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## STUDIES ON OPTICAL BLEACHING OF X-RAY IRRADIATED NaCl CRYSTALS

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### ABSTRACT

The regions of fast first stage bleaching and the slow second stage bleaching of F-centres in 'as cleaved' X-ray irradiated NaCl crystals at room temperature are not clearly separated out in the optical bleaching curves. These curves are explained by a simple relation of the form  $\Delta \alpha_F / \alpha_F = k \log t$ ,  $\Delta \alpha_F$  being the change in absorption coefficient at the F-band peak after bleaching the colored crystal for  $t$  minutes,  $\alpha_F$  being the absorption coefficient at the F-band peak before bleaching and  $k$  being the constant dependent on the time of X-ray irradiation. The two regions are distinctly separated out in the case of heat-treated NaCl crystals. A possible mechanism of bleaching is suggested to explain the results of optical bleaching.

### INTRODUCTION

IT is well established by several authors<sup>1-8</sup> that F-centres are formed in alkali halides by X-rays by two distinct processes. In one of them the negative ion vacancies initially present in the crystal, trap electrons liberated by X-rays and these are uniformly distributed in the volume of the crystal. In the other process, new vacancies are generated during irradiation and these in turn may trap electrons and form additional F-centres. These F-centres are formed perhaps near some defects and are highly localized in small regions of the crystal having very high concentration of these F-centres.

The optical bleaching of F-centres also supports the idea of two stages of coloration. The studies on optical bleaching of F-centres by Markham *et al.*<sup>9</sup> on additively colored KBr crystals at low temperatures, by Ueta and Werner Kanzio<sup>10</sup> on additively colored, deformed KCl crystals, and by Bron<sup>5</sup> on the relation between X-ray coloration and optical bleaching indicate that optical bleaching of F-centres also takes place in two stages. During the first stage of bleaching the F-band decreases rapidly and this can be attributed to the bleaching of first type F-centres. During the second stage of bleaching, the decrease in F-band is much

slower and this can be attributed to the bleaching of second type F-centres.

In the present paper optical bleaching curves of F-centres have been studied systematically to investigate the nature of these two stages of bleaching at room temperature in X-irradiated Harshaw NaCl crystal (as cleaved and heat-treated crystals).

### EXPERIMENTAL

Sodium chloride crystals used in the present study were aged about 8 to 10 years. Systematic experiments were conducted to find the origin of these crystals. Rabin and C. C. Klick<sup>11</sup> have studied the F-band growth curves for NaCl crystals of different origins. The F-band growth curve obtained from our experiments agreed well with that obtained by Rabin and Klick for Harshaw NaCl crystals.

NaCl crystals were cut and cleaved to the size required from a big block. The thickness of the crystals used was less than 0.4 mm.

Heat treatment of NaCl crystals consisted in raising their temperature to about 600°C and maintaining them at that temperature for 7 to 8 hours, then quenching immediately by withdrawing them from the furnace and cooling on a copper plate.

The continuous X-ray spectrum from a copper target tube operated at 39 kV and 10 mA

was employed to produce the coloring. The cleaved crystals, wrapped in black paper were placed close to the window of the X-ray tube. The irradiation time varied from 10 minutes to 12 hours.

Progressive optical bleaching of previously X-irradiated crystals was carried out by placing the crystals within about 8 cm from a 250 V 60 W incandescent bulb with an electric fan nearby to keep the crystal cool.

Optical absorption measurements were made using DU-2 Beckmann non-recording type Spectrophotometer in the wavelength range from 400 m $\mu$  to 900 m $\mu$ . The optical density  $\log_{10} I_0/I$  at various wavelengths and the absorption coefficient  $a_F$  at the F-band peak were determined. F-centre concentrations were computed from Smakula's formula using an oscillator strength of 0.8. In our experiments the density of F-centres was in the range  $10^{17}$  to  $10^{18}/\text{cm}^3$ .

### RESULTS

X-ray irradiation and optical bleaching were carried out as explained before. Figure 1 represents optical bleaching curves for 'heat-treated' as well as 'as cleaved' NaCl crystals.

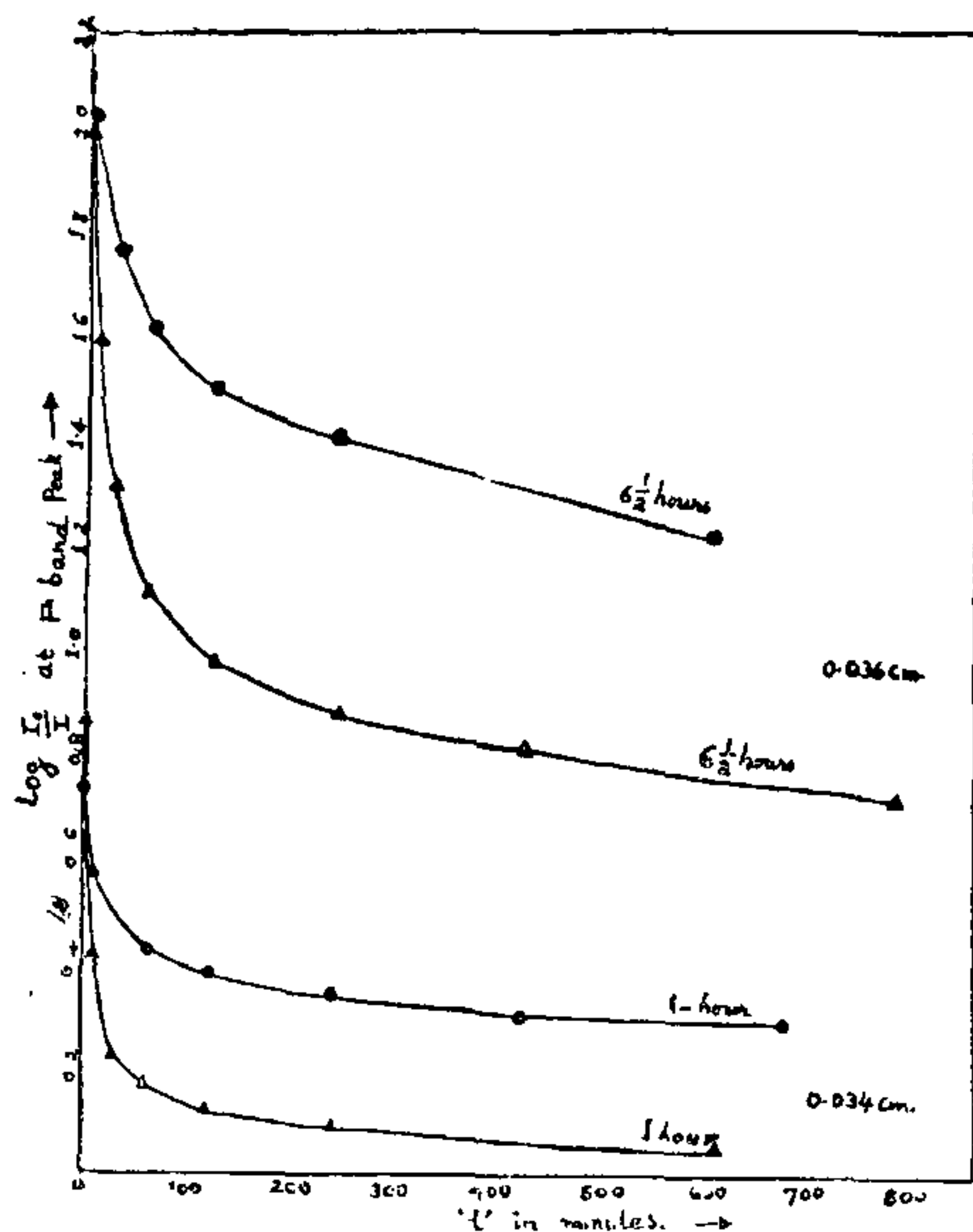


FIG. 1. Representing the optical bleaching curves for 'heat-treated' and 'as cleaved' NaCl crystals. ● Bleaching curves of 'as cleaved' NaCl crystals. △ Bleaching curves of 'heat-treated' NaCl crystals. Time of X-ray exposure and the thickness of the crystals are mentioned on the curves.

Regions of fast and slow bleaching are clearly indicated in the case of heat-treated crystals. In our experiments, the optical bleaching curves can be explained by a simple relation of the form  $\Delta a_F/a_{F0} = k \log t$ . Figure 2 shows a plot

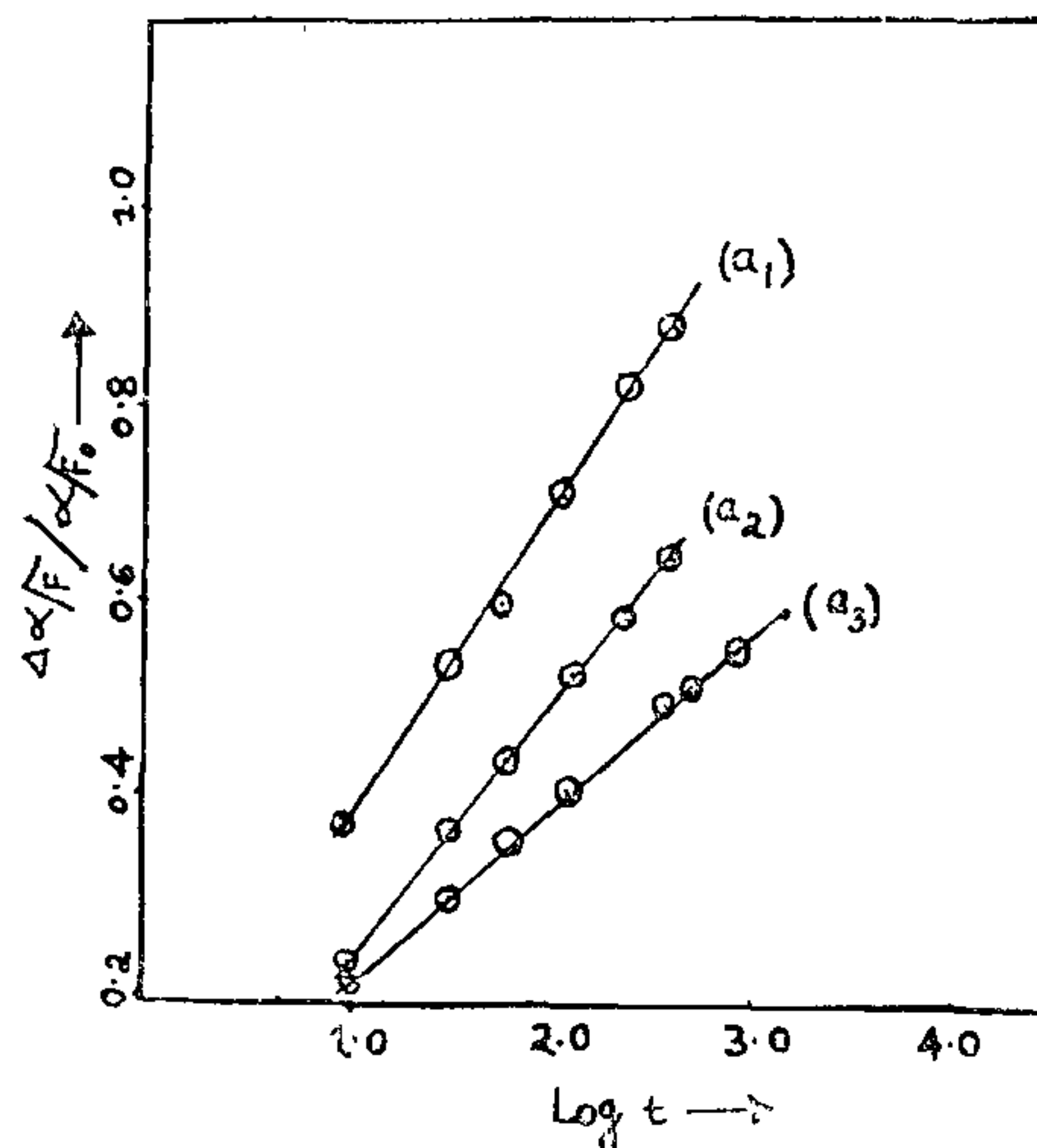


FIG. 2. Results obtained with 'as cleaved' NaCl crystals (a<sub>1</sub>)—10 minutes X-ray irradiation. (a<sub>2</sub>)—20 minutes X-ray irradiation. (a<sub>3</sub>)—7 hours X-ray irradiation. Thickness of the crystal used = 0.034 cm.

of  $\Delta a_F/a_{F0}$  versus  $\log t$  for "as cleaved" NaCl crystals,  $\Delta a_F/a_{F0}$  being the fractional change in absorption coefficient at the F-band peak and  $t$  being the time of bleaching in minutes. Irrespective of X-ray irradiation time, the plot is a straight line. (Only 3 graphs are shown as samples.) In Fig. 3 the graph (b) represents the plot of  $\Delta a_F/a_{F0}$  versus  $\log t$  for a heat-treated NaCl crystal and graph (a) represents that for an 'as cleaved' crystal. Graph (b) consists of two parts, one of which has got nearly the same slope as that of (a). We need at least two slopes to explain the bleaching curve obtained with heat-treated crystals. This indicates that the nature of bleaching in the initial stage is different from that in the later stage and that the mechanism of bleaching in the later stage is similar to that in the case of 'as cleaved' crystals.

### DISCUSSION

To explain the mechanism of optical bleaching several theories have been put forward by earlier workers<sup>1-10</sup>. But a more rigorous one is that due to Bron and Nowick<sup>13</sup>. According to them the transfer of electrons from



F-centres to some pre-existing traps, present only in X-ray irradiated crystals (hole traps-V-centres which are produced along with F-centres in X-ray irradiated crystals), is considered to occur during the initial, very rapid part of the first stage of bleaching. Since the initial vacancies and hence the first type F-centres are widely distributed in the volume of the crystal, an ejected electron from an F-centre by a photon will have a very small chance of being recaptured by another vacancy before it combines with a hole trap. As the hole traps become fully occupied with electrons, bleaching becomes dependent on the rate of formation of the secondary centres like, R, M, N.

The mechanism which slows down the second stage of bleaching will be as follows: The second type F-centres generated by X-rays during the second stage of coloration are of high concentration in certain localized areas of the crystal. During bleaching, a liberated electron will have a high probability of being recaptured by a nearby vacancy with no net loss of F-centre. Quantum efficiency measurements<sup>6,12,13</sup> also support the above mechanism of bleaching.

In 'as cleaved' crystals of NaCl, the number of vacancies present prior to irradiation is very much dependent on the origin of these crystals. In the case of Harshaw NaCl crystals, this number is of the order of  $10^{15}$  to  $10^{16}/\text{cm}^3$ . (The same order of initial number of vacancies was estimated from graphical extrapolation for Harshaw NaCl crystals by Rabin<sup>4</sup> in his studies on expansion of colored NaCl crystals having different origins.) Thus the concentration of first type F-centres can be only of the order of  $10^{15}$  to  $10^{16}/\text{cm}^3$  or even less. In our experiments the density of F-centres is as high as  $10^{17}/\text{cm}^3$  for X-irradiation of 10 minutes. When the crystal is being optically bleached, the first type F-centres are perhaps bleached within a few seconds and later the bleaching occurs only by forming F-centre aggregates like M, N, R centres. The study of absorption spectrum shows definitely that as the F-band decreases, the M-band gradually increases first and later the N-band appears at the expense of both F-band and M-band. So, the regions of fast first stage bleaching and the second stage bleaching are not separated out in the case of 'as cleaved' NaCl crystals as shown in Fig. 1. From Fig. 2 it is evident that the mechanism of bleaching is the same for all the 'as cleaved' crystals of NaCl irrespective of X-ray irradiation time and the only change observed is in their slope which decreases as the X-irradiation period increases. This can be explained from the fact that as the density of second type F-centres increases, the recapture of an ejected electron from an F-centre by a vacancy without net loss of F-centre becomes more prominent and hence the fractional change in absorption coefficient  $\Delta\alpha/\alpha_0$  becomes much less for the given time of bleaching.

It is known that quenching of NaCl crystals at a particular temperature increases the initial number of vacancies. The effect is much greater at higher temperatures. This may be attributed to the 'quenching in' of vacancies

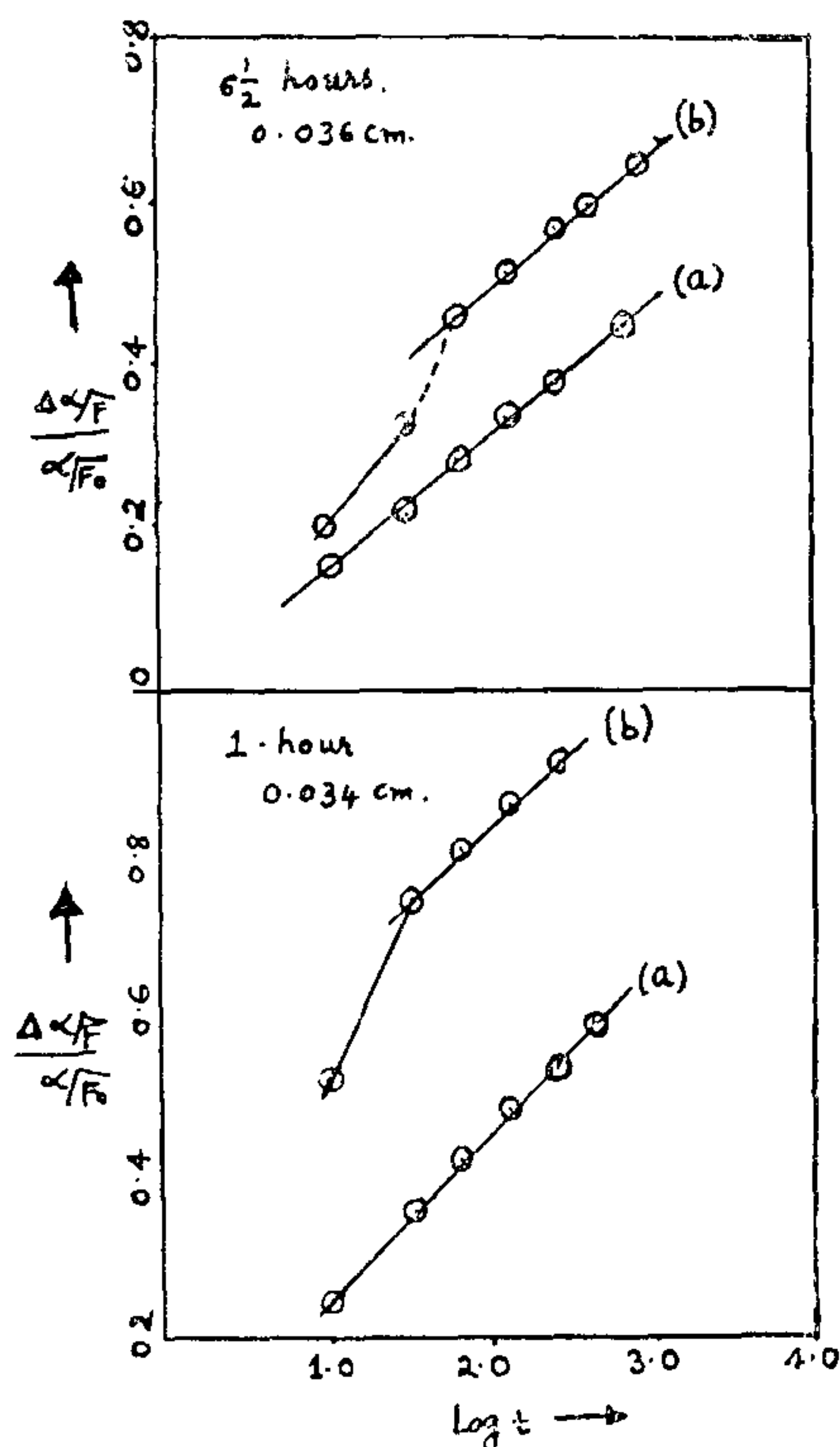


FIG. 3. A comparison of results obtained with 'as cleaved' and 'heat-treated' NaCl crystals (a) 'as cleaved' crystals; (b) 'heat-treated' crystals. X-ray irradiation time and the thickness of the crystals are mentioned on the graphs.

Since the second type F-centres have very high local density, it is not unreasonable that these F-centres should unite to form F-centre aggregates like M, N, R centres as they are bleached.

which were in equilibrium at high temperatures. It is supposed that these vacancies are unable to coalesce. It is well established<sup>3,6</sup> that initial vacancies and those induced by heat treatment are similar and are widely distributed in the volume of the crystal. Thus in heat-treated crystal of NaCl, the concentration of the first type F-centres will enhance considerably when they are colored. Optical bleaching of these crystals clearly indicates that there are two distinct stages of bleaching. The rate of bleaching is faster in the initial stage and later the mechanism of bleaching is similar to that in the case of 'as cleaved' crystals.

In conclusion, it may be said that even though the regions of first stage and the second stage bleaching are not separated out in 'as cleaved' crystals of NaCl, distinct separation can be obtained by quenching the crystal at high temperatures. The results obtained from heat-treated NaCl crystal support the fact that the optical bleaching also takes place in two stages. Firstly, the fast bleaching of first type F-centres occurs and then in the second stage,

the second type of F-centres are bleached with the formation of secondary centres like M, N, R.

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#### DIRECTOR, RAMAN RESEARCH INSTITUTE

The Board of Trustees of the Raman Research Institute has appointed V. Radhakrishnan to the position of Director of the Institute. Radhakrishnan, who is at present with the CSIRO Division of Radio Physics in Sydney, is known for his significant contributions to Radio Astronomy for over a decade, particularly those relating to Pulsars, to interstellar neutral hydrogen and to Jupiter's radiation belt. He has been out of India for the last 18 years working in England, Sweden, the United States, and for the last 6 years, in Australia.

Radhakrishnan will be returning to India early next year to take up his appointment. Until then, S. Ramaseshan (Deputy Director, National Aeronautical Laboratory, Bangalore) will act for him and run the affairs of the Institute.