac{dn}{dx} = q \cdot n(0)$$

where q = rate of the non-radiational capture of excitons on the surface of the crystal through which the excitation penetrates the crystal, and

$$x = \infty, \quad n = D \frac{dn}{dx} = 0.$$

can lead to an expression for the diffusion length of the excitons,

$$l = \sqrt{\tau D} = \frac{(1 - \alpha_{ac}) [c(1 - \alpha_{ab}) + b - a \alpha_{ab}] - (1 - \alpha_{ab}) [b(1 - \alpha_{ac}) + c - a \alpha_{ac}]}{b(1 - \alpha_{ab})(c - a \alpha_{ac}) - c(1 - \alpha_{ac})(b - a \alpha_{ab})} \quad \text{-----}(20)$$

where α_{ab} , α_{ac} , are the ratios of the intensity of luminescence for such wavelengths as $\alpha_{ab} = \frac{I_a}{I_b}$, $\alpha_{ac} = \frac{I_a}{I_c}$.

To determine the magnitude of l we must know the absorption coefficients of the naphthalene crystals for non-polarized light, and the relative intensities of the exciting light.

Agranovich and Faidysh⁷ considered the diffusion equation in the presence of an impurity concentration c_p . Let us consider the simplest case of the solution of the diffusion equation when only free excitons are considered and that the diffusion character of the localized ones is neglected. If the probability of capture of a free exciton (λ_0^2) is proportional to the impurity concentration we get

$$\lambda_0^2 = \mu_0 + \mu_1 c_p.$$

If J_a and J_n are proportional to the luminescence yield of the impurity and the base material respectively they find that:

$$J_n = \frac{A_1}{1 + \sqrt{\mu_0 + \mu_1 c_p}} + \frac{A_2}{(1 + \sqrt{\mu_0 + \mu_1 c_p}) \sqrt{\mu_0 + \mu_1 c_p}} + A_3$$

$$J_a = \frac{A_4 c_p}{(1 + \sqrt{\mu_0 + \mu_1 c_p}) \sqrt{\mu_0 + \mu_1 c_p}}, \quad \text{-----}(21)$$

where A_1, A_2, A_3, A_4 are constants independent of the impurity concentration. Then, letting

$$a_1 = \frac{A_1}{A_4}, \quad a_2 = \frac{A_2}{A_4}, \quad a_3 = \frac{A_3}{A_4}$$

Then

$$c_p \frac{J_n}{J_a} = (a_1 + a_3) \sqrt{\mu_0 + \mu_1 c_p} + a_3(\mu_0 + \mu_1 c_p) + a_2 \quad \text{-----}(22)$$

consider

$$\lim_{c_p \rightarrow \infty} \frac{J_n}{J_a} = a_3 \mu_1 = c_1 \quad \text{-----}(23)$$

which is independent of c_p .

For small $c_p \rightarrow 0$

$$c_p \frac{J_n}{J_a} = (a_1 + a_3) \sqrt{\mu_0} + a_3 \mu_0 + a_2 = c_2 \quad \text{-----}(24)$$

or

$$c_p \propto \frac{J_a}{J_n} \quad \text{-----}(25)$$

For small c_p but > 0 such that $\mu_0 > \mu_1 c_p$

$$\begin{aligned} \sqrt{\mu_0 + \mu_1 c_p} &= \mu_0 \left(1 + \frac{\mu_1 c_p}{\mu_0} \right)^{1/2} \\ &\approx \sqrt{\mu_0} \left(1 + \frac{\mu_1 c_p}{2\mu_0} \right) \quad \text{-----}(26) \end{aligned}$$

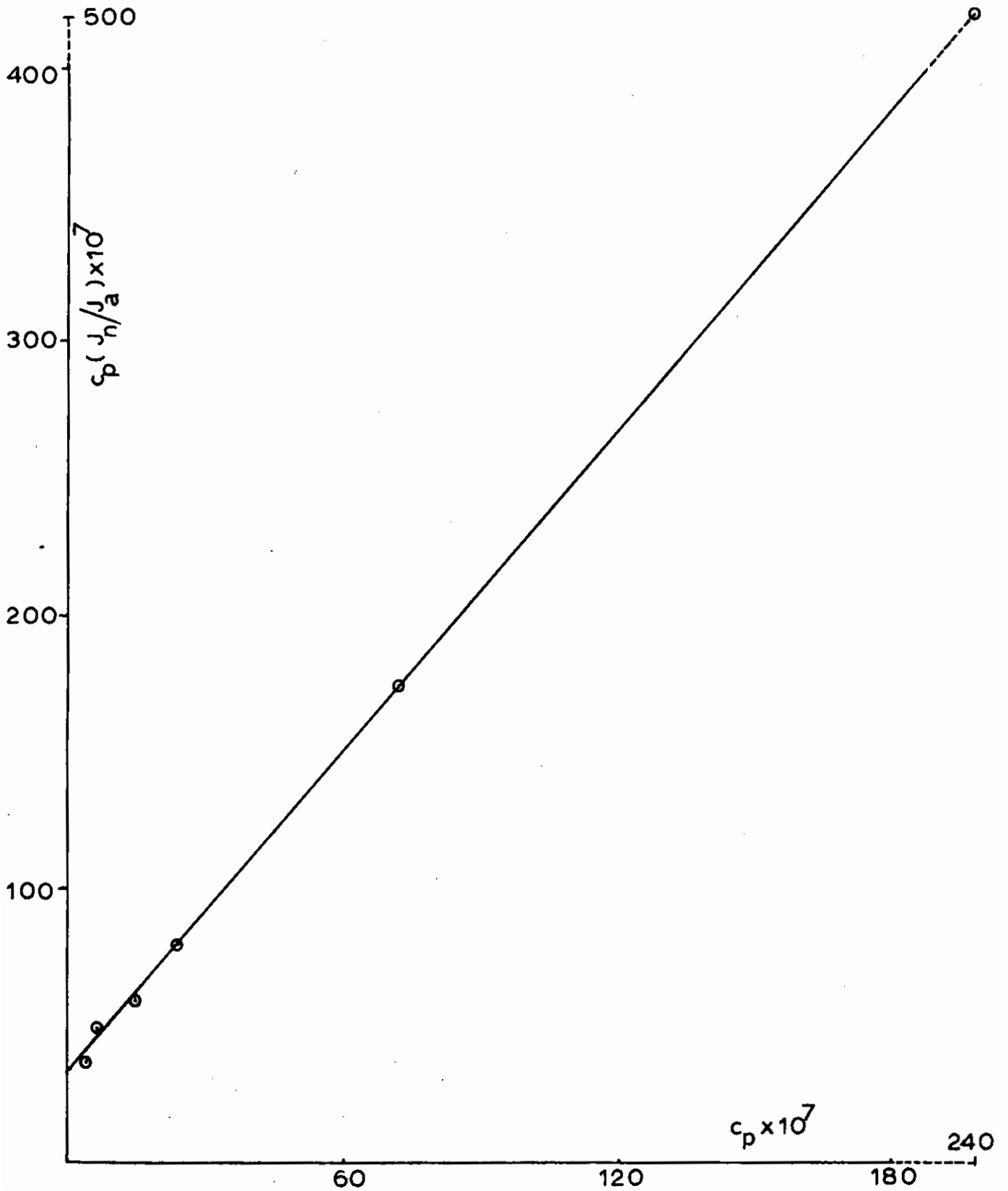
Then

$$c_p \frac{J_n}{J_a} = (a_1 + a_3) \left(1 + \frac{\mu_1 c_p}{2\mu_0} \right) \sqrt{\mu_0} + a_3 (\mu_0 + \mu_1 c_p) + a_2$$

$$\therefore c_p \frac{J_n}{J_a} = \left[(a_1 + a_3) \mu_0 + a_3 \mu_0 + a_2 \right] + c_p \left[\sqrt{\mu_0} \frac{\mu_1}{2\mu_0} (a_1 + a_2) + a_3 \mu_1 \right]$$

$$\begin{aligned} &= c_2 + c_p \left[c_1 + \frac{\mu_1 a_1}{2\sqrt{\mu_0}} + \frac{c_1}{2\sqrt{\mu_0}} \right] \\ &= c_2 + c_p c_3 \end{aligned} \quad \text{-----(27)}$$

The behaviour predicted by equations 27, 25 is in agreement with our experimental results as shown in Figs. 14 and 15.

Fig.14. J_h/J_a vs. c_p

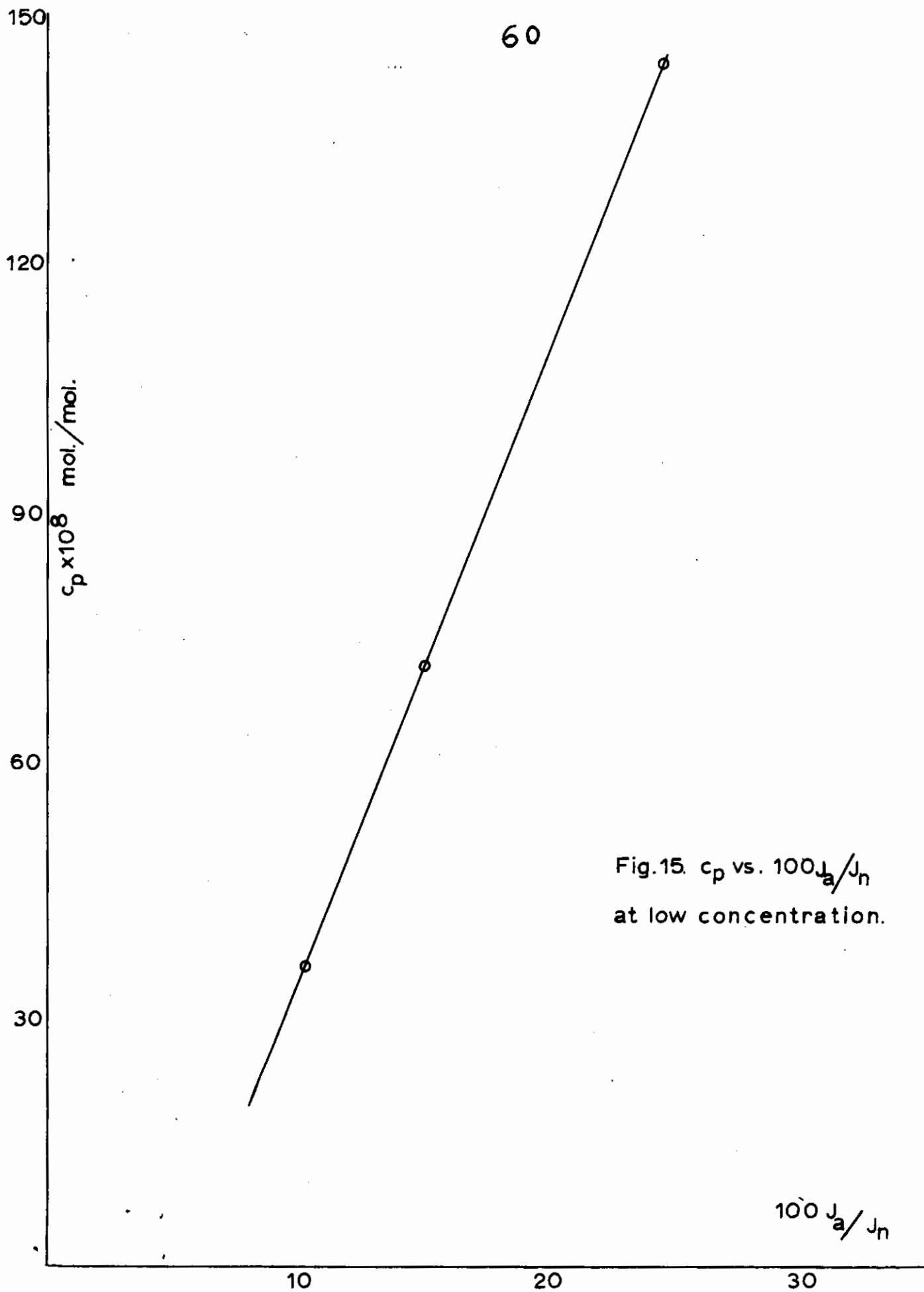


Fig.15. c_p vs. $100 J_a/J_n$
at low concentration.

(1) Dependence of Naphthalene Crystal Emission on the Extinction Coefficient:

The absorption spectra of naphthalene crystals has not been reported in the literature in unpolarized light and at 300°K. Lyons (private communication to Dr. A. Zahlan) states that the absorption spectra depends on thickness. It is, however known that the extinction coefficient (k) increases with decreasing wavelength in the region 3200-2600 Å.

Using the data of table V Fig. 11 shows a plot of the ratio of $\left(\frac{J_a}{J_n}\right)$ in the region of high extinction coefficient to that at 3020 Å (where k is lower). It is apparent that the dependence on k is not uniform. In general, the prediction of Agranovich and Faizysh⁷ holds. This can be seen from the analysis of equation (21) and the fact that the constants $A_1, A_2, A_3,$ and A_4 depend on the extinction coefficients in an inverse sense. The very few points in Fig. 11 which do not satisfy this prediction must be due to some other complication beyond our control (such as surface effects and non-uniformity in the distribution of impurity) which is introducing the fluctuations. More experiments have been made to investigate this point further. The data is given in Table VI. Fig. 12 shows the dependence of (J_a/J_n) as a function of wavelength of the exciting light and extinction coefficients for "pure" naphthalene grown and sublimed "crystals". The impurity is anthracene (most probably) and the concentration is about 10^{-8} or less. Hence these graphs indicate exciton trapping at very low concentrations. We note the following results:-

- i) Pure Grown Crystals: A peak is observed in the region of 3020 Å which is the region of the first electronic transi-

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- i) Pure Grown Crystals: A peak is observed in the region of 3020 Å which is the region of the first electronic transi-

tion with a low extinction coefficient. This result then indicates that the impurity is uniformly distributed in the crystal.

ii) Pure Sublimed Crystals:

There we note that the peaks in the curves are shifted to lower wavelength or the region of high extinction coefficient contrary to the prediction of Agranovich and Faidysh, as well as contrary to the above results for grown crystals. At high extinction coefficient more of the excitons are generated near or on the surface. Hence if the impurity is uniformly distributed it will capture fewer excitons.

However the observation that the capture has increased for high k and decreased for low k (quite sharply) signifies that the impurity is more concentrated in the surface of the microcrystals than in the bulk and hence is not uniformly distributed.

2. Dependence on Film Thicknesses:

Data given in Table VI shows that the naphthalene luminescence efficiency increases with decreasing the thicknesses of the films and that the anthracene fluorescence in general decreases. Consequently J_a/J_n decreases for smaller thicknesses. Fig. 12 indicates this behavior clearly. Fig. 13 throws more light on this phenomenon. The ratios J_a/J_n are compared for the same wavelength but at different thicknesses. For thicknesses below

$10\mu \frac{J_a}{J_n}$ is rather constant. For thicknesses larger than 10μ J_a/J_n increases very sharply. This indicates a very fundamental behavior, which can be explained as follows:

Since the excitons incident on the surface result in luminescence of the base material, a decrease in the film thickness should lead to an increase in the luminescence of the base material, and consequently to a decrease in the ratio J_a/J_n . For thicknesses below 10μ reabsorption is no more a problem and not much change can be due to that cause. For thicknesses greater than 10μ the decrease of the luminescence of the base material (or the increase of J_a/J_n) is due to the increase of the reabsorption of luminescence by the molecules of the base material themselves.

Faidysh and Zima²³ reported that at an impurity concentration of 10^{-6} (tetracene/anthracene) the anthracene luminescence is almost independent of the crystal thickness between $0.2 - 40\mu$, but at higher impurity levels, the luminescence of anthracene decreases with increasing thickness. According to the foregoing this is the same phenomenon which we have indicated above.

On the other hand we disagree with the statement that the base material luminescence at a concentration of 10^{-6} is independent of the thickness. What our data shows is that

not only at an impurity concentration 10^{-6} such a phenomenon exists but it is observed at much lower impurity concentrations, of the order of 10^{-8} . It also indicates that exciton trapping occurs at very low impurity concentrations, which demonstrates the large value of the mean free path of the free excitons.

3. Dependence on Anthracene Concentration:

i) Grown Crystals.

Equation (23) as deduced from the theory presented by Agranovich and Faidysh⁷ indicates that at very high concentration of anthracene the ratio $\frac{J_a}{J_n}$ is independent of the impurity concentration. Fig. 8 shows that this is true.

In the region of high concentration (about 10^{-3}) the ratio $\frac{J_a}{J_n}$ is almost constant and does not increase with increasing concentration. At such a limit we can say that all the free excitons have been trapped by the anthracene. Comparison with Fig. 9 we see that at such concentration the anthracene emission is about 50% of the total luminescence of the naphthalene. But since the quantum yield of the naphthalene is only 70% and that of the anthracene is 90%, hence the actual amount of the anthracene fluorescence compared with the amount of the light originally absorbed by the naphthalene is about 40%.

This shows that the localized excitons do not interchange with the free excitons when all the free ones are captured by the impurity molecules. If this did take place the curve

in Fig. 8 could not have a plateau (showing the exhaustion of free excitons) but should find a smooth curve. The assumption of Agranovich and Faidysh therefore holds. If the impurity concentrations increases the ratio starts to increase rather sharply. It seems that the trapping in this case is caused by other means than that caused by the free excitons. We think that this behavior is due to the capture of the localized excitons. At a higher impurity concentration the probability of capture of the localized excitons is appreciable, since the separation between any two impurity particles is small, and of the order of their mean free path.

ii) Sublimed Films.

The graph of J_a/J_n vs c_p shown on Fig. 10 for the sublimed films raises several points. In comparison with Fig. 8 for grown crystals, the experimental points show considerable scattering. The effect is partly due to differences in the thicknesses of the sublimed films. The following points should be noted:-

- a) The irregularities in the rate of sublimation of the naphthalene and the anthracene.

Anthracene does not sublime at the same temperature as naphthalene. The assumption that anthracene is carried by naphthalene is not correct except probably for small quantities of the impurity. The points on Fig. 10 obtained for low impurity concentration ($< 10^{-6}$) show lower dispersion.

- b) Surface Effects.

Sublimed films have a large surface to volume ratios

compared with grown crystals. Therefore there is a higher probability that the free excitons are quenched on the surface. Since the size of the microcrystals vary from film to film the importance of quenching varies from film to film.

c) Effects due to light scattering.

Since the films are microcrystalline in structure, light scattering caused by the film is not negligible. This, also, depends on the size of the microcrystals.

From the above mentioned points one can also expect to have lower J_a/J_n compared with the cases of grown crystals, which is exactly what was observed.

Note that because of the large fluctuations of J_a/J_n in the case of sublimed films the plateau does not appear clearly one can easily miss it. This might indicate why no previous workers on such films noticed the effect. Results obtained using such films are not as reliable as the results which can be obtained by using grown crystals.

The complete analysis of the results presented in this thesis requires accurate values for the extinction coefficients and might require the use of a computer. The results are capable of giving us an order of magnitude estimate of the mean free path for free and localized excitons. The minimum concentration of anthracene required to reduce the free exciton fluorescence by one half is 10^{-6} . $1/c_p = 10^6$ is the number of

steps the free exciton makes before it encounters an impurity molecule. Assuming the average distance between molecules²² to be 7.5A, the mean free path (ℓ_{free}) is:

$$7.5 \times \sqrt[3]{10^6} = 750 \text{ \AA}.$$

In the case of localized excitons the trapping begins at an impurity concentration of 2×10^{-3} . The value of (ℓ_{loc}) is then about 60A. This is the first experimental determination of a localized exciton mean free path. The value of 750A is close to Borisov and Vishnevski's who found 2000 - 3000A in thick crystals.

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References

1. Simpson, O. Proc. of Royal Soc., A, vol. 238, 402-411 (1956).
2. Borisov, M.D. and Vishnevski, V.N. Ukr. Phys. Journal, (1956).
3. Wolf, H.C. Zeit. fur Phys., 145, 166-174, (1956).
4. Ganguley, S.C., J. Chem. Phys. 13, 128 (1945).
5. Bowen, E.J., Nature, 159, 706 (1947).
6. Lipsett, F.R. and Dekker, A.J. Can. J. of Phys., 30, 165-173, (1952).
7. Agranovich, V.M. and Faidysh A.N. Optika i Spektroskopiya, 1, 983-987, (1956).
8. Frenkel, IA. I. Phys. Rev. 37, 17, 1276, (1931).
9. Davydov, A.S., J. Exptl. Theoret. Phys. (U.S.S.R.) 18, 210 (1948).
10. Forster, Th. Fluorescence organischer Verbindungen, Vandenhvech & Ruprecht, Gottingen (1951).
11. Mott, N.F. and Gurney, R.W., Electronic Processes in Ionic Crystals, Clarendon Press, Oxford, (1940).
12. Gross, E.F., AN U.S.S.R., vol. 28, No. 10, 11-19, (1958).
13. Northrop, Simpson, O. Proc. Roy. Soc., A, 234, 124 (1956).
14. Sidman, J.W. Phys. Rev., vol. 102, No. 1, 96, (1956).
15. Nikitine, S., Philosophical magazine, vol. 4, No. 37, 1, (1959).
16. Sponer, H. and Nordheim, P. Disc. Faraday Soc., 9, 19, (1950).
17. Wolf, H.C., Solid State Physics, vol., 9, London, Academic Press, Inc., (1959).
18. Afriedel, R.A. and Orchin, M., Ultraviolet Spectra of Aromatic Compounds, John Wiley & Sons, Inc., New York, (1951).
19. Dammers, A., Thesis, University of Amsterdam, (1956).

20. Gilmore, E.H., Gibson, G.E. and McClure, D.S. *J. Chem. Phys.* vol. 20, No. 5, 829-836, (1952).
21. Wolf, H.C. *Zeits, fur Physik*, Bd. 145, 116-124, (1956).
22. Winchell, A.N. *The Optical Properties of Organic Compounds*, Academic Press, Inc., (1954).
23. Faidysh, A.N. and Zima, V.L., *Opt. & Spect.* 6, 58, (1959).