Chapter II

EXPERIMENTAL, RESULTS AND DISCUSSIONS
In the present investigations, the effect of reactor radiations on the fluorescence spectra of several uranyl salts is studied first. There were no apparent changes in the nature of the fluorescence spectra of the uranyl salts $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{UO}_2(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cs}_2\text{UO}_2\text{Cl}_4$ and $\text{Cs}_2\text{UO}_2(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ after irradiation in the core of Apsara reactor for various durations. The intensity of fluorescence spectrum as a whole seems to have decreased after irradiation. However, marked (and similar) changes were observed in the fluorescence spectra of reactor core irradiated Cs$\text{UO}_2(\text{NO}_3)_3$ and Rb$\text{UO}_2(\text{NO}_3)_3$. Experiments have been done using a few other sources of radiation in order to find out which component of the reactor radiations is mainly responsible for the observed changes. These spectral changes have been studied and a mechanism responsible for these changes postulated.

1. Irradiation in Apsara reactor core.

The Apsara reactor (at Trombay) is a light water moderated enriched uranium fueled swimming pool type reactor, designed to work at a maximum power level of 1 MW. The core configuration as it existed when most of the irradiations were carried out, is shown in Figure 19(a). Many samples of uranyl salts namely $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cs}_2\text{UO}_2\text{Cl}_4$, $\text{UO}_2(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$,
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**FC** - FISSION COUNTER  
**F** - FUEL ELEMENT  
**RA** - ROD A  
**RB** - ROD B  
**RC** - ROD C  
**RF** - ROD FINE  
**REF** - REFLECTORS  
**□** GRAPHITE  
**☑** BeO  
**IRR** - IRRADIATION POSITION  
**L.T.** - LONG TIME, **S.T.** - SHORT TIME

**FIG. 19 (a)**
FLUORESCENCE SPECTRA AT 77°K

a) CsUO$_2$(NO$_3$)$_3$ (UNIRRADIATED)
b) CsUO$_2$(NO$_3$)$_3$ (IRRADIATED - 3hrs)
c) Cs$_2$UO$_2$(NO$_3$)$_4$ (SYNTHESIZED)

FIG. 20.
SHARP BANDS

DIFFUSE BANDS

a) CsUO₂(NO₃)₃ (UNIRRADIATED)
b) CsUO₂(NO₃)₃ (20hr. IRRADIATED) 6 WEEKS
c) CsUO₂(NO₃)₃ (20hr. IRRADIATED) 16 WEEKS

FIG. 19
Cs$_2$UO$_2$(SO$_4$)$_2$·3H$_2$O, CsUO$_2$(NO$_3$)$_3$ and RbUO$_2$(NO$_3$)$_3$ were irradiated at the $A_4$ position of the core. At this position the total neutron flux (consisting of both fast and slow neutrons) is about $10^{12}$ n/cm$^2$/sec, at the reactor power level of 300 KW at which most of the irradiations have been carried out. At $A_4$ position in the core of Apsara reactor the ratio of fast to thermal neutrons almost equals unity. The energy spectrum of the neutrons in a reactor core is complex, varying from a fraction of an electron volt to about 20 Mev, with an average energy of 2 Mev.

To irradiate a sample in the core of the reactor the following procedure was followed. The sample (usually about 500 mg. by weight) was sealed in a vycor' tube. This tube was in turn sealed in a polythene bag and it was placed in a Harwell type watertight aluminium can. The can was suspended in the core of the Apsara reactor at the $A_4$ position for a specified time. After irradiation, the sample is taken out of the reactor core and allowed to 'cool' for a week or more by which time most of the short lived radioactivity would have died down. At the end of one week, the sample still showed an activity of 50 mr to 100 mr/hr. (mostly gamma activity) and proper care was therefore taken in handling these for further work. The samples were usually handled in the same
hoods meant for radioactive work.

Among the uranyl salts the absorption and fluorescence spectra of CsUO$_2$(NO$_3$)$_3$ have been studied in great detail$^1$. Therefore this uranyl salt has been taken up first for investigating the effects of reactor radiations. A small crystal of CsUO$_2$(NO$_3$)$_3$ was irradiated for 20 hrs. at the A$_4$ position in the core of Apsara reactor working at an average power level of 300 KW. The CsUO$_2$(NO$_3$)$_3$ sample showed the following changes$^2$. (i) The single crystal of CsUO$_2$(NO$_3$)$_3$ had crumbled down to powder form (ii) The colour of CsUO$_2$(NO$_3$)$_3$ changed from yellowish green to yellowish brown (iii) The irradiated salt showed a high level of activity of 150 mr/hr. soon after the irradiation. It was therefore cooled for about two weeks before the spectrum of the sample was taken.

The fluorescence spectra of the irradiated CsUO$_2$(NO$_3$)$_3$ were recorded at 77$^\circ$K on a three prism glass Steinheil spectrograph after two weeks, six weeks and sixteen weeks after irradiation. The fluorescence spectrum after two weeks consisted of a continuum and the spectrum after six weeks showed continuous emission between 5600 Å and 6200 Å with intensity maximum at about 5800 Å and a weak broad band at 4894 Å. The original spectrum of CsUO$_2$(NO$_3$)$_3$ was completely absent.
The fluorescence spectrum recorded after sixteen weeks showed (Figure 19), (1) a set of diffuse bands separated by an interval of \( \sim 840 \text{ cm}^{-1} \) (Table 2-), (ii) a set of sharp bands with a repetition frequency of about \( \sim 855 \text{ cm}^{-1} \) and (iii) a set of bands identical with the fluorescence spectrum of the unirradiated \( \text{CsUO}_2(\text{NO}_3)_3 \). It was thought that the twenty hour irradiation in the reactor core might have been too much for the changes observed and that a smaller dose might bring out these changes better. Therefore another sample of \( \text{CsUO}_2(\text{NO}_3)_3 \) (multicrystals) was irradiated in the \( A_1 \) position of the Apsara reactor (power level 300 KW) for only 3 hours. Some microcrystals had undergone a change in colour from yellowish green to yellowish brown whereas the others did not.

The fluorescence spectrum of three hour irradiated \( \text{CsUO}_2(\text{NO}_3)_3 \), recorded at 77°K showed the following features. (1) A set of bands identical with the fluorescence spectrum of unirradiated \( \text{CsUO}_2(\text{NO}_3)_3 \) (ii) A set of sharp band groups with a frequency interval of \( \sim 855 \text{ cm}^{-1} \) between the groups. This set of sharp bands was identical with the set of sharp bands observed in the 20 hr. irradiated \( \text{CsUO}_2(\text{NO}_3)_3 \) (iii) A continuous emission appeared in the wavelength range of 5600 \( \AA \) to 6200 \( \AA \) with a maximum of 5800 \( \AA \) as in the case of 20 hr. irradiated sample of
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b = broad
CsUO$_2$(NO$_3$)$_3$. The diffuse bands observed in the fluorescence spectrum of 20 hr. irradiated CsUO$_2$(NO$_3$)$_3$ were completely absent here. One of the brownish crystals was picked out of the 3 hr. irradiated sample of CsUO$_2$(NO$_3$)$_3$ and its fluorescence spectrum recorded at 77°K (Figure 20). It showed features two and three mentioned above but not feature one. Feature two in the fluorescence spectrum has the usual characteristics of the spectrum of UO$_{2}^{++}$ ion and a comparison of the vibrational frequencies obtained from this spectrum with those of dirubidium uranyl nitrate indicated that these sharp bands might belong to the analogous caesium salt namely dicaesium uranyl nitrate compound. The Cs$_2$UO$_2$(NO$_3$)$_4$ was not known when these investigations were carried out and it seemed that the attempts to synthesize this salt previously had not been successful. An attempt was therefore made by us to synthesize Cs$_2$UO$_2$(NO$_3$)$_4$ in our laboratory which proved successful. The fluorescence spectrum of the synthesized Cs$_2$UO$_2$(NO$_3$)$_4$ salt has been recorded at 77°K and compared with that of the three hour irradiated CsUO$_2$(NO$_3$)$_3$. It can be seen from Figure 20 that the sharp set of band groups observed in three hour irradiated CsUO$_2$(NO$_3$)$_3$ are identical in all respects with the fluorescence spectrum of Cs$_2$UO$_2$(NO$_3$)$_4$. This seemed to suggest that the
brownish crystals in the irradiated CsUO$_2$(NO$_3$)$_3$ could be Cs$_2$UO$_2$(NO$_3$)$_4$ i.e., a portion of CsUO$_2$(NO$_3$)$_3$ has been converted to Cs$_2$UO$_2$(NO$_3$)$_4$ by irradiation in reactor core. To test this further, X-ray powder diffraction patterns of the brown crystals in the irradiated CsUO$_2$(NO$_3$)$_3$ and synthesized Cs$_2$UO$_2$(NO$_3$)$_4$ have been obtained and compared. These patterns have been found to be identical (Figure 21). All the above results strongly suggest that CsUO$_2$(NO$_3$)$_3$ is changed to Cs$_2$UO$_2$(NO$_3$)$_4$ under reactor core irradiation. As will be seen in more detail below a similar situation holds good in case of Rubidium salts (of course the fluorescence spectrum of Rb$_2$UO$_2$(NO$_3$)$_4$ is already well known). When RbUO$_2$(NO$_3$)$_3$ is irradiated for 10 hrs. in the A$_1$ position of the Apsara reactor core (power level 300 KW), the crystals undergo a change in colour. There thus additional bands due to Rb$_2$UO$_2$(NO$_3$)$_4$ introduced in the irradiated RbUO$_2$(NO$_3$)$_3$ salt (Figure 21). Similar considerations lead one to wonder whether the set of diffuse bands in the 20 hr. irradiated CsUO$_2$(NO$_3$)$_3$ do not belong to the next higher form of Cs$_2$UO$_2$(NO$_3$)$_4$ namely the triaesium uranyl nitrate Cs$_3$UO$_2$(NO$_3$)$_5$. Cs$_3$UO$_2$(NO$_3$)$_5$ is not known. Our attempts to synthesize this salt have not been successful yet. Then attempts were made to synthesize Rb$_3$UO$_2$(NO$_3$)$_5$ and K$_3$UO$_2$(NO$_3$)$_5$. Attempts to synthesize K$_3$UO$_2$(NO$_3$)$_5$ appear
to be successful (Appendix 2). The salt synthesised has a complex fluorescence spectrum. There is sole similarity between diffuse bands in the fluorescence spectrum of the 20 hr. irradiated CsUO$_2$(NO$_3$)$_3$ and that of K$_3$UO$_2$(NO$_3$)$_5$ in the value of the repetition frequency which is the same for both. While the diffuse bands in irradiated CsUO$_2$(NO$_3$)$_3$ bands appear to be simple, the fluorescence bands of K$_3$UO$_2$(NO$_3$)$_5$ are more complex. To summarise the above results (1) CsUO$_2$(NO$_3$)$_3$ salt irradiated in the core of reactor for 20 hrs. (power level 300 KW), shows in its fluorescence, bands due to CsUO$_2$(NO$_3$)$_3$, Cs$_2$UO$_2$(NO$_3$)$_4$ and probably due to Cs$_3$UO$_2$(NO$_3$)$_5$. (11) CsUO$_2$(NO$_3$)$_3$ salt irradiated for 3 hrs. in the reactor core shows in its fluorescence spectrum a set of bands attributable to Cs$_2$UO$_2$(NO$_3$)$_4$ apart from those of CsUO$_2$(NO$_3$)$_3$.

Apart from the above changes in the fluorescence spectra there is a general decrease in fluorescence intensity after irradiation in the reactor core.

In the core of the reactor, the neutrons have a wide energy spectrum, varying from a fraction of an electron volt to about 20 Mev. In addition to neutrons of different energies, the reactor core has beta and gamma radiations. Fission fragments of wide energy ranges also exist. To understand as to which of these
was primarily responsible for the type of radiation observed above, the CsUO$_2$(NO$_3$)$_3$ salt was subjected to some individual types of irradiations detailed below.

(1) **Thermal neutron irradiation:** The CsUO$_2$(NO$_3$)$_3$ sample was irradiated with different doses of thermal neutrons in the thermal column of the Apsara reactor. The fast neutron flux in the thermal column was negligible (~1%). The thermal neutron flux at the position in the thermal column where most of the samples were irradiated was $\sim 10^8$ neutrons/cm$^2$/sec., when the reactor was running at a power level of 400 KW.

Thermal neutron irradiation of CsUO$_2$(NO$_3$)$_3$ showed the same type of changes that occurred in the 3 hr. core-irradiated sample of CsUO$_2$(NO$_3$)$_3$ except that the colour of the sample did not show any appreciable change from that of unirradiated salt.

(ii) **Irradiation by 14 Mev neutrons:** The CsUO$_2$(NO$_3$)$_3$ samples were subjected to irradiation by 14 Mev neutrons for different durations. The 14 Mev neutrons were obtained making use of the deuterons accelerated in the 1 MV Cockroft-Walton type accelerator at the Tata Institute. The high energy deuteron beam hits the target containing tritium and the following nuclear reaction yields monoenergetic neutrons of 14 Mev.

$$ _1^1H^3 + _1^1H^2 \rightarrow _0^1n^1+^2He^4 + 17.6 \text{ Mev} $$
For irradiation, the CsUO$_2$(NO$_3$)$_3$ sample was kept about 2 inches away from the tritium containing target. The maximum usable neutrons flux was $\sim 10^7$ neutrons/cm$^2$/sec. A sample of CsUO$_2$(NO$_3$)$_3$ irradiated by 14 Mev neutrons to a integrated dose of $\sim 10^{10}$ showed in its fluorescence spectrum, bands due to Cs$_2$UO$_2$(NO$_3$)$_4$. The intensity of this Cs$_2$UO$_2$(NO$_3$)$_4$ spectrum was however poor as compared to that of the Cs$_2$UO$_2$(NO$_3$)$_4$ spectrum obtained in the fluorescence of the CsUO$_2$(NO$_3$)$_3$ sample irradiated by approximately the same dose of thermal neutrons.

(I) Irradiation by 'Gamma' radiations: A CsUO$_2$(NO$_3$)$_3$ sample was irradiated by gamma rays from the 150 K.Rad/hr. Cobalt-60 source at CIRUS at Trombay, to a total dose of $\sim 10^6$ Rads. The fluorescence spectrum of the salt did not show any change in the structure after irradiation.

The above experiments show that irradiation of CsUO$_2$(NO$_3$)$_3$ with thermal neutrons brings about the same changes in its fluorescence spectrum as irradiation for 3 hours in the A$_1$ position of Apsara reactor core (power level 300 KW) and that irradiation by gamma rays or 14 Mev neutrons has either no effect or very little effect. It is probably unlikely that the thermal neutron component of the reactor core is solely
responsible for the observed changes in the fluorescence spectrum of the reactor core irradiated CsUO$_2$(NO$_3$)$_3$, but the fact that similar changes are brought about by irradiating CsUO$_2$(NO$_3$)$_3$ with thermal neutrons gives us a basis for further postulating the mechanism that might be responsible. $^{235}$U nucleus has a large cross section for fission ($\sim$580 barns) by thermal neutrons and therefore it was of interest to see whether fission of $^{235}$U plays any part in the radiation damage of CsUO$_2$(NO$_3$)$_3$. With this in view, a set of samples of CsUO$_2$(NO$_3$)$_3$ enriched in $^{235}$U to 1.6%, 2.5%, 5% and 10% were irradiated simultaneously by the same dose of thermal neutrons. This experiment was repeated at different doses of neutron irradiation. It was found that the intensity of bands attributable to Cs$_2$UO$_2$(NO$_3$)$_4$ in the fluorescence spectrum of the irradiated CsUO$_2$(NO$_3$)$_3$ was enhanced as (i) enrichment of $^{235}$U in the sample increased and (ii) as the thermal neutron dose increased. The results are shown in Figure 22 wherein the intensity ratios of Cs$_2$UO$_2$(NO$_3$)$_4$ bands to CsUO$_2$(NO$_3$)$_3$ bands are plotted against the product of percentage $^{235}$U enrichment and thermal neutron dose. The graph is not a straight line but this could be due to one or more of several factors. For instance, the values of the thermal neutron flux used are very
approximate. However, it can be clearly seen that the intensity ratio $\text{Cs}_2 : \text{Cs}_1$ increases as the value of the product of $^{235}\text{U}$ enrichment and thermal neutron flux increases. This result points out that fission of $^{235}\text{U}$ could indeed be involved in the radiation damage of $\text{CsUO}_2(\text{NO}_3)_3$.

**Radiation damage mechanism:** From the results of the various experiments mentioned above, one is gradually led to the assumption that fission of the $^{235}\text{U}$ nucleus is probably at the root of the radiation damage of $\text{CsUO}_2(\text{NO}_3)_3$ as evidenced in the change in the fluorescence spectrum of irradiated $\text{CsUO}_2(\text{NO}_3)_3$. Before postulating a probable mechanism of radiation damage, it is necessary to have an idea of the number of fissions taking place, the amount of energies involved etc.

Assuming that 0.589 gm. of $\text{CsUO}_2(\text{NO}_3)_3$ (one over one hundredth of the molecular weight) is irradiated for 10 hrs. in the $A_1$ position of the Apsara reactor working at a power level of 300 KW (neutrons flux $\sim 10^{12}$ n/cm$^2$/sec.). We have the following results:

- Thermal neutron flux at $A_1$ position $\sim 5 \times 10^{11}$ n/cm$^2$/sec.
- Integrated thermal neutron flux for 10 hrs. irradiation $\sim 18 \times 10^{15}$ n/cm$^2$.

Assuming an effective area of 2 cm$^2$ for 0.589 gm. of $\text{CsUO}_2(\text{NO}_3)_3$, the thermal neutron flux at $A_1$ position is $5 \times 10^{11}$ n/cm$^2$/sec.
the total thermal neutron flux incident on 0.589 gm. of CsUO$_2$(NO$_3$)$_3$ $\approx 36 \times 10^{15}$ n.

Number of $^{235}\text{U}$ atoms in 0.589 gm. of CsUO$_2$(NO$_3$)$_3$ = $4.216 \times 10^{18}$.

Therefore number of $^{235}\text{U}$ fissions = $1.46 \times 10^{13}$.

A large number of fissions is thus taking place. Each fission process releases a large amount of energy ($\approx 205$ Mev) distributed as follows:

1. Kinetic energy of fission fragments $167\pm5$ Mev
2. Kinetic energy of fast neutrons $\approx 1$ Mev
3. Instantaneous gamma radiation $\approx 1$ Mev
4. Gamma from fission products (delayed) $1\pm1$ Mev
5. Betas from fission products (delayed) $7.4\pm0.5$ Mev
6. Neutrino energy (delayed) $1\pm2$ Mev
7. Total $205$ Mev

It is to be noted that two heavy fission fragments carry away most of the energy released in fission. It is therefore these that will be primarily responsible for the observed radiation damage. The range of such high energy fission fragments in uranium is usually of the order of a few microns. It is expected that for uranium compounds the range does not differ appreciably.

Thus the large amount of energy is dissipated in a short range in the material. Here the concept of thermal spike or displacement spike can be used as a mechanism for the explanation of radiation damage.
Outlines are given below of a possible mechanism that might explain the observed facts in the radiation damage of \( \text{CsUO}_2(\text{NO}_3)_3 \). In view of the fact that so little is known about the processes going on in a material placed inside a reactor, it is not claimed that the following scheme is a satisfactory explanation of the experimental observations. It is only a tentative scheme evolved in attempts to understand the experimental results. The thermal spike concept as applied to a typical case indicates that with the amount of energy released in a single fission event about \( 10^4 \) atoms will be heated to about \( 1000^\circ \text{K} \) in a period as short as \( 10^{-11} \) sec. This rapid local heating is followed by local recrystallisation. During the recrystallisation a different compound may be formed from the constituents of the original one arranged in different proportions. If these regions of recrystallisation are large and overlap, the damage appears to be a macrophenomenon and the damaged microcrystals can be picked out, as was done in the present investigations. If, on the other hand, the recrystallisation takes place in a very small region, it will not be possible to separate the damaged regions from the unaffected ones. If during the recrystallisation, following the thermal spike, the
mixing up of the constituents of the original molecule (atoms and atomic groups) is not much one expects after recrystallisation, mostly the original compound. If, on the other hand, the mixing is high as, for instance, in the case of a heavy dose of irradiation, the process of recrystallisation may yield not only the original compound but other compounds possible from a rearrangement of the constituents of the original one. Then, the most probable form into which the recrystallisation occurs, is the form of lowest symmetry possible with the constituents, because this involves the least energy. Thus it is that $\text{Cs}_3\text{UO}_2(\text{NO}_3)_5$ may be responsible for the set of diffuse bands observed in the fluorescence spectrum of highly irradiated $\text{CsUO}_2(\text{NO}_3)_3$ as it is likely to have the lowest symmetry among compounds containing Cs, U, O and NO$_3$. As the annealing progresses, more and more compounds of increasing symmetry are crystallised. Thus the appearance of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ crystals is expected to occur next to that of $\text{Cs}_3\text{UO}_2(\text{NO}_3)_5$. However, if the mixing is not very much, it is expected that recrystallisation into $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ takes place in preference to $\text{CsUO}_2(\text{NO}_3)_3$ because the former has a lower symmetry than the latter. Thus in such cases only the formation of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ is observed. The recrystallisation into $\text{CsUO}_2(\text{NO}_3)_3$ which belongs to the most symmetrical
form of caesium uranyl nitrate comes as the third and last step in reocrystallisation.

Radiation damage in $\text{RbUO}_2(\text{NO}_3)_3$: The radiation damage in $\text{RbUO}_2(\text{NO}_3)_3$ is very similar to that of $\text{CsUO}_2(\text{NO}_3)_3$. $\text{RbUO}_2(\text{NO}_3)_3$ was irradiated in the core of Apsara reactor at 300 KW power level for 20 hrs., for 10 hrs., by thermal neutrons from Apsara reactor, by 14 Mev neutrons and by gamma radiations. Thermal neutron irradiation and 10 hr. core irradiation indicated the formation of $\text{Rb}_2\text{UO}_2(\text{NO}_3)_4$ after irradiation (Figure 21). This was as expected.

The observation that similar irradiation has no effect on the fluorescence spectra of $\text{Cs}_2\text{UO}_2\text{Cl}_4$, $\text{Cs}_2\text{UO}_2(\text{SO}_4)_2\cdot 3\text{H}_2\text{O}$, $\text{UO}_2(\text{SO}_4)_2\cdot 3\text{H}_2\text{O}$, $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ can now be understood in harmony with the above mechanism because other possible compounds (formed with the constituents of the original compounds) are all unstable. Thus in the absence of other stable compounds, the reocrystallisation has to take place in the original compound only. As a result, the salts appear not to have undergone any change. To test the above postulate still further a large varieties of uranyl compounds have to be studied for their radiation damage.

Possible analytical application: The experimental observation (mentioned above) that the fluorescence spectrum of reactor irradiated $\text{CsUO}_2(\text{NO}_3)_3$, the intensity
ratio of bands attributable to $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ and those due to $\text{CsUO}_2(\text{NO}_3)_3$ increases with the amount of $^{235}\text{U}$ in the sample offers the possibility of developing a simple spectrographic method for the isotopic assay of uranium. A lot of further work in this direction has to be done before the workability of the method is established.

Further systematic study of the radiation damage in uranium containing materials is likely to throw some more light on damage mechanism and this can be used with advantage to study some aspects of the solid state of matter.
Figure 21

(a) RbUO$_2$(NO$_3$)$_3$ (UNIRRADIATED)
(b) RbUO$_2$(NO$_3$)$_3$ (IRRADIATED)
(c) Rb$_2$UO$_2$(NO$_3$)$_4$ (SYNTHESIZED)

Fluorescence spectra at 77°K
A
If) O)
CM ro
O) O)
"cm ii
GO m
**
CD
oTf yD
CO CO
"cm V
< <
20695
20708
*
FIG 24

A_2^* = 846, B_2^* = 925
A_1^* = 860, B_1^* = 939

FIG 24
REFERENCES


