

STUDY OF THE OPTICAL ABSORPTION AND DICHROISM
OF COLOR CENTERS IN GAMMA-IRRADIATED LiF:Mg

by

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I. INTRODUCTION

In the past few decades there has been considerable interest in the properties of color centers which are associated with divalent impurities in alkali halide crystals. The Z centers, which were found in alkali halide doped with alkaline earth impurities (1, 2) have received most attention. Studies of the optical properties (3, 4, 5, 6), luminescence (7), photoconductivity (8), electron spin resonance (9, 10) and dichroism (11, 12, 13) of these centers have provided useful information on the electronic structure of the centers, as well as on the nature of the point defects associated with them.

The thermoluminescence of LiF doped with Mg has important application as a radiation dosimetry technique (14). Harshaw Chemical Co., Cleveland, Ohio has developed thermoluminescent grade LiF with 100 ppm Mg impurity as a radiation dosimeter for gamma rays (14). These crystals are marketed as TLD-100. The X or gamma irradiated LiF:Mg shows a dominant F center absorption band at 5.0 eV, a V_3 band at 11.0 eV and additional absorption bands at 3.24 eV, 4.0 eV and 5.5 eV which are thought to result from Mg-related trapping centers (15, 16, 17). Mehta concluded in his work that the centers responsible for the 3.24 eV, 4.0 eV and the 5.5 eV absorption bands in TLD-100 are Z_2' , Z_2 and Z_3 centers respectively (18).

Studies of TL glow curves and optical absorption of TLD-100 showed the correlation between two important glow peaks near 200 °C and 4.0 eV absorption band (19). Study of this color center has been an important tool in investigating the TL process in TLD-100.

The fact that Z_2 center is a two-electron center (6) raises the possibility that dichroic behavior may be observed in optical bleaching with

polarized light. Past work has shown dichroism of Z_2 band in NaCl:Sr (11), KCl:Sr (12) and KCl:Ba (13) along [010] direction.

The purpose of this research is to study the bleaching behavior of gamma radiation induced absorption bands in LiF:Mg. Particularly, the objective of this work is to determine if the 4.0 eV absorption band--- Z_2 center absorption band, exhibits dichroism.

II. THEORY

Lithium Fluoride is an ionic compound, and like most of the alkali halides crystallizes in the rock salt or NaCl structure. In this structure each cation (lithium ion) is surrounded by six nearest-neighbor anions (fluoride ions), and each anion by six nearest-neighbor cations. The cations and anions are each situated on separate face-centered cubic lattices, and the two lattices are interleaved with each other.

At normal temperatures, LiF is a highly insulating solid and is optically transparent from the vacuum ultraviolet to the far infrared. In the band picture of solids, LiF is described by a filled valence band and an empty conduction band separated by a forbidden energy gap of about 13.5 eV (20, 21). Passage of ionizing radiation through the crystal releases electron-hole pairs. Color centers are formed by the trapping of these charges at the crystal imperfections and impurity sites. These color centers introduce energy levels in the forbidden region and can absorb photons which normally are transmitted by the crystal (22).

2.1. Color Centers in LiF

The principle color center produced in alkali halide by the passage of ionizing radiation is the F center. At room temperature the maximum of the F center absorption band in LiF is at 5.0 eV (22). The ground and excited states of the F center are localized energy levels in the forbidden energy gap. Recent works (20, 21) have shown that, in LiF, the ground state of the F center is approximately 8.5 eV below the conduction band minimum, and that it can not be optically bleached by illumination at 5.0 eV.

The F center absorption band is a bell-shaped absorption band whose spectral position and width depend on the nature of the alkali halide and on

the temperature. For alkali halides having the NaCl structure, the positions of the peaks of the F center absorption band at room temperature are given by the empirical relation (23),

$$\lambda_{\max} = 703 d^{1.84}, \quad (I)$$

where d is the lattice constant of the alkali halide. Both λ_{\max} and d are in Angstrom units. As the temperature is decreased, the F center absorption band becomes narrower and its peak position shifts to shorter wavelengths (24).

If we assume that the centers giving rise to the absorption do not interact with one another, the area under the absorption curve is directly proportional to the concentration of the centers. Smakula treated the F center as a damped oscillator according to classical dispersion theory, and obtained the following equation (25) relating the number of F centers per cm^3 , N , to the absorption coefficient in cm^{-1} at the peak of the F center absorption band, α_{\max} ,

$$Nf = \frac{n}{(n^2 + 2)^2} \alpha_{\max} W 1.29(10^{17}), \quad (II)$$

where

f = "oscillator strength," a factor which is related to the probability of the optical transition producing the absorption,

W = the half-width of the absorption band in eV,

and n = the refractive index of the crystal for the wavelength at the peak of the F center absorption band.

Dexter's analysis (26) took into account that the width of the absorption band arises from interactions of the center with lattice vibrations rather than from classical dispersion considerations, and that the F center absorption band is more Gaussian in shape rather than Lorentzian. From this viewpoint, the numerical factor should be $0.87 (10^{17})$ rather than $1.29 (10^{17})$.

Besides the prominent F center absorption band, the optical absorption measurement of irradiated LiF shows a dominant absorption band centered at 11.0 eV (15). The 11.0 eV absorption band has been identified as the V_3 center absorption band which is molecular fluorine resulting from two trapped holes. In the study of the thermoluminescence mechanism in LiF, Mayhugh found that the V_3 centers are intimately involved in the thermoluminescence process (15).

Recent works done by Marrs (27) and Richter (28) on the optical absorption of irradiated LiF have shown that a small absorption band, which appeared as a shoulder on the low energy side of the F center absorption band, is the Y center absorption band. At room temperature, this absorption band is centered approximately at 4.4 eV. A Y center is an electron captured at a halogen ion vacancy adjacent to an interstitial aluminum ion. The model of Y center shows a dipole axis along either $[0\bar{1}1]$ or $[011]$ direction. Marrs (27) and Richter (28) both observed a difference in absorbances at 4.4 eV in optical absorption spectra of irradiated LiF measured with $[0\bar{1}1]$ polarized light and with $[011]$ polarized light before optical bleaching. Optical bleaching with unpolarized light at 254 nm results in disappearance of this dichroism. The exact mechanism causing the dichroism of Y center is not known.

In some alkali halides, bleaching of the F center absorption band at low temperature results in reduction of the F center absorption band with a growth of a broad absorption band on the low energy side of the F center absorption band. This new absorption band is called the F' center absorption band (22), and is not thermally stable. The F' center is a F center which has captured an additional electron. The F' center absorption band has not been observed in LiF.

When an alkali halide crystal containing only the F center absorption band is illuminated in this band at room temperature, a broad absorption band arises at the low energy side of the F center absorption band. This absorption band is called M center absorption band (22), and is thermally unstable at temperatures somewhat above room temperature. The M center consists of two adjacent F centers, and in LiF, the M center is observed at 2.8 eV (444 nm) (17).

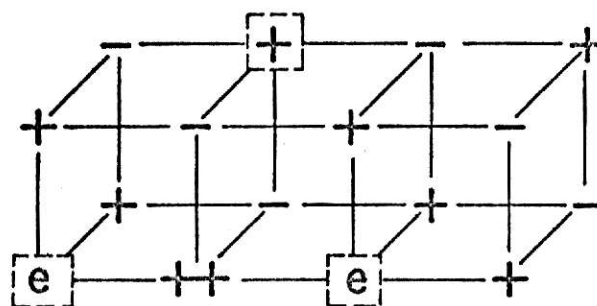
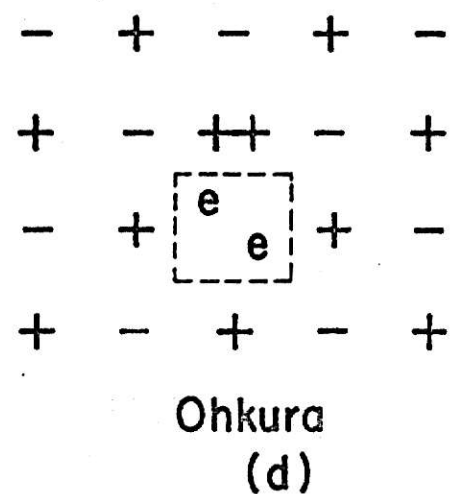
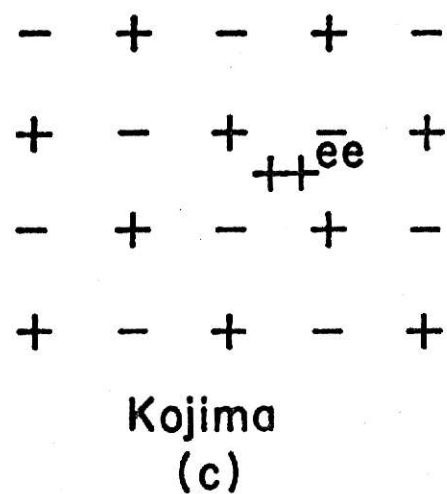
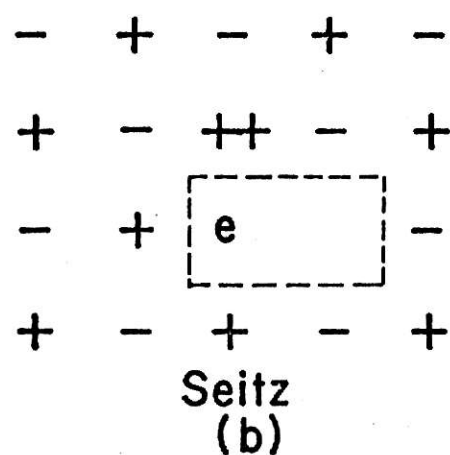
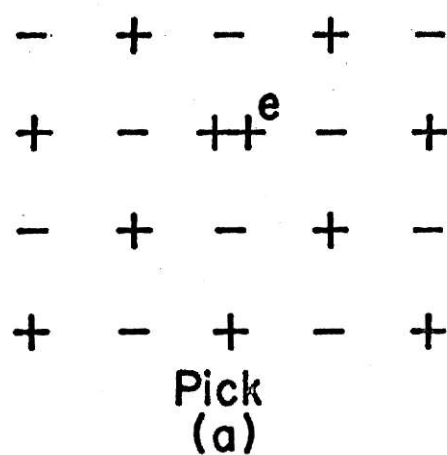
2.2 Models of Z Centers

When a divalent impurity is added substitutionally to an alkali halide crystal, additional absorption bands are observed. These absorption bands were first observed by Pick (1), and the centers producing these absorption bands are called Z centers. When an alkali halide crystal containing any of the alkaline earth impurities is additively colored, it exhibits the F center absorption band. Bleaching of the F center absorption band at room temperature results in the formation of an absorption band due to centers called Z_1 centers on the low energy side of the F center absorption band. If this crystal is then warmed up to $\sim 100^\circ\text{C}$, the Z_1 center absorption band disappears, the F center absorption band is further reduced, and a new absorption band called a Z_2 center absorption band is observed on the low energy side of the F center absorption band. The Z_2 center absorption band can also be formed in additively colored crystals, quenched from 400°C in the dark. If the bleaching is done at liquid nitrogen temperature instead of room temperature, the Z_3 center absorption band is observed on the high energy side of the F center absorption band.

Various models of Z centers have been proposed by Pick (1), Seitz (2), Kojima (5), Ohkura (6, 10) and Adlhart et al. (13). Models of Z_2 centers proposed by these authors, shown in Fig. 1, can be classified as one electron and two electron models in addition to vacancy-centered and impurity-centered models.

Figure 1

Models for the Z_2 centers proposed by Pick, Seitz,
Kojima, Ohkura, and Adlhart et al.



Adlhart et al.
(e)

Pick (1) suggests that the Z_1 center consists of an F center next to a substitutional divalent ion, and that the Z_2 and Z_3 centers consist of one and two electrons respectively trapped at a substitutional divalent ion. The Seitz model for the Z_1 center is identical to Pick's model for the Z_2 center. Seitz's model for the Z_2 center is a monovalent alkaline earth ion which is associated with an adjacent vacancy pair, and trapping of an electron by this center converts it into a Z_3 center.

West and Compton (7) have measured the degree of polarization of the emission induced by excitation with polarized light in the Z_2 center absorption band at 77 °K in KCl:Sr crystal and stated that the Z_2 center is one of high symmetry. Thus they supported the high symmetry model of the Z_2 center proposed by Pick. G. Chiarotti et al. (4) bleached with [010] polarized light in the Z_2 center absorption band at dry ice temperature, but failed to find any dichroism after 25 percent bleaching of Z_2 center absorption band. Remaut et al. (11) and Ishiguro et al. (12) have found dichroic behavior of the Z_2 center absorption band occurred in NaCl:Sr and KCl:Sr, and thus supported the Seitz' model of Z_2 center. The Pick's and Seitz' models of Z_2 center are both one-electron models, and can be converted into a Z_3 center by trapping of second electron.

The two electron model of Z_2 center was first proposed by Ohkura and Murase (10). The electron spin resonance (ESR) studies of the Z_2 center indicated that this center is diamagnetic (10). Studies of the formation of the Z_2 and Z_3 center absorption bands in KCl and KBr doped with Sr^{++} have shown that Z_3 center is the product of photoionization of the Z_2 center (6). Ohkura concluded on the basis of the above observations that the Z_2 and Z_3 centers consist of two electrons and one electron respectively trapped at a halogen ion vacancy next to a substitutional divalent cation. The experimental results of Kojima (5) are similar to those obtained by Ohkura. She

has suggested a two electron model of Z_2 center with electrons captured at an interstitial divalent cation.

Later work done by Adlhart et al. (13) on electron spin resonance measurements has shown different symmetry axes of Z_2 centers in different crystals: [100] in KCl:Ca, KCl:Sr and NaCl:Ca; and [100], [011] and $[0\bar{1}1]$ for NaCl:Sr. They also found in the optical measurements of Z_2 centers in KCl:Ba that the symmetry axis is in [100] direction. A model of Z_2 center was proposed to fit their observations. The two electrons of this Z_2 center model are partly localized at the divalent ion sites, and each located at an halogen ion vacancy at each side of the divalent ion with an alkali ion vacancy located at position as shown in Fig. 1e.

2.3. Color Centers in LiF:Mg

The crystals of LiF:Mg, marketed as TLD-100, contain about 100 ppm of magnesium as the prominent impurity (17, 29). After X or gamma irradiation, these TLD-100 crystals show absorption bands centered at 3.24 eV, 4.0 eV, and 5.5 eV, in addition to the F center and V_3 center absorption bands (15, 16, 30). The absorption bands centered at 3.24 eV, 4.0 eV and 5.5 eV do not appear in irradiated pure LiF (27, 28) and have been correlated with the presence of magnesium in TLD-100 (15, 16, 17, 30). The optical bleach of the 4.0 eV absorption band leads to the growth of the 5.5 eV absorption band, indicating that the 5.5 eV absorption band is due to the color center of the same type as 4.0 eV center. The 5.5 eV absorption band can also increase at the expense of 4.0 eV and 5.0 eV absorption bands by illuminating at 5.0 eV at room temperature (18).

Recent work done by Mehta (18) concluded that the color centers responsible for the 3.24 eV, 4.0 eV and 5.5 eV absorption bands are Z_2' , Z_2 and Z_3 centers respectively. The models used by Mehta were the models proposed by Ohkura (6).

The Z_2 center consists of two electrons trapped at a halogen ion vacancy next to a substitutional divalent cation. The Z_2' center is a Z_2 center with an extra electron (or Z_2^- center) and the Z_3 center is a Z_2 center which has lost an electron (or Z_2^+ center).

It was observed (18) that on annealing at 100 °C the 4.0 eV absorption band grows but all other absorption bands diminish, and the 3.24 eV absorption band was completely eliminated. The electrons were transferred from other color centers to form Z_2 center and cause the growth of the 4.0 eV absorption band. It is also observed (18) that in optical bleaching of the 3.24 eV absorption band at room temperature or near liquid nitrogen temperature, the 4.0 eV and 5.0 eV absorption bands both grow at the expense of 3.24 eV absorption band. The interconversion of these absorption bands of TLD-100 will be further studied in this research with light polarized in the $[0\bar{1}1]$, $[010]$, $[011]$ and $[001]$ directions.

The thermoluminescence of TLD-100 has been receiving wide application in radiation dosimetry (14), and has been used as an important tool in study of the color centers in gamma irradiated TLD-100 crystals. The 3.24 eV and 4.0 eV absorption bands were correlated with the 100 °C and 200 °C thermoluminescence peaks respectively (17, 19, 30). Mayhugh et al. found that the centers causing the 200 °C thermoluminescence appear to have two excited states, i.e. having absorption bands at 4.0 eV and under the F center absorption band at 5.0 eV (19). The observation of reduction of the F center absorption band in gamma irradiated TLD-100 by room temperature bleaching at 5.0 eV (15, 16, 18, 19) is in contrast with the fact that the F center of LiF can not be optically bleached (20, 21, 27, 28). This indicates that an additional absorption band may be buried under the F center absorption band.

III. EXPERIMENTAL PROCEDURE

Optical absorption spectra of magnesium doped LiF single crystals, TLD-100, were measured in the spectral range of 700 nm to 200 nm at room temperature or near liquid nitrogen temperature (LNT). The measurements were made before and after the crystal was irradiated with ^{60}Co gamma rays followed by thermal annealing at 100 °C, and after it was optically bleached. In each step, five spectra were measured in the order: unpolarized light, $[0\bar{1}1]$ polarized light, $[010]$ polarized light, $[011]$ polarized light, and $[001]$ polarized light. In this chapter, we will deal with the materials and the methods used in these experiments.

3.1 Experimental Samples

Crystals of TLD-100, obtained from Harshaw Chemical Corp, in 1972, were 1.0 x 1.0 cm in cross-sectional area. The thickness varied from 0.2 cm to 0.5 cm.

3.2 Thermal Treatment

Prior to gamma irradiation all samples were annealed at 400 °C for 24 hours. They were then quick quenched to room temperature, in air, by placing the Pyrex beaker containing the samples on a large piece of stainless steel. The purpose of the quick quenching was to freeze in the defects formed during the high temperature anneal.

After the gamma irradiation, the sample was annealed at 100 °C for 30 minutes and then quick quenched again to room temperature. The purpose of this anneal was to destroy the unstable larger aggregates so as to eliminate any possible interactions between these centers and the centers of interest.

3.3 Gamma Irradiation

Gamma irradiations were carried out in the irradiation chamber of the Gamma cell (AECL 220).

A polyethylene disk about 1/2 inch thick made to fit inside the irradiation chamber was used to irradiate the TLD-100 samples. The purpose of this disk was to position the sample in the irradiation chamber so that the sample would receive the same dose as if they had been placed at the center of the chamber. This position is located at 2 3/4 inches above the base of the chamber and 2 inches away from its axis (34). The dose rate at this position was 1.28 kilorad per minute, as of March 1, 1976.

3.4 Optical Absorption Measurements

A Cary-14 Recording Spectrophotometer was used to measure the optical absorption spectra. The measurements were made at temperatures of 300 °K and 90 °K. Figure 2 shows the schematic of the dewar used as sample holder. The outer wall of the vacuum jacket at the bottom of the dewar was connected by a $\frac{1}{8}$ 29/42 joint to a glass tube having two fused quartz windows. The inner wall of the vacuum jacket was silver soldered through a Kovar-to-glass graded seal to a copper sample holder. The sample was held on the sample holder by Eccotherm TC-4 conducting grease, made by Emmerson and Cummings, Inc., Canton, Massachusetts. The dewar was held in a wooden box which was made to fit firmly into the top of the Cary-14 sample chamber such that the sample was positioned normal to the measuring beam.

Every crystal sample was first examined and marked as shown in Fig. 3. The mark defines the (100) surface and the (001) surface which will be attached to the sample holder. Optical absorption spectrum was always taken with measuring beam incident on (100) surface along $[\bar{1}00]$ direction.

FIGURE 2

Glass dewar sample holder for optical absorption measurements.

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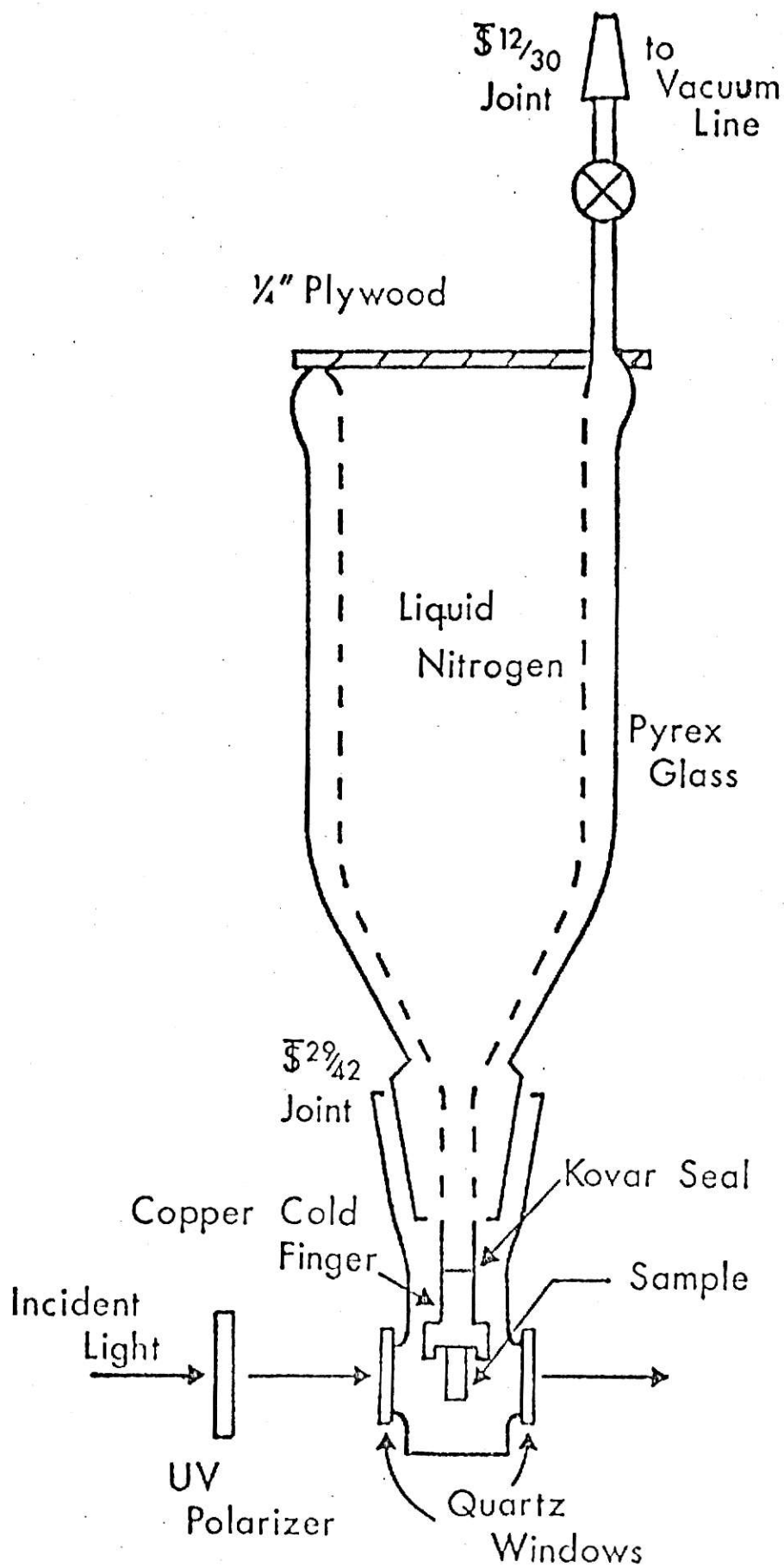
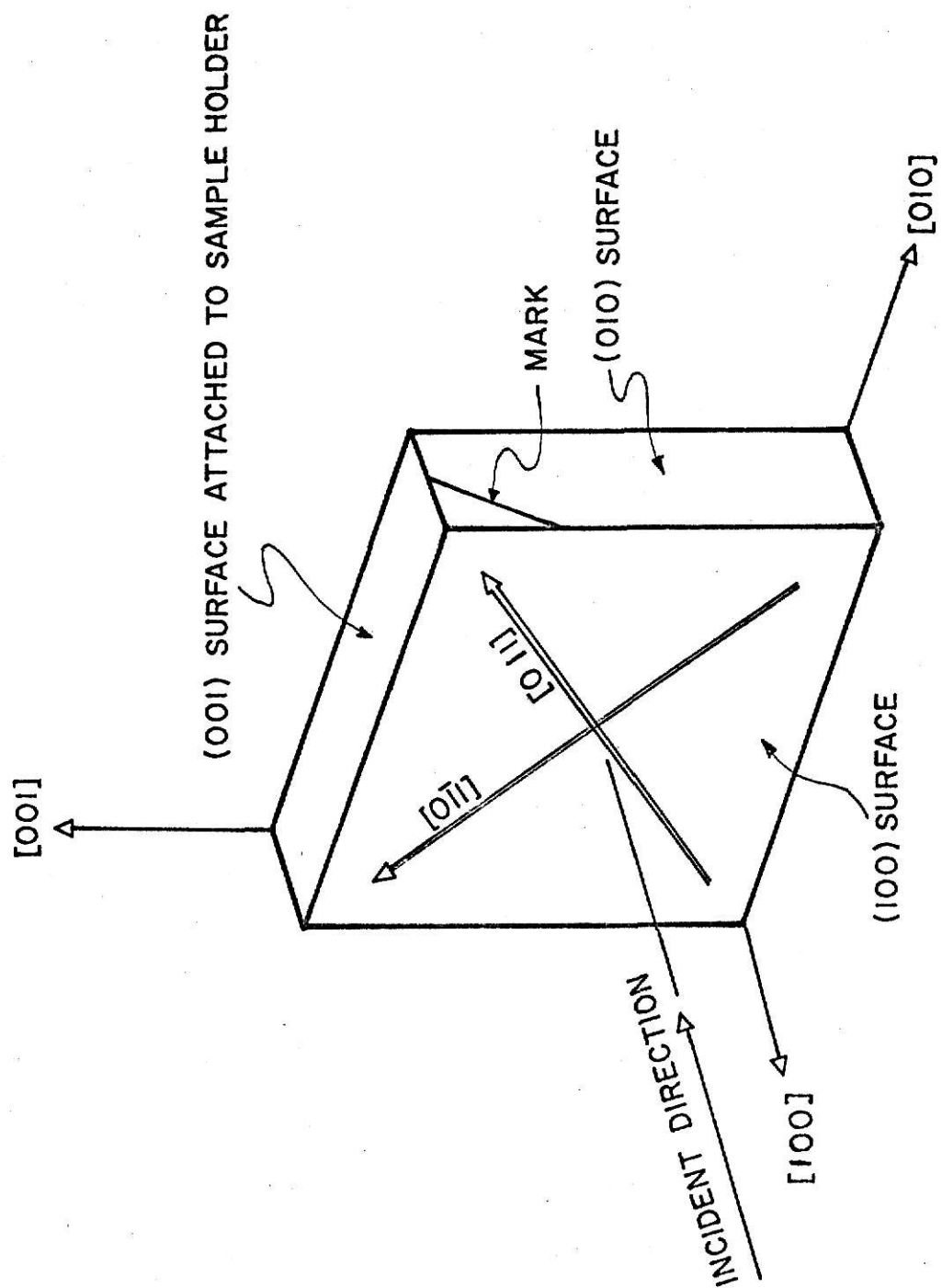


FIGURE 3

Crystallographic representation of the direction of propagation and the direction of the polarization of the incident light. The orientation of the crystal is defined by the engraved mark on the (010) surface.



The absorption measurements were made before and after gamma irradiation, and after optical bleaching. In each step, five measurements were made with unpolarized light, $[0\bar{1}1]$ polarized light, $[010]$ polarized light, $[011]$ polarized light and $[001]$ polarized light in this order.

The absorption spectra taken before gamma irradiation was used as background which was then subtracted from those spectra taken after gamma irradiation.

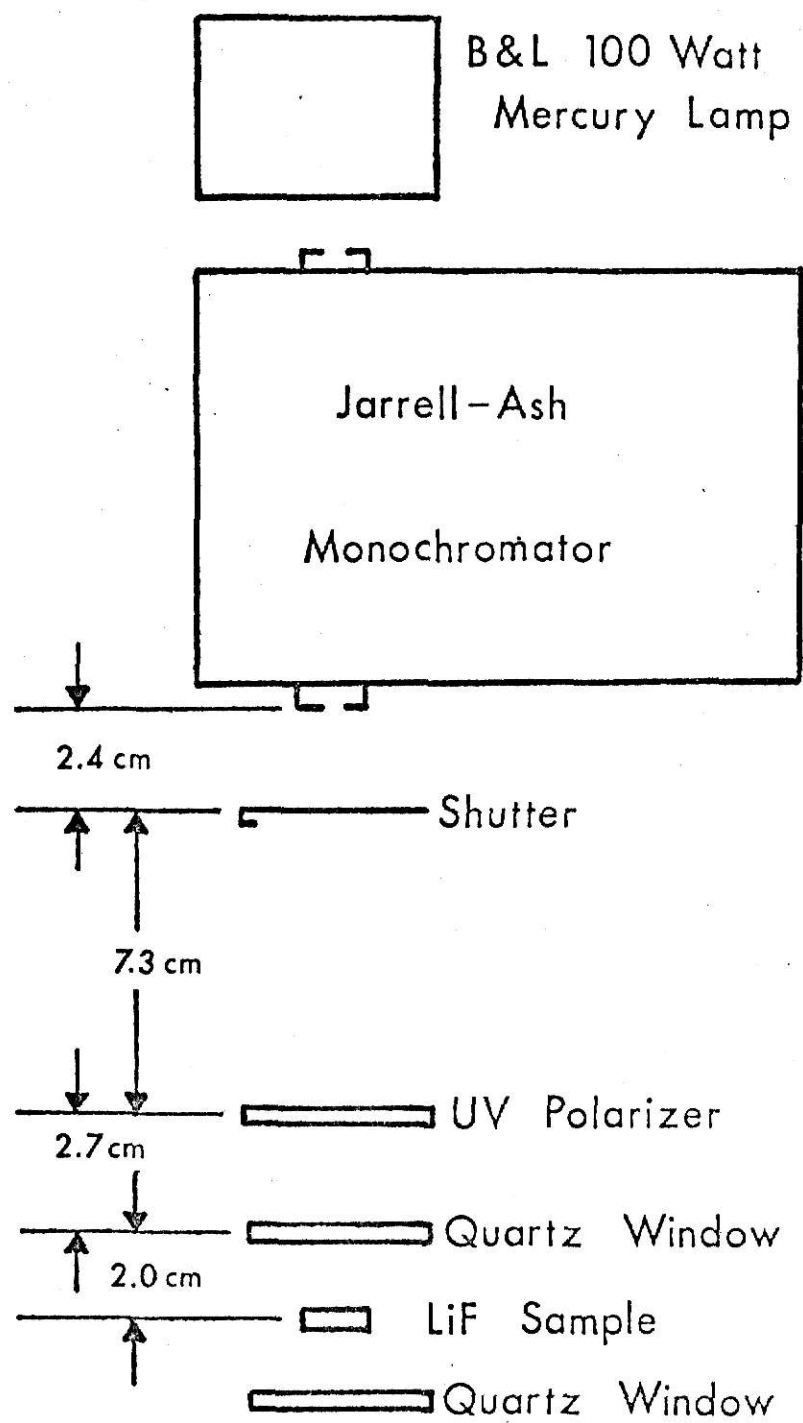
3.5 Optical Bleaching

Figure 4 shows the experimental arrangement for optically bleaching the samples. The bleaching light was obtained from a Bausch and Lomb, Model HP-100, 100 watt Mercury Arc Lamp and Power Supply. The light then went through a Jarrell-Ash, Model 82-410, 0.25 meter Ebert Monochromater and a quartz condensing lens. The Jarrell-Ash monochromater has a dispersion of 1.6 nm/mm in the ultraviolet. A one millimeter exit slit gave a bandpass of about 1.6 nm. The position of the condensing lens was adjusted such that the width of the bleaching light is slightly larger than that of measuring beam of the Cary-14 Spectrophotometer.

The samples were optically bleached with unpolarized light or polarized light at the selected wavelength. To obtain the polarized light beam a linear polarizer made by Polacoat Inc. was used. The orientation of the polarization vectors and the k-vector of the light beam relative to the crystal axes is shown in Fig. 3. The k-vector of the incident light was in the $[\bar{1}00]$ direction.

FIGURE 4

Experimental arrangement used to optically bleach LiF:Mg (after
Reference 27)



IV. RESULTS AND DISCUSSION

The absorbance of TLD-100 single crystal was studied before and after optical bleaching at 300 °K or 90 °K. The optical absorption spectra were measured in the spectral range of 700 nm to 200 nm with unpolarized light and light polarized in the directions of $[0\bar{1}1]$, $[010]$, $[011]$ and $[001]$ relative to the crystal axes. Optical bleaches were carried out at 250, 280, and 310 nm.

A Neutron Activation Analysis was run on a sample of TLD-100, used in this work, to determine the impurity concentrations. The results show that the crystals contain magnesium and aluminum at concentrations of about 127.0 ppm and 20.8 ppm respectively. A small amount of titanium was also found in TLD-100 crystal at a concentration of about 10 ppm.

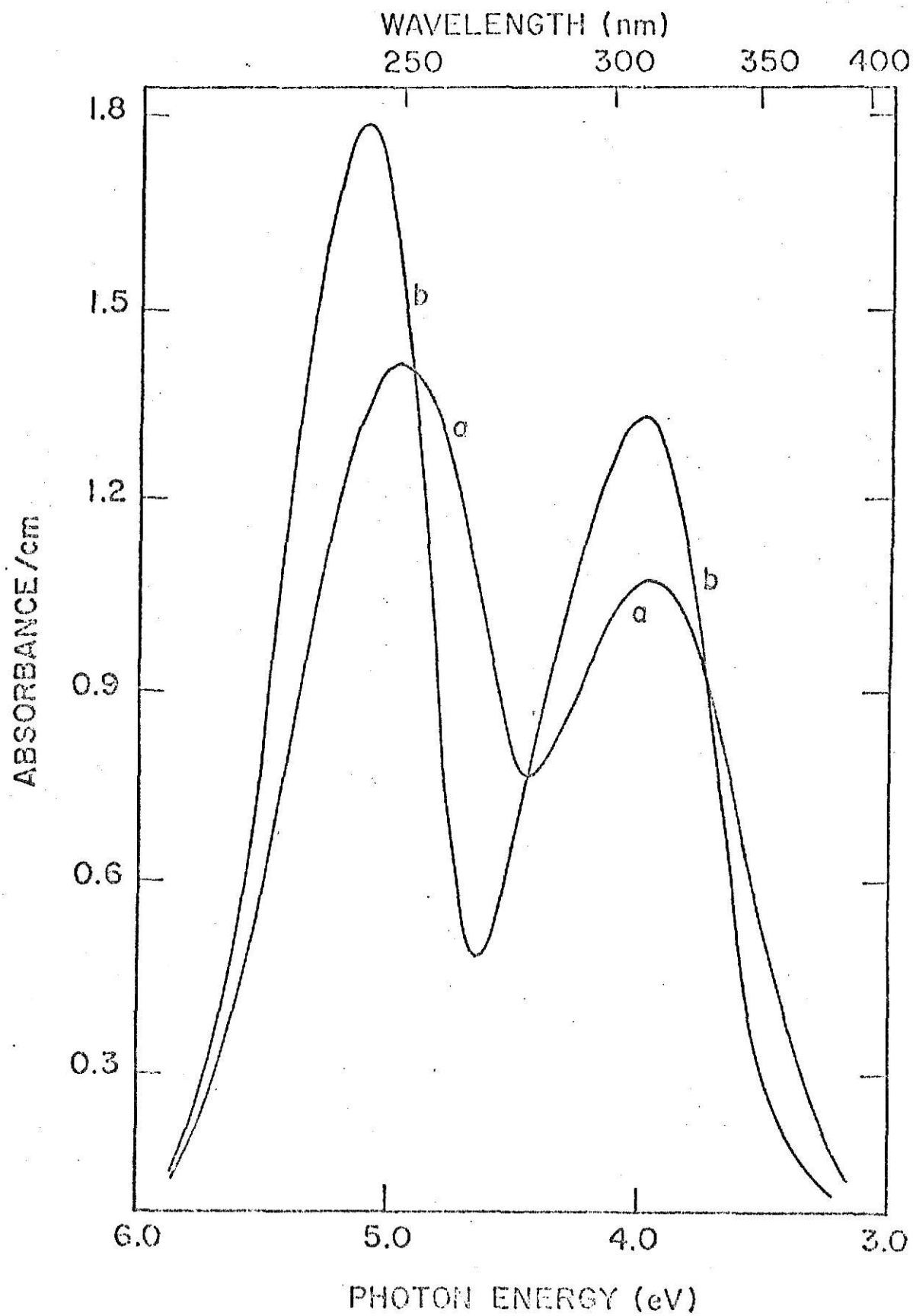
4.1 Optical Absorption of Gamma-Irradiated TLD-100

Figure 5 shows the optical absorption of TLD-100 versus photon energy after exposure to 50 kilorad of gamma radiation followed by 30 minutes thermal annealing at 100 °C. Curve a shows the absorbance measured at 300 °K and curve b the absorbance at 90 °K. Both were measured with unpolarized light.

Both curves show the prominent absorption band peaking at 5.0 eV at 300 °K and at 5.1 eV at 90 °K. The center which causes the 4.0 eV absorption band was described as a Z_2 center by Mehta (18). He used Ohkura's model, which is a center trapping two electrons at an anion vacancy adjacent to a divalent cation impurity.

FIGURE 5

Optical absorption spectra of gamma-irradiated TLD-100 measured with unpolarized light at 90 °K and 300 °K. Curve (a) is the optical absorption spectrum measured at 300 °K. Curve (b) is the optical absorption spectrum measured at 90 °K. Absorbed Dose-50 kilorad.



It is noticed, in Fig. 5, that near liquid nitrogen temperature both the Z_2 center absorption band and the F center absorption band have narrowed, and that the F center absorption band has shifted to higher energy. The shift and narrowing of F center absorption band with decreasing temperature have also been observed in pure LiF by Mehta (18), Marrs (27) and Richter (28). This temperature dependence of the F center absorption band has been also observed in other alkali halides (22).

A particle-in-a-box model of F center can be used to qualitatively explain the shift and narrowing of F center absorption band. For this model of the F center, the particle is the trapped electron and the box is the negative ion vacancy. The difference in energy between the ground state and the first excited state of the electron is inversely proportional to the square of the size of the box. Decreasing the temperature will reduce the size of the unit lattice cell or the box. The reduction of the size of the box will result in increasing the difference between energy levels, and consequently the peak position of the absorption band will shift to higher energy.

Decreasing the temperature also decreases the amplitude of thermal vibrations of the Li^{+1} ions surrounding the trapped electron. Since the range of possible values for the size of the box is a function of the amplitude of thermal vibration, decreasing the temperature will result in a smaller range of possible values of the size of the box. The full width at half maximum (FWHM) which is related to the probability distribution of the size of the box therefore becomes smaller when the temperature is decreased.

The area under the F center absorption band is proportional to the concentration of the F centers (22). In pure LiF, Marrs (27) found that

the concentrations of the F centers at 300 °K and 90 °K are about same. For LiF:Mg, the absorption spectra are more complicated because of the overlapping of F center absorption band with 4.0 eV absorption band and other absorption bands (19).

Results of Neutron Activation Analysis show the existence of aluminum in TLD-100 at a concentration of 21 ppm. Richter found that the LiF, which contained aluminum at concentration of 22.5 ppm, exhibited an absorption band at 4.4 eV (27). This absorption band is due to a perturbed F center, called a Y center. The model of the Y center is a F center with an aluminum ion occupying an interstitial site. Although the Y center absorption band is not seen in Fig. 5, the existence of Y center in TLD-100 can not be ruled out.

4.2 Optical Bleaching of TLD-100 with Unpolarized Light at 254 nm

Figures 6, 7, and 8 shows the effect of optical bleach on TLD-100 with unpolarized light at 254 nm at 300 °K for 20 hours. The optical absorption spectra measured with unpolarized light are shown in Fig. 6. Curve a is the spectrum measured before the bleach, and curve b measured after the bleach. The results show the same effect of bleaching with unpolarized light at 250 nm at 300 °K as that observed by Mehta (18). Reduction of 5.0 eV absorption band is greater than that of 4.0 eV absorption band, and an absorption band around 5.5 eV grows at the expense of 4.0 eV and 5.0 eV absorption bands.

The absorption spectra were also measured with $[0\bar{1}1]$ polarized, $[010]$ polarized, $[011]$ polarized and $[001]$ polarized light. The analysis of the change of each individual absorption band is complicated due to overlapping of the absorption bands. However it is observed that the 4.0 eV absorption bands measured with different polarizations of light before optical bleach

FIGURE 6

Optical absorption spectra of irradiated TLD-100 measured with unpolarized light at 300 °K before and after an optical bleach with unpolarized light at 254 nm at 300 °K. Curve (a) is the optical absorption spectrum before the bleach. Curve (b) is the optical absorption spectrum after a 20 hour bleach at 254 nm. Absorbed Dose-50 kilorad.

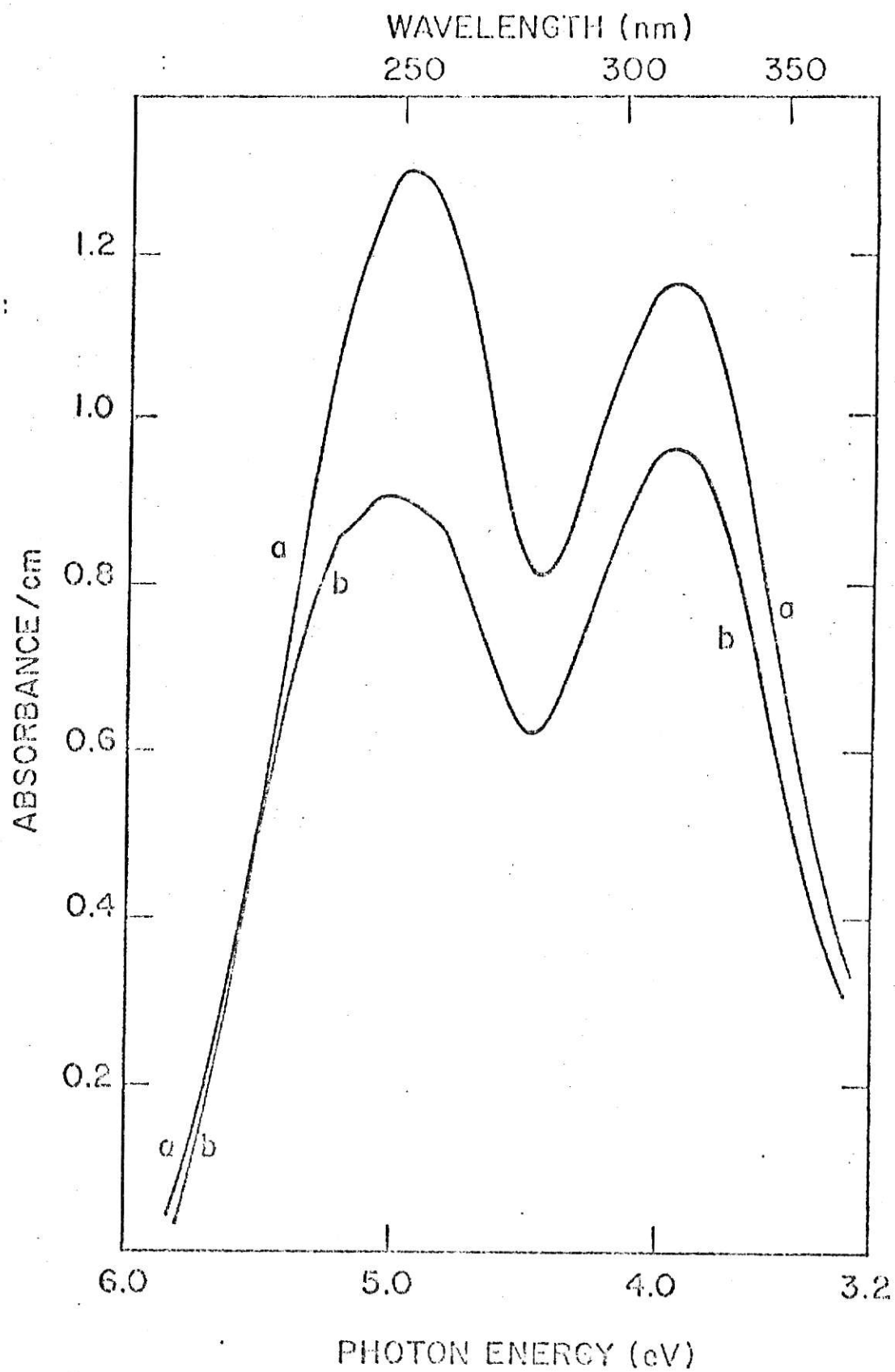


FIGURE 7

Optical absorption spectra of irradiated TLD-100 measured with [011] polarized light at 300 °K before and after an optical bleach with unpolarized light at 254 nm at 300 °K. Curve (a) is the optical absorption spectrum before the bleach. Curve (b) is the optical absorption spectrum after a 20 hour bleach at 254 nm. Absorbed Dose-50 kilorad.

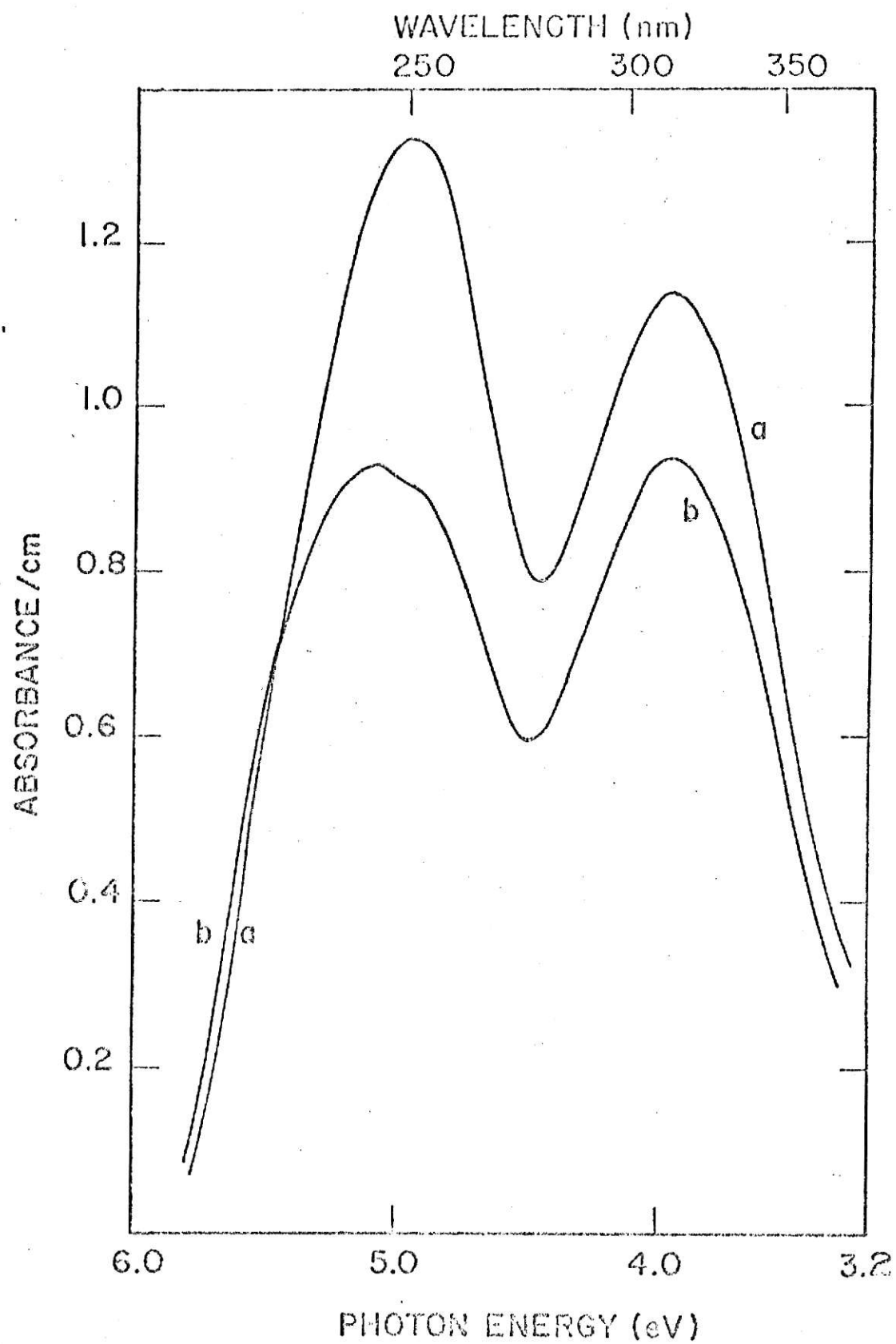
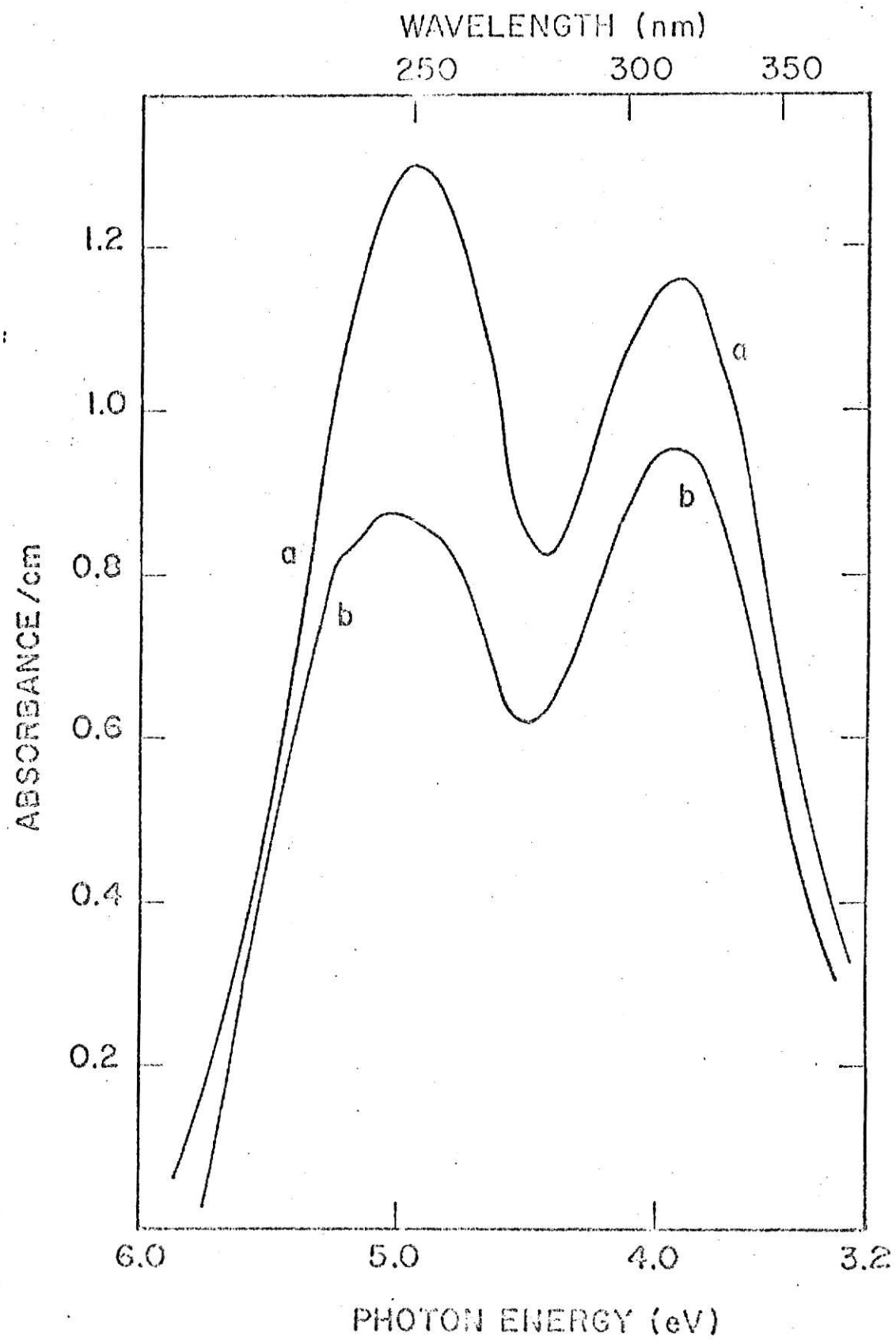


FIGURE 8

Optical absorption spectra of irradiated TLD-100 measured with $[0\bar{1}1]$ polarized light at 300 °K before and after an optical bleach with unpolarized light at 254 nm at 300 °K. Curve (a) is the optical absorption spectrum before the bleach. Curve (b) is the optical absorption spectrum after a 20 hour bleach at 254 nm. Absorbed Dose-50 kilorad.



have the same peak height, and that the reduction of these absorption bands caused by bleaching with unpolarized light at 254 nm at 300 °K are the same. Figure 7a is the optical absorption spectrum measured with [011] polarized light, and Figure 8a is the optical absorption spectrum measured with $[0\bar{1}1]$ polarized light before the optical bleach. Figures 7b and 8b are the respective optical absorption spectra measured after the bleach. The absorbance at 5.0 eV measured with $[0\bar{1}1]$ polarized light (Fig. 8b) is a little greater than that measured with [011] polarized light (Fig. 7b). This difference in absorbance would seem to indicate dichroism, but it seems unlikely that dichroism would be produced by bleaching with unpolarized light. The peak of the absorbance shifts from 4.95 eV to about 5.05 eV and this is due in part to the growth of the Z_3 center absorption band around 5.5 eV. This was also observed by Mehta (18). A Z_3 center is the product of photoionization of Z_2 center (6), and consists of one electron captured at a halide ion vacancy adjacent to a substitutional divalent ion. The reduction of the 5.0 eV absorption band measured with unpolarized light and light polarized in the [010] direction and in the [001] direction are about the same (not shown). The peak position of the 4.0 eV absorption band does not shift as a result of bleaching with unpolarized light at 254 nm.

The reasons for the seeming dichroism of 5.0 eV absorption band induced in TLD-100 by bleaching with unpolarized light at 254 nm, and for the preference of dichroism for $[0\bar{1}1]$ and [011] directions are not known. The fact that the F center absorption band in LiF can not be bleached with light at 254 nm (20,21) suggests that there are other absorption bands overlapping the F center absorption band. Marrs (27) and Richter (28) have both observed the bleaching of the Y center absorption band on the low energy side of the F center absorption band with unpolarized

light at 254 nm in pure LiF. Mayhugh et al. (19) have suggested that the Z center in TLD-100 which has an absorption band at 4.0 eV, also absorbs light at 5.0 eV. The bleaching of these two centers could explain the decrease in the absorbance at 5.0 eV. The bleaching of these two centers plus the growth of the Z_3 center could explain the shift of the peak position from 4.95 eV to about 5.05 eV.

Samples of TLD-100, bleached at room temperature with polarized light at 254 nm for 40 hours, did not exhibit dichroism. The light was polarized in the [011] direction and in the [001] direction. Ishiguro et al. (12) used light polarized in the [010] direction which was absorbed either by Z_2 centers or F centers in NaCl:Sr and KCl:Sr. They observed an initial induced dichroism in these centers, followed by a decrease in the dichroism and finally a disappearance of the induced dichroism.

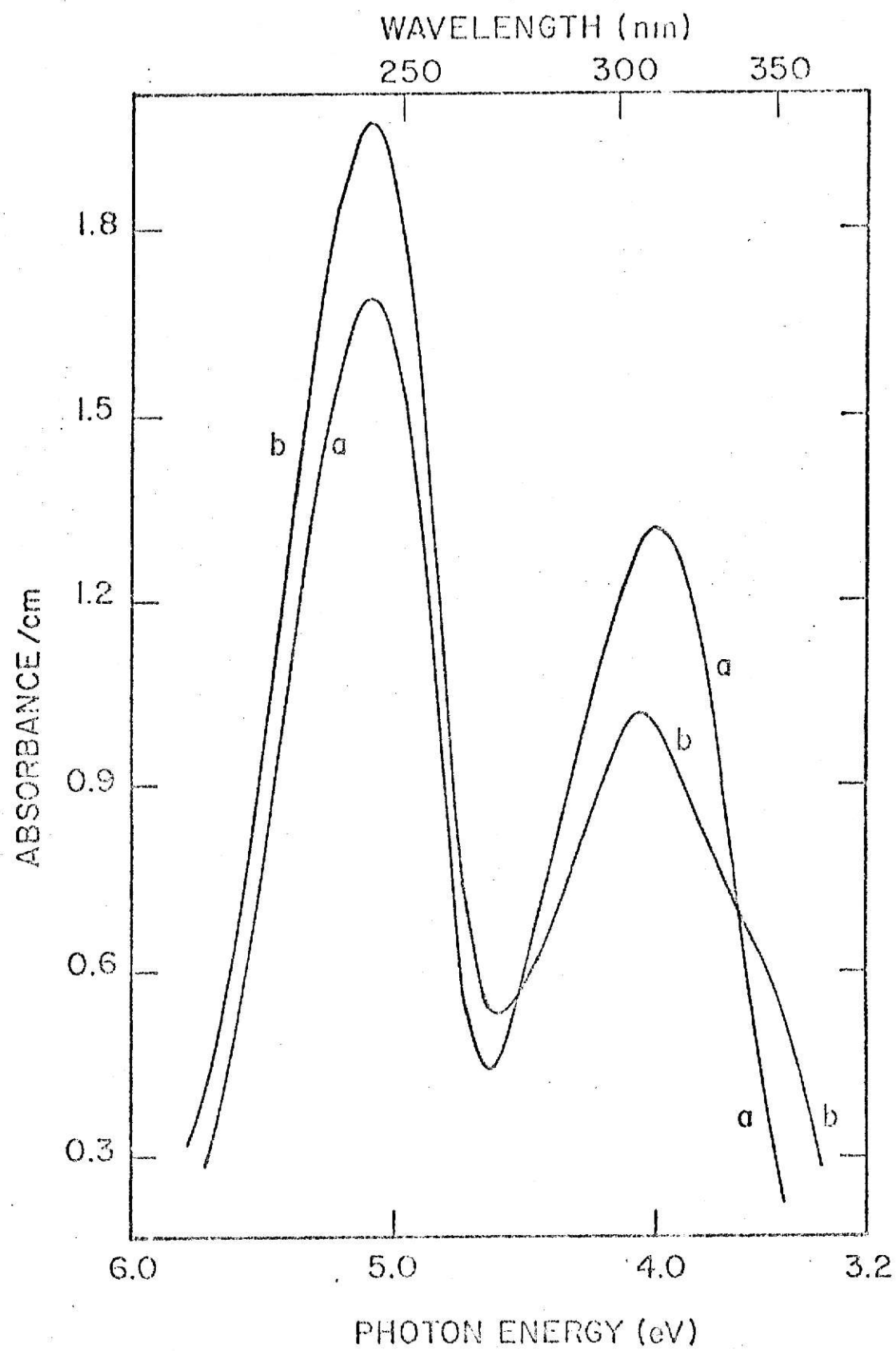
4.3. Optical Bleaching of TLD-100 with Unpolarized Light at 313 nm and 280 nm

Optical bleaches on TLD-100 with unpolarized light at 313 nm were carried out at liquid nitrogen temperature. Figure 9 shows the effect of optical bleach with unpolarized light at 313 nm at 90 °K for 3 hours. Curves a and b of Fig. 9 are the absorption spectra taken before and after the bleach, respectively. The 4.0 eV absorption band decreases as a result of bleach, while the 5.0 eV absorption band increases.

It is noticed that a new absorption band grows at the low energy side of the 4.0 eV absorption band. This absorption band centered at about 3.5 eV was also observed by Mehta (18). Warming up to room temperature and then cooling down to liquid nitrogen temperature results in disappearance of this band and slight increase of 4.0 eV absorption band (not shown). This reverse reaction indicates that the 3.5 eV absorption band is unstable at room temperature, and that it is closely related with the 4.0 eV absorption

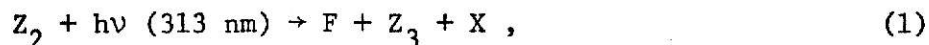
Figure 9

Optical absorption spectra of irradiated TLD-100 measured with unpolarized light at 90 °K before and after an optical bleach with unpolarized light at 313 nm at 90 °K. Curve (a) is the optical absorption spectrum before the bleach. Curve (b) is the optical absorption spectrum after a 3 hour bleach at 313 nm. Absorbed Dose-50 kilorad.



band. Since the Z_2 center, which is responsible for the 4.0 eV absorption band is trapped electron center, the center which absorbs at 3.5 eV may also be trapped electron center. The structure of this center is not known.

The study of optical absorption bands of TLD-100 done by Mehta shows that bleaching of the 4.0 eV absorption band results in the increase of the F center absorption band and of the absorption band around 5.5 eV (18). The low temperature bleaching with light in the Z_2 center absorption band in other alkali halides produces the Z_3 center absorption band on the high energy side of the F center absorption band (1, 2, 5, 6). Mehta concluded in his work that the absorption band at 5.5 eV is due to the Z_3 center which is the product of photoionization of the Z_2 center. He represented the overall bleaching behavior of TLD-100 at 313 nm by the following equation (18),



where X represents the 3.5 eV center. In Fig. 9, the increase in the 5.5 eV absorption band can not be easily separated out from the increase in the F center absorption band.

There has been a significant increase in the absorbance at 4.4 eV as a result of the bleaching. It is observed from Fig. 9 that the absorption band peaking at 4.0 eV shifts to higher energy. The shift of the peak position of this absorption band can be explained in a manner similar to the explanation of the shift of 5.0 eV absorption band to higher energy during room temperature bleaching at 254 nm. Before optical bleaching, the 4.0 eV absorption band is the combination of the prominent Z_2 center absorption band at 4.0 eV and other minor bands such as the Y center absorption band at 4.4 eV. When bleaching with light at 313 nm, some of the electrons released from the Z_2 centers may be trapped at ionized Y centers. Therefore the Y center absorption band grows while the Z_2 center absorption band decreases

and may finally become dominant after longer bleaching. The maximum of the new combination of Z_2 and Y center absorption bands thus shifts to higher energy.

Bleaching with light at 280 nm causes the reverse reaction, that is, populating Z_2 centers at the expense of Y centers, and the shift of peak position back to the original position. This is shown in Fig. 10. Curve a of Fig. 10 is the optical absorption spectrum of TLD-100 after gamma irradiation to a dose of 50 kilorad and thermally annealed at 100 °C for 30 minutes. Curve b is the spectrum measured after bleaching with light at 313 nm for 80 minutes, and curve c is the spectrum measured after bleaching with light at 280 nm for 90 minutes following the bleaching at 313 nm.

The absorbance at 6.0 eV has increased during the optical bleaching with light at 313 nm and with light at 280 nm. There is an absorption band centered at 6.0 eV in unirradiated TLD-100 (18, 19, 30). The absorbance of unirradiated and thermally annealed TLD-100 is shown in Fig. 11. This absorption band is not seen in the other figures of this thesis because the spectrum of unirradiated TLD-100 was used as background and was subtracted from those spectra taken after gamma irradiation. However, the increase of absorbance at 6.0 eV indicates that more color centers associated with this absorption band have been produced by bleaching.

The 5.0 eV absorption band, which may consist at least two absorption bands, increases by bleaching with light at 313 nm, but stays unchanged when bleached with light at 280 nm following bleach at 313 nm, as shown in Fig. 10. If the TLD-100 crystal is bleached with light at 280 nm after gamma irradiation and thermal annealing at 100 °C for 30 minutes, the spectrum after bleach shows an increase of absorbance at 5.0 eV, instead of staying

Figure 10

Optical absorption spectra of irradiated TLD-100 measured with unpolarized light at 90 °K before and after optical bleaches with unpolarized light at 313 nm and with unpolarized light at 280 nm at 90 °K. Curve (a) is the optical absorption spectrum before the bleach. Curve (b) is the optical absorption spectrum after a 80 minute bleach at 313 nm. Curve (c) is the optical absorption after a subsequent 90 minute bleach at 280 nm. Absorbed Dose-50 kilorad.

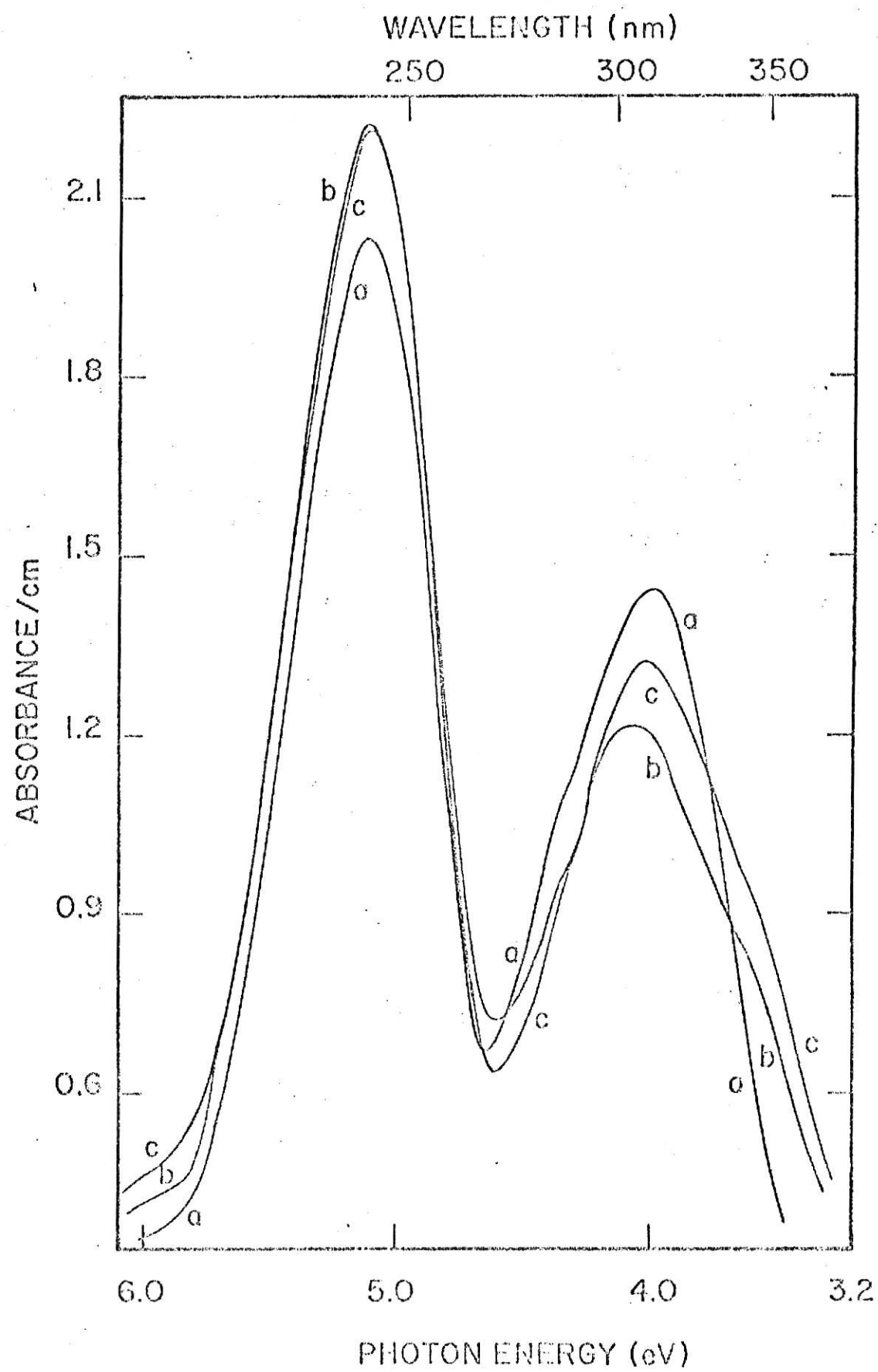
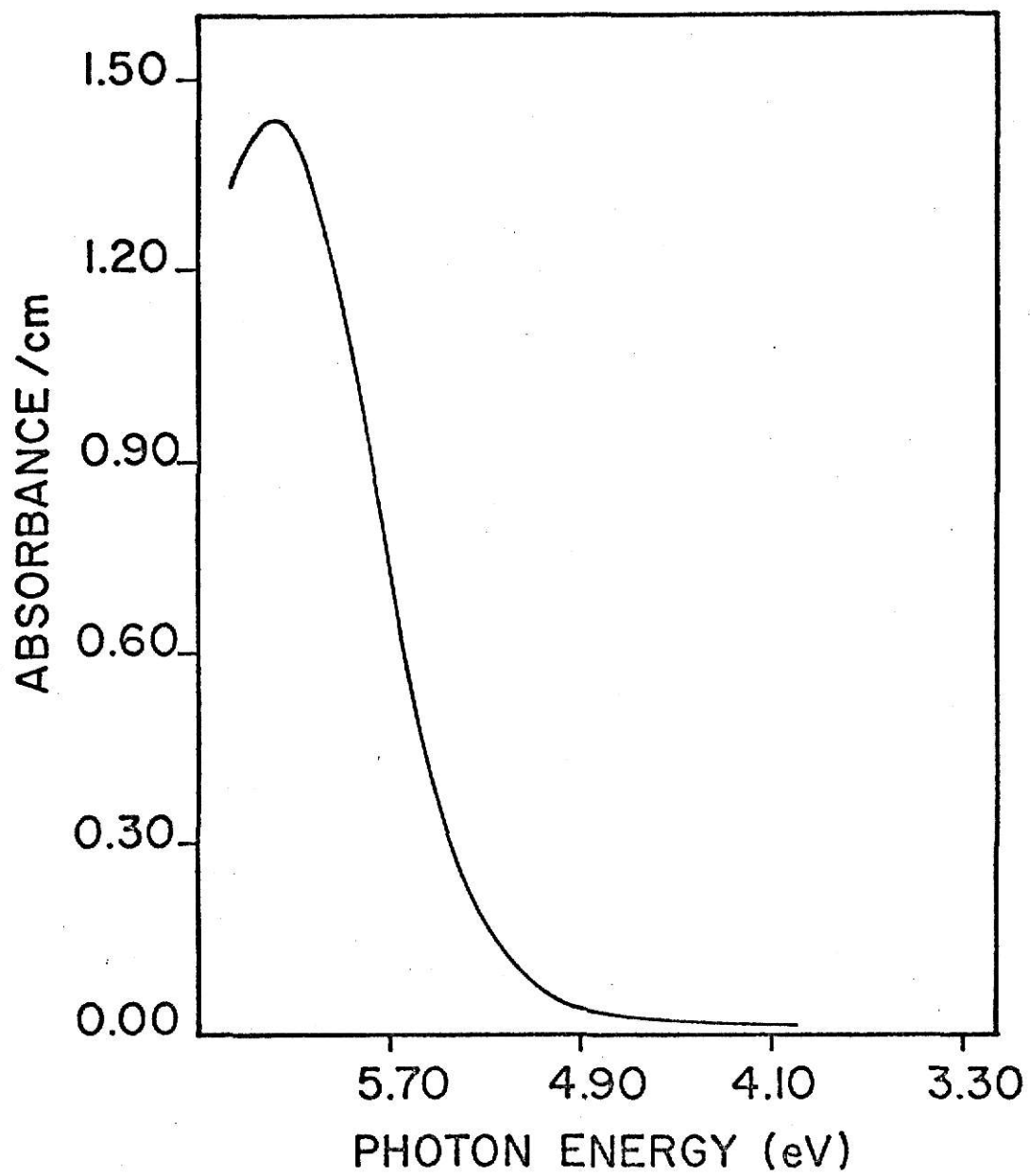


Figure 11

Optical absorption spectrum of unirradiated TLD-100 measured with unpolarized light at 300 °K, after 400 °C anneal for 16 hours. Measurement at liquid nitrogen temperature showed no change in absorbance.



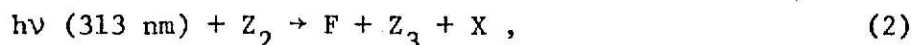
unchanged as in the previous case. Figures 12a and 12b are the absorption spectra measured before and after bleaching with unpolarized light at 280 nm, respectively. The absorption bands centered at 3.5 eV and 5.0 eV increase at the expense of Y center absorption band at 4.4 eV.

4.4 Study of Dichroism of the Z_2 Center in TLD-100

4.4.1 Optical Bleaches with Polarized Light at 313 nm and with Unpolarized Light at 254 nm

The gamma-irradiated TLD-100 crystal was first bleached with light at 313 nm polarized in the $[0\bar{1}1]$ direction, then with unpolarized light at 254 nm, near liquid nitrogen temperature. The optical absorption spectra were measured with unpolarized light and light polarized in the $[0\bar{1}1]$ direction, the $[010]$ direction, the $[011]$ direction and the $[001]$ direction at 90 °K, before and after bleaching.

Figure 13 shows the absorption spectra measured with unpolarized light at 90 °K. Curves a and b show the effect of the bleaching of TLD-100 at 313 nm near liquid nitrogen temperature discussed in the previous section, that is, an increase of 3.5 eV, 4.4 eV, 5.0 eV and 5.5 eV absorption bands at the expense of 4.0 eV absorption band. Curve c shows the effect of a subsequent bleach at 254 nm for 2 hours. The 4.4 eV and 5.0 eV absorption bands diminish and the 4.0 eV absorption band grows. Mehta had also observed the same effect as he successively bleached the TLD-100 with unpolarized light at 310 nm and 250 nm (18). He used the following equations to represent these reactions,



and

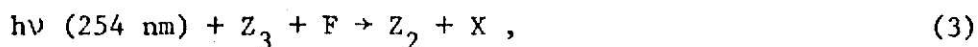


Figure 12

Optical absorption spectra of irradiated TLD-100 measured with unpolarized light at 90 °K before and after an optical bleach with unpolarized light at 280 nm at 90 °K. Curve (a) is the optical absorption spectrum before the bleach. Curve (b) is the optical absorption spectrum after a 60 minute bleach at 280 nm. Absorbed Dose-48 Kilorad.

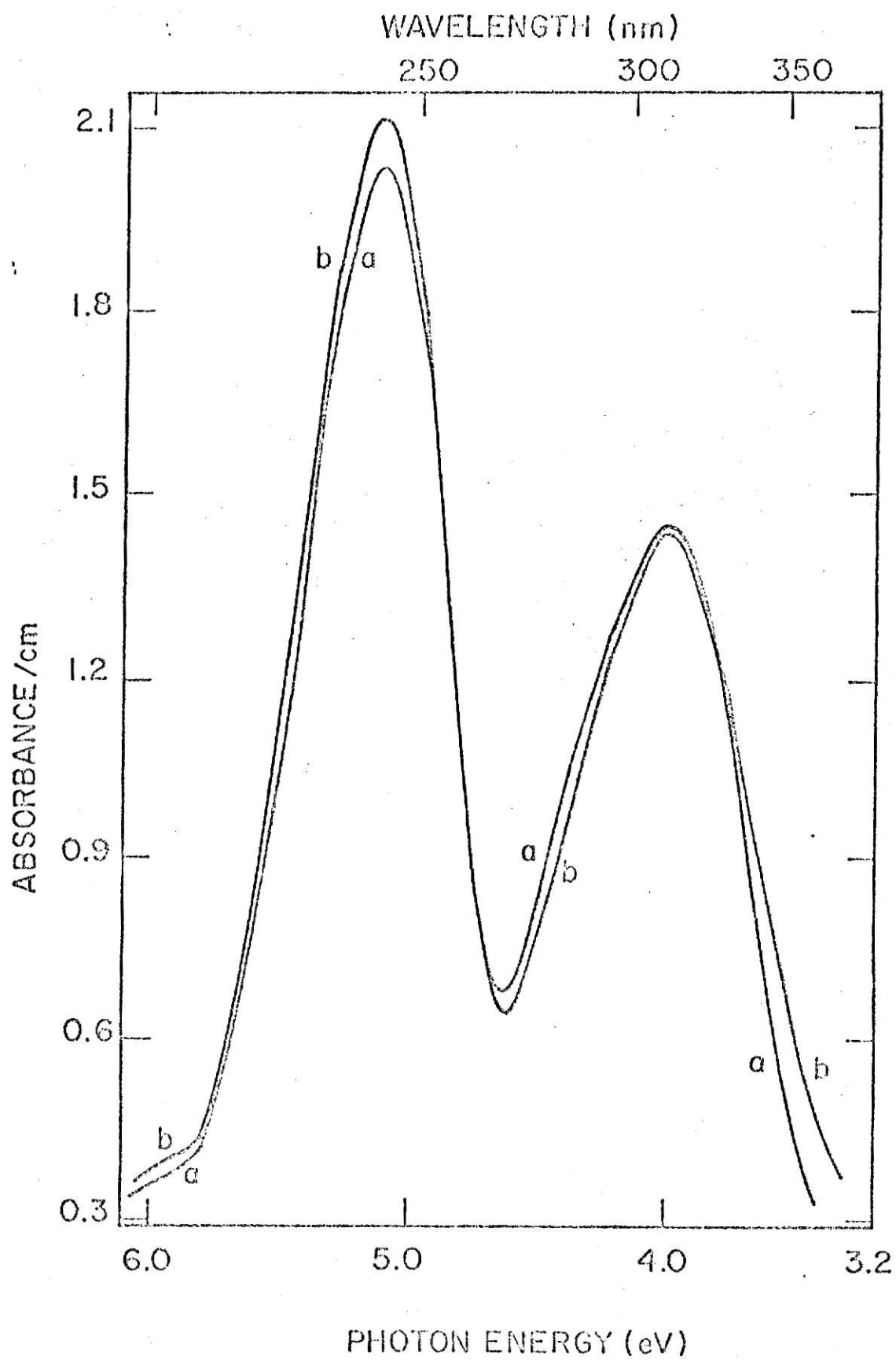
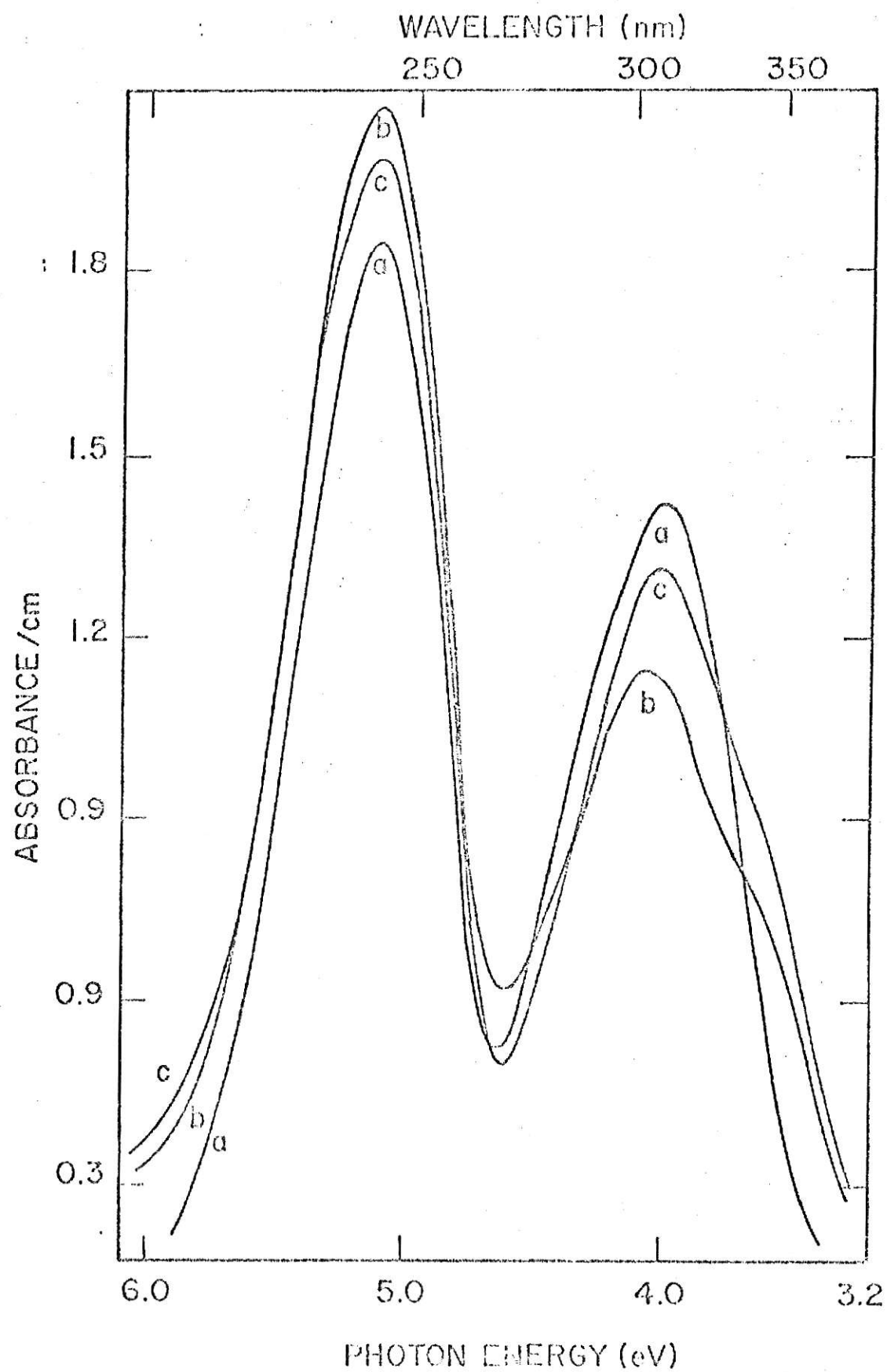
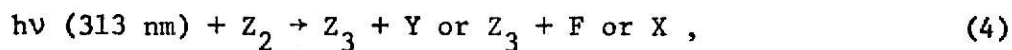


Figure 13

Optical absorption spectra of irradiated TLD-100 measured with unpolarized light at 90 °K before and after optical bleach with $[0\bar{1}1]$ polarized light at 313 nm and with unpolarized light at 254 nm at 90 °K. Curve (a) is the optical absorption spectrum before the bleach. Curve (b) is the optical absorption spectrum after a 3 hour bleach at 313 nm. Curve (c) is the optical absorption spectrum after a subsequent 2 hour bleach at 254 nm. Absorbed Dose-50 Kilorad.



where X in the above equations represents the 3.5 eV center. Since the F center in LiF can not be optically bleached and the Y center can be bleached with light at 254 nm, the F center in the second equation may be replaced by the Y center. The equations would be written as follows,



and



The electron released from a Z_2 center by bleaching at 313 nm may be trapped again at a negative ion vacancy adjacent to an interstitial aluminum ion to form a Y center, or at a negative ion vacancy to form a F center. The second equation shows that bleaching at 254 nm releases the electron from a Y center, and this electron is then captured by a Z_3 center to form a Z_2 center. It is also noticed in Fig. 13 that the peak position of Z_2 center absorption band shifts to higher energy by bleaching at 313 nm and then returns to its original position by the subsequent bleach at 254 nm. This can be explained by the same reason used in the previous section for the case of successive bleaches at 313 nm and 280 nm, that is, the changes in the concentration of the Y center as a result of bleaching.

The absorption spectra measured with $[011]$ polarized light and with $[0\bar{1}1]$ polarized light, before and after the TLD-100 was bleached with $[0\bar{1}1]$ polarized light at 313 nm show the dichroism of Z_2 center absorption band. Curves a and b of Fig. 14 are respectively the absorption spectra of TLD-100 measured with $[011]$ polarized light and with $[0\bar{1}1]$ polarized light before the bleach. Curves a and b of Fig. 15 are the respective optical absorption spectra measured after the optical bleach with $[0\bar{1}1]$ polarized light at 313 nm. As shown in Fig. 14, the absorption spectra of TLD-100 measured with $[011]$ polarized light and with $[0\bar{1}1]$ polarized light before the bleach are about the

Figure 14

Optical absorption spectra of irradiated TLD-100 measured with $[011]$ polarized light and with $[0\bar{1}1]$ polarized light at 90 °K before the bleach. Curve (a) is the optical absorption spectrum measured with $[011]$ polarized light. Curve (b) is the optical absorption spectrum measured with $[0\bar{1}1]$ polarized light. Absorbed Dose-50 Kilorad.

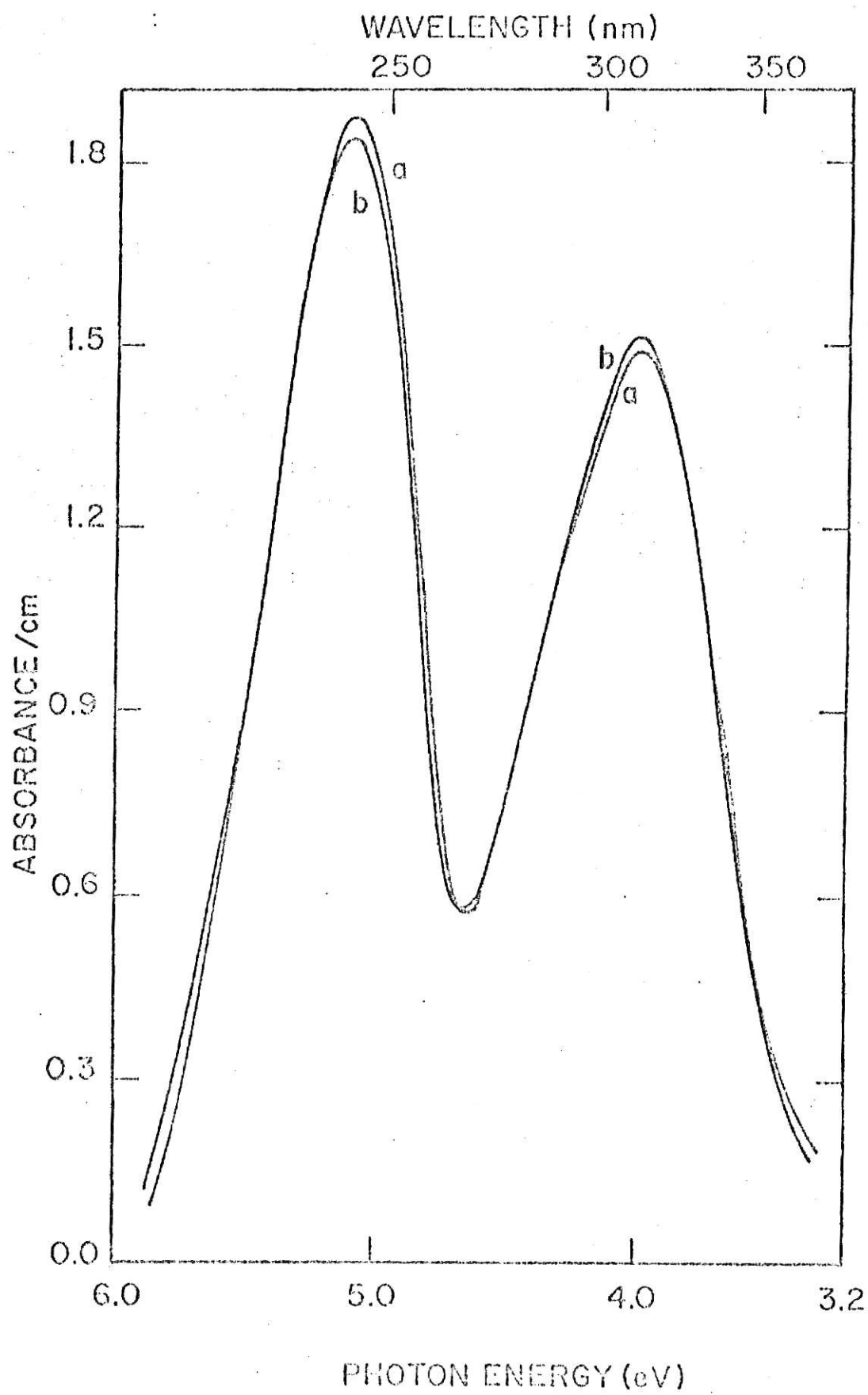
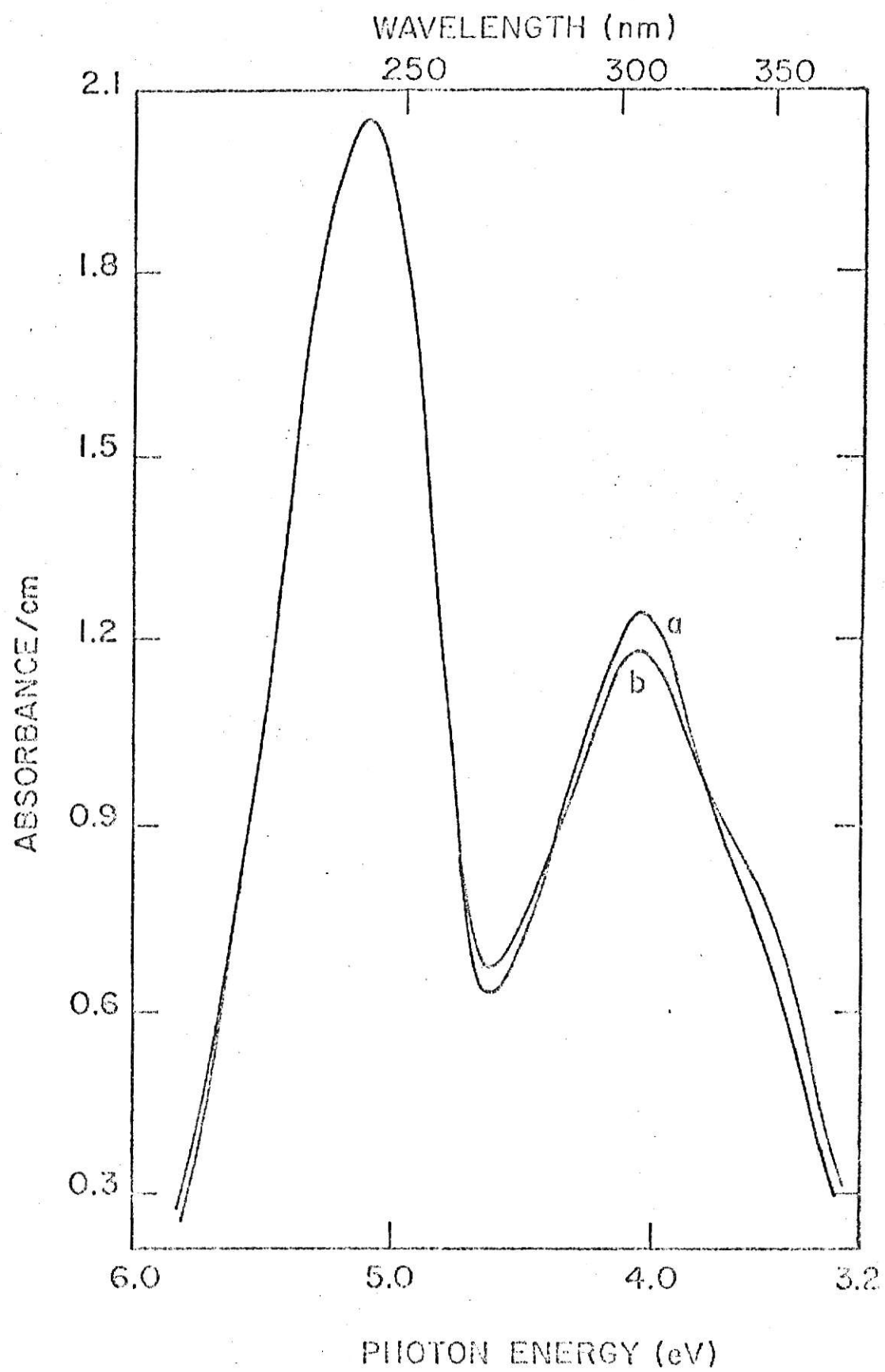


Figure 15

Optical absorption spectra of irradiated TLD-100 measured with $[011]$ polarized light and with $[0\bar{1}1]$ polarized light at 90 °K after an optical bleach with $[0\bar{1}1]$ polarized light at 313 nm at 90 °K. Curve (a) is the optical absorption spectrum measured with $[011]$ polarized light. Curve (b) is the optical absorption spectrum measured with $[0\bar{1}1]$ polarized light. Absorbed Dose-50 Kilorad.



same, indicating that no dichroism was induced during treatments of thermal annealing and gamma irradiation. This is in contrast to Marr's and Richter's observations (27, 28) of dichroic behavior of Y center in LiF before optical bleaching. In their work on gamma irradiated pure LiF, the dichroic behavior of the Y center was removed by optical bleaching, while in this work the dichroism of the Z_2 center was induced by optical bleaching of Z_2 center absorption band with polarized light. As shown in Fig. 15, the reduction of Z_2 center absorption band measured with light polarized in $[0\bar{1}1]$ direction is greater than the reduction of this band measured with light polarized in $[011]$ direction.

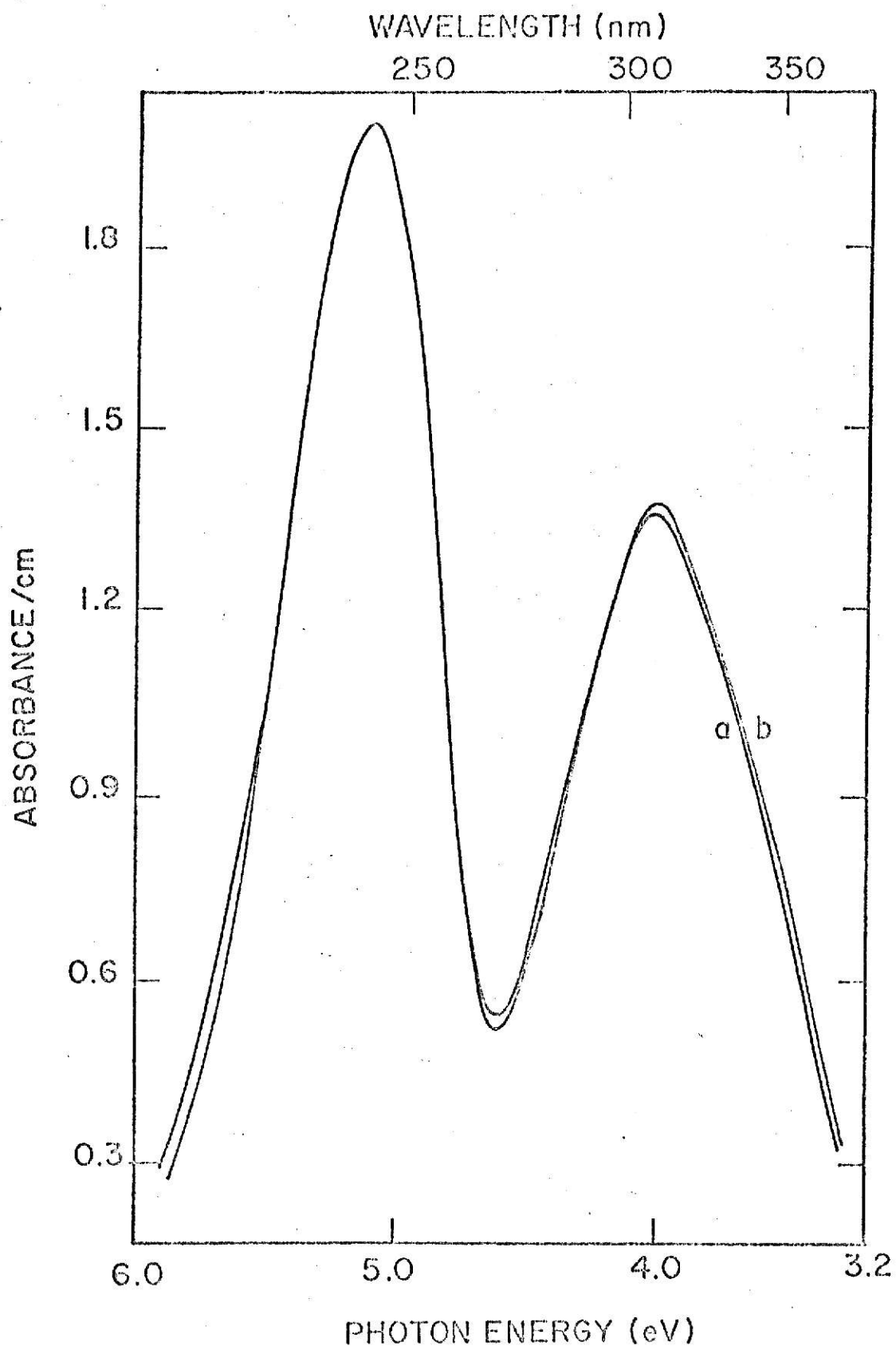
The observation made by W. Adlhart et al. (13) that electrons freed by ionization and trapped by other centers would absorb isotropically is supported by the results shown in next section. However, Fig. 15 shows a difference in absorbance at each side of the Z_2 absorption band. No explanation can be presented for this difference in absorbance.

The dichroism of Z_2 absorption band can be removed by subsequent bleach with unpolarized 254 nm light. This is shown in Fig. 16. Curves a and b of Fig. 16 are the absorption spectra of TLD-100 bleached with unpolarized 254 nm light following optical bleaching with $[0\bar{1}1]$ polarized light at 313 nm, measured with $[011]$ polarized light and $[0\bar{1}1]$ polarized light respectively.

The dichroism behavior of Z_2 center in TLD-100 induced by optical bleaching with light polarized in other directions has also been studied. It is observed that the decrease in absorption is always greater when the measuring light is polarized in the same direction as the bleaching time. The details will be discussed in next section.

Figure 16

Optical absorption spectra of irradiated TLD-100 measured with $[011]$ polarized light and with $[0\bar{1}1]$ polarized light at 90 °K after an optical bleach with unpolarized light at 254 nm at 90 °K following the bleach with $[0\bar{1}1]$ polarized light at 313 nm at 90 °K. Curve (a) is the optical absorption spectrum measured with $[011]$ polarized light. Curve (b) is the optical absorption spectrum measured with $[0\bar{1}1]$ polarized light. Absorbed Dose-50 Kilorad.



4.4.2 Optical Bleaches at 313 nm with Light Polarized in [010] and in [001] Directions

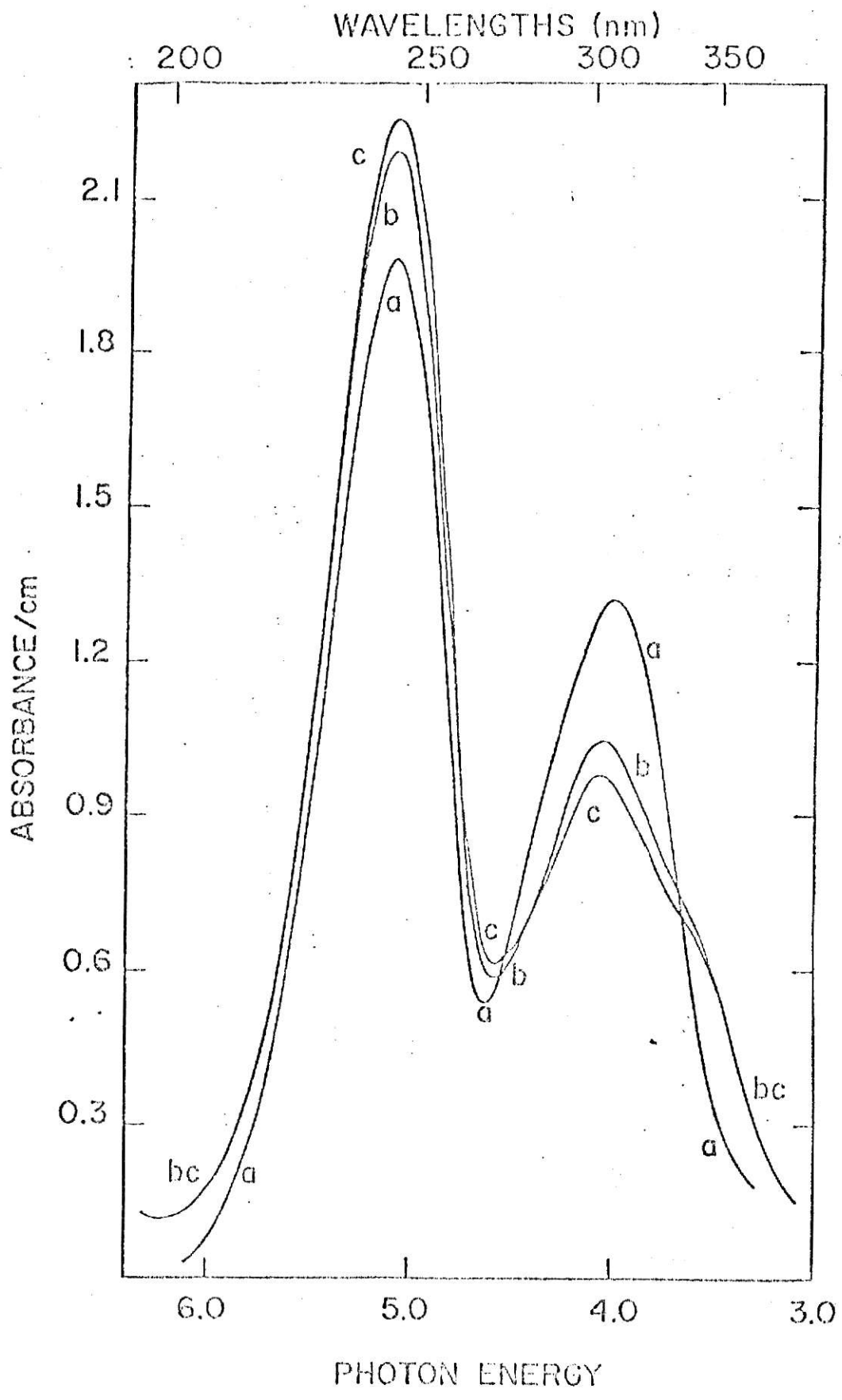
A gamma-irradiated TLD-100 crystal was bleached at 90 °K first with light polarized in one selected direction, and then with light polarized at 90 degrees from the selected direction. All four directions, $[0\bar{1}1]$, $[010]$, $[011]$ and $[001]$ were used. The absorption spectra were measured with unpolarized light and with light polarized in $[0\bar{1}1]$, $[010]$, $[011]$ and $[001]$ directions at 90 °K, before and after each of the bleaches.

Figures 17, 18 and 19 show the effects of optical bleach of TDL-100 with $[010]$ polarized light at 313 nm and a subsequent bleach with $[001]$ polarized light at 313 nm. Figure 17 shows the absorption spectra measured with unpolarized light at 90 °K. Curve a is the absorption spectrum measured after gamma irradiation to a dose of 45 kilorad, thermal annealing at 100 °C for 30 minutes, followed by quick quenching to room temperature. Curve b is the absorption spectrum measured after optical bleaching with $[010]$ polarized light at 313 nm for 3 hours at 90 °K, and curve c is the absorption spectrum measured after a subsequent bleach with $[001]$ polarized light at 313 nm for 3 hours at 90 °K. The results of these bleaches measured with unpolarized light, shown in Fig. 17, are the same as that discussed in section 4.3, that is, an increase of the 3.5 eV, 4.4 eV, 5.0 eV, 5.5 eV and 6.0 eV absorption bands at the expense of the 4.0 eV absorption band. The position of the peak in the absorption band has also shifted to higher energy. It is observed that for the same amount of bleaching time, the effect of the first bleach is greater than that of the subsequent bleach. The reason for this result is the decreasing population of Z_2 centers by the optical bleaching of the 4.0 eV absorption band.

Figures 18 and 19 show the absorption spectra measured at 90 °k with $[010]$ polarized light and $[001]$ polarized light, respectively. Curves a of Fig 18 and 19 are the absorption spectra measured before the bleaches.

Figure 17

Optical absorption spectra of irradiated TLD-100 measured with unpolarized light at 90 °K before and after optical bleaches with [010] polarized light at 313 nm and with [001] polarized light at 313 nm at 90 °K. Curve (a) is the optical absorption spectrum before the bleach. Curve (b) is the optical absorption spectrum after a 3 hour bleach with [010] polarized light at 313 nm. Curve (c) is the optical absorption spectrum after a subsequent 3 hour bleach with [001] polarized light at 313 nm. Absorbed Dose-45 Kilorad.



n

Figure 18

Optical absorption spectrum of irradiated TLD-100 measured with [010] polarized light at 90 °K before and after optical bleaches with [010] polarized light at 313 nm and with [001] polarized 313 nm light at 313 nm at 90 °K. Curve (a) is the optical absorption spectrum before the bleach. Curve (b) is the optical absorption spectrum after a 3 hour bleach with [010] polarized light at 313 nm. Curve (c) is the optical absorption spectrum after a subsequent 3 hour bleach with [001] polarized light at 313 nm. Absorbed Dose-45 Kilorad.

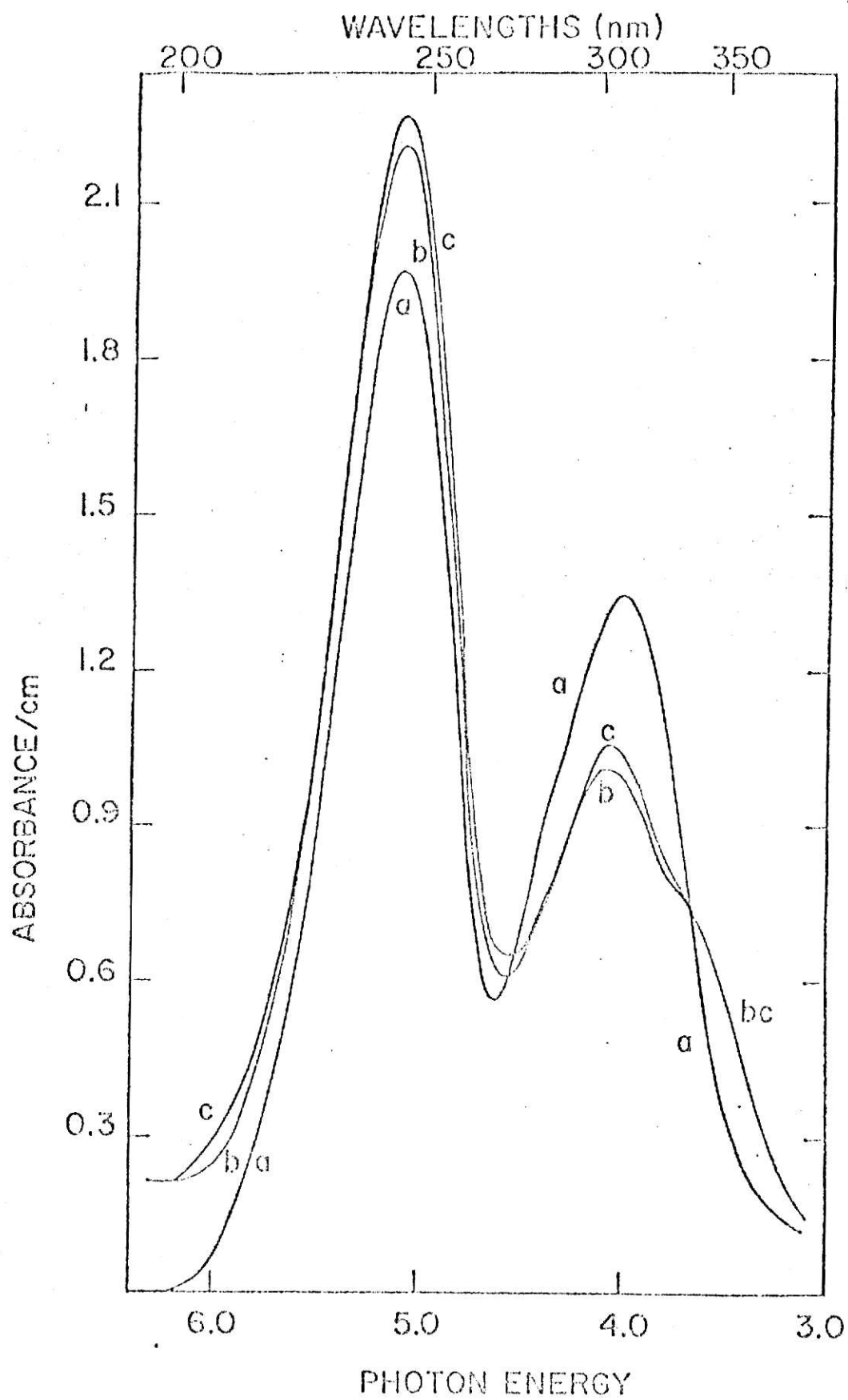
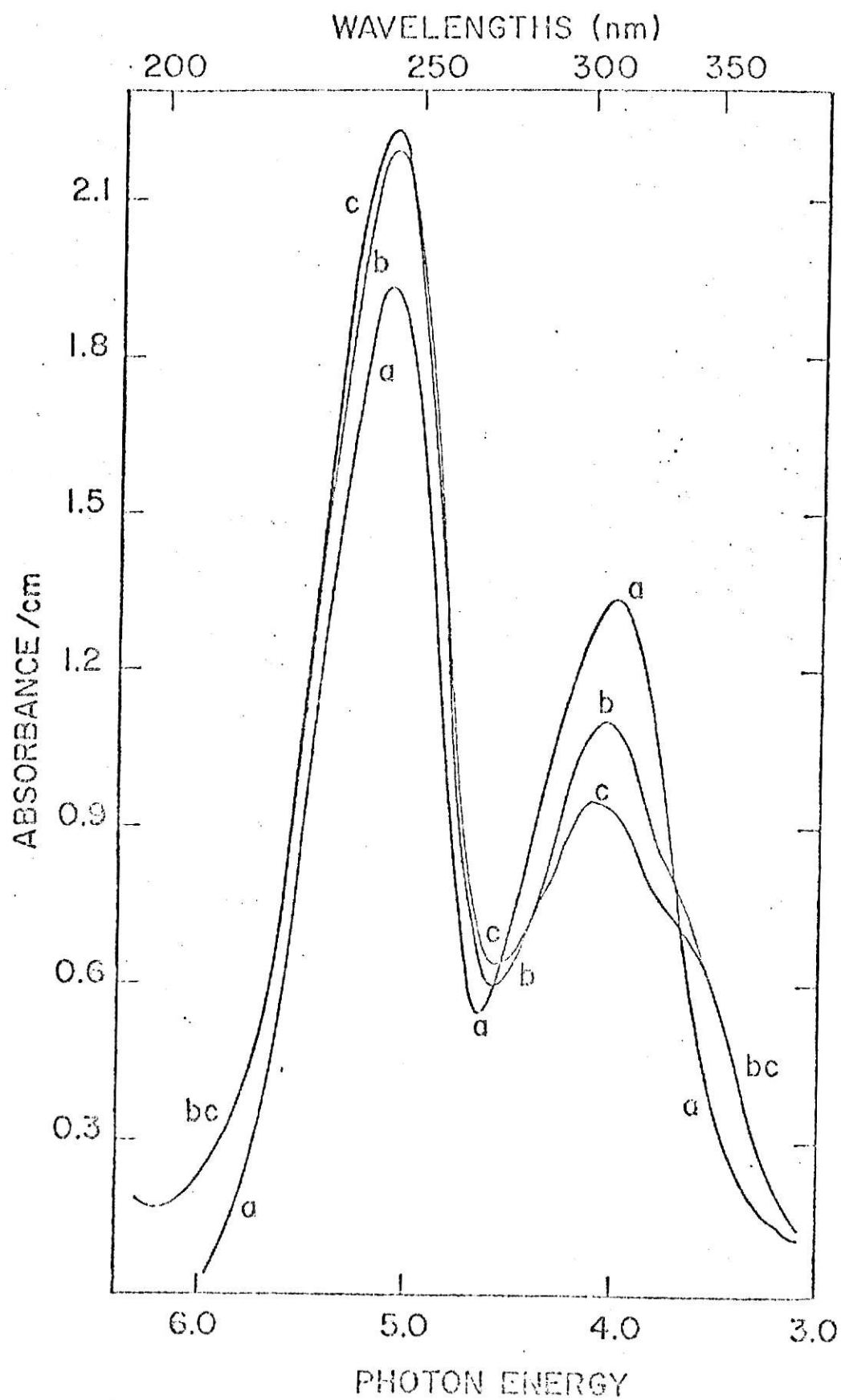


Figure 19

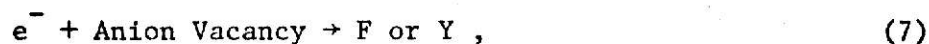
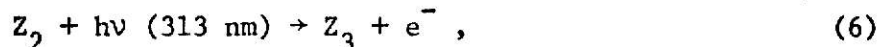
Optical absorption spectra of irradiated TLD-100 measured with [001] polarized light at 90 °K before and after optical bleaches with [010] polarized light at 313 nm and with [001] polarized light at 313 nm at 90 °K. Curve (a) is the optical absorption spectrum before the bleach. Curve (b) is the optical absorption spectrum after a 3 hour bleach with [010] polarized light at 313 nm. Curve (c) is the optical absorption spectrum after a subsequent 3 hour bleach with [001] polarized light at 313 nm. Absorbed Dose-45 Kilorad.



Curve b of Fig. 18 is the absorption spectrum measured with [010] polarized light, after optical bleaching at 313 nm with light polarized in [010] direction, and curve c of Fig. 18 is the absorption spectrum after subsequent bleaching at 313 nm with light polarized in [001] direction. Curves b and c of Fig. 19 are the respective absorption spectra measured with [001] polarized light. Similar to the results of bleaching with $[0\bar{1}1]$ polarized 313 nm light discussed in previous section, Figures 18 and 19 show that the absorption spectra measured before bleaching are about the same, and that the dichroism of Z_2 center absorption band has been induced by bleaching. The Z_2 center (4.0 eV) absorption band measured with [001] polarized light is greater than that measured with [010] polarized light (compare 18b and 19b). The absorption bands centered at 3.5 eV, 4.4 eV, 5.0 eV, 5.5 eV, and 6.0 eV exhibit no dichroism. W. Adlhart et al. (13) observed that electrons freed by ionization and trapped at other centers would absorb isotropically. Therefore no dichroism can be induced in the absorption bands which are not optically bleached.

It is observed from Figures 18 and 19 that the dichroism of Z_2 center induced by bleaching at 313 nm with light polarized in [010] direction is reversed by the subsequent bleaching with [001] polarized light at 313 nm. After the second bleach, the Z_2 center absorption band measured with [001] polarized light is reduced and the Z_2 center absorption band measured with [010] polarized light has increased such that the Z_2 center absorption band measured with [001] polarized light is less than that measured with [010] polarized light. (Compare Figures 18c and 19c). The changes in the absorbance, measured with $[0\bar{1}1]$ polarized light and $[011]$ polarized light (not shown), show the same results as that measured with unpolarized light. Since a Z_3 center is formed when a Z_2 center loses one electron, and a Z_2 center is

formed when one electron is trapped at a Z_3 center, the effect of bleaching at 313 nm can be described by the following equations,



When the crystal is first bleached with [010] polarized light at 313 nm, the Z_2 centers with a dipole in [010] direction will be preferentially bleached. For each Z_2 center destroyed by bleaching, there is one Z_3 center created. The electron may be trapped at a vacancy to form a F center or a Y center. As the concentration of the Z_3 centers increases, some electrons can be trapped at Z_3 centers, forming Z_2 centers. However, the net number of Z_3 centers keeps increasing as the optical bleach continues.

If the bleaching is then changed to light polarized in the [001] direction, the Z_2 centers with dipoles in [001] direction will be preferentially bleached, and those with dipoles in [010] direction will be bleached to a lesser extent. Therefore, the population of Z_2 centers with dipole in [001] direction is decreased further (see Fig. 19c). Since the concentration of Z_3 centers was increased by the first bleach, it can compete with the vacancy for the freed electrons. More Z_2 centers are formed in $Z_3 \rightarrow Z_2$ reaction thus it is possible that the Z_2 centers with dipole in [010] will be created faster than destroyed, and cause the increase in Z_2 center absorption band measured with [010] polarized light (Fig. 18c).

Similar results as shown in Fig. 17, 18 and 19 are observed in other bleaching experiments, with light polarized in the [001] direction and then in the [010] direction, with light polarized in [011] direction and then in the $[0\bar{1}1]$ direction, and with light polarized in $[0\bar{1}1]$ direction and then in the [011] direction. Dichroic behavior is induced in the Z_2 center by

bleaching with polarized light. The decrease in absorbance is always greatest in the direction that the sample was bleached with polarized light. There was an increase in absorbance after the second bleach when measured with light polarized perpendicular to the polarized bleach. In all cases, the changes in absorbance were the same for the two polarization directions not involved in bleaching.

V. SUMMARY AND CONCLUSIONS

Neutron activation analysis shows that aluminum is present in TLD-100 at the concentration of about 21 ppm. The aluminum related Y center absorption band has been observed in pure LiF by Marrs (27) and Richter (28). Although the Y center absorption band is not seen in the optical absorption spectra of irradiated TLD-100, the existence of the Y center in TLD-100 can not be ruled out.

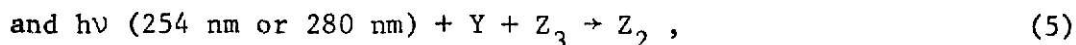
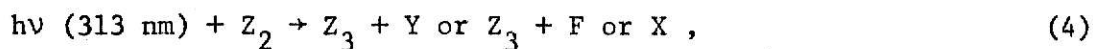
The optical bleaching of TLD-100 with unpolarized light at 254 nm at 300 °K decreases the 5.0 eV and 4.0 eV absorption bands, and the 5.5 eV absorption band grows as the results of this bleach. The absorbance at 5.0 eV measured with $[0\bar{1}1]$ polarized light is a little greater than that measured with $[011]$ polarized light. This difference in absorbance would seem to indicate dichroism. The reasons for this apparent dichroism of the 5.0 eV absorption band and for the preference of dichroism for $[0\bar{1}1]$ and $[011]$ directions are not known. The 5.0 eV absorption band of TLD-100 has been suggested as due to F centers. However, the bleaching behavior of this absorption band does not agree with the fact that F center in LiF can not be optically bleached (20, 21, 27, 28). It is therefore suggested that there are other absorption bands overlapping the F center absorption band which could explain the decrease and shift of the 5.0 eV absorption band.

Mayhugh et al. (19) has suggested that the Z_2 center in TLD-100 which has an absorption band at 4.0 eV, also absorbs light at 5.0 eV. The studies of dichroism of Z_2 center in this work did not show any correlation between the bleaching behaviors of the 4.0 eV and the 5.0 eV absorption bands which would support this suggestion.

The optical bleaching at 313 nm at 90 °K results in the increase of the 3.5 eV, 4.4 eV, 5.0 eV, 5.5 eV and 6.0 eV absorption bands at the expense

of the 4.0 eV absorption band, and the shift of peak position of the 4.0 eV absorption band to higher energy. This indicates that electrons have been transferred from the Z_2 centers to other color centers. The growth of the Y center absorption band and the reduction of the Z_2 center absorption band explain the shift of peak position. A subsequent bleaching at 280 nm at 90 °K reverses the change in peak position, that is, populating Z_2 centers at the expense of Y centers, and the shift of peak position back to the original position.

Bleaching at 254 nm after bleaching at 313 nm with light polarized in the $[0\bar{1}1]$ direction at 90 °K shows similar results as that observed in successive bleaching at 313 nm and 280 nm at 90 °K. Representing the structure of the 5.5 eV, 5.0 eV, 4.4 eV and 4.0 eV centers as Z_3 , F, Y, and Z_2 respectively, the low temperature bleaching behavior of TLD-100 can be represented by the following equations,



where X represents the 3.5 eV center. Absorbing a photon at 313 nm, the Z_2 center ejects one electron and turns into a Z_3 center. The released electron can be trapped again at a negative ion vacancy adjacent to an interstitial aluminum ion to form a Y center, or at a negative ion vacancy to form a F center. The second equation shows that electron can be released from a Y center by bleaching at 254 nm or 280 nm, and then trapped at a Z_3 center to form a Z_2 center.

The growth of the 3.5 eV absorption band was observed at liquid nitrogen temperature bleaching. If the sample is warmed up to room temperature, this absorption band disappears. When the sample is cooled down to liquid nitrogen

temperature, this absorption band is no longer present and there is a slight increase of 4.0 eV absorption band. This indicates that the 3.5 eV absorption band is thermally unstable and that, like the 4.0 eV center, it may be a trapped electron center. The structure of this center is not known.

The study of dichroism of Z_2 center of TLD-100 was made by optical bleaching at 313 nm at 90 °K with light polarized in one direction, and then with light polarized perpendicular to the initial direction. All four directions, $[0\bar{1}1]$, $[010]$, $[011]$ and $[001]$ were used. The dichroism is induced in the Z_2 center by bleaching with polarized light. The decrease in absorbance is always greatest in the direction that the sample was bleached with polarized light. There was an increase in absorbance after the second bleach when measured with light polarized perpendicular to the direction that the sample was bleached. The changes in absorbance were the same for the two polarization direction not involved in bleaching.

The dichroic behavior of the Z_2 centers in TLD-100 shows the existence of symmetry axes along the directions: $[0\bar{1}1]$, $[010]$, $[011]$ and $[001]$. None of the proposed models, shown in Fig. 1, are capable of explaining the induced dichroism of the Z_2 center. Since there are four symmetry axes involved in this center, it must be a complex center.

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APPENDIX A

Relation Between the Absorbance and the Absorption Coefficient

This work involves the study of optical absorption spectra of LiF:Mg (TLD-100). The quantity that is measured by the Cary-14 Spectrophotometer is the "Optical Density," O. D., or the "Absorbance," A, (34).

$$A = \log_{10}(I_0/I) , \quad (A.1)$$

where

I_0 = intensity of the light incident on the crystal,

I = intensity of the light transmitted by the crystal.

The absorption coefficient, α , (cm^{-1}) is defined as,

$$I = I_0 e^{-\alpha x} , \quad (A.2)$$

where

I and I_0 have the same meaning as that defined in equation (A.1),

x = optical path length in cm.

From equation (A.2) one obtains the equation

$$\alpha(\text{cm}^{-1}) = [\log_e(I_0/I)]/x(\text{cm}) . \quad (A.3)$$

Therefore the relation between the absorbance, A, and the absorption coefficient α , is

$$\alpha = (\log_e^{10}) A/x , \quad (A.4)$$

or

$$\approx 2.3026 A/x . \quad (A.5)$$

The quantity A/x was calculated and then plotted against the photon energy.

APPENDIX B

Neutron Activation Analysis of TLD-100 Samples

Neutron Activation Analysis was carried out on the samples of TLD-100 to determine the impurity concentrations. Magnesium, aluminum and titanium were expected to be found as impurities in TLD-100 crystals. The samples of TLD-100 and reference materials MgO , Al_2O_3 and TiO were individually placed in small polyethylene vials. Iron wires were attached to the outside of each vial to monitor the flux. The samples, reference materials and flux monitors were irradiated in the rotary specimen rack of the Kansas State University TRIGA Mark II nuclear reactor. After irradiation, activities were measured for two consecutive periods of time by a Camberra Ge(Li) detector together with a Northern Scientific 636 pulse height analyzer.

Gamma rays with energies 0.322, 0.843, 1.012 and 1.774 MeV were detected. The half-life of $^{51}_{22}\text{Ti}$ is 5.8 minutes and it decays by beta emission accompanied by a 0.320 MeV gamma ray. $^{27}_{12}\text{Mg}$ has a 9.5 minute half-life and decays by beta emission accompanied by 0.840 and 1.013 MeV gamma rays. $^{28}_{13}\text{Al}$ has a 2.3 minute half-life and decays by beta emission accompanied by a 1.78 MeV gamma ray. The TLD-100 samples were found to contain magnesium, aluminum and titanium as impurities.

The impurity concentration in parts per million (ppm) can be determined by the method developed by Steven D. Howe (35). If all the activities were measured for the same amount of time, and the area under the photoelectric peak which is equivalent to the total number of counts due to gamma rays emitted by the activated isotope is known, the concentration can be determined by the following equation (35),

$$(\text{ppm})_{i,s} = \frac{N_s}{N_r} \cdot \frac{N_r'}{N_s'} \cdot (\text{ppm})_{i,r} \quad (\text{B.1})$$

with

$$N_s = (\text{area})_{i,s} \cdot e^{\lambda_i t_s} / \text{mass of sample} ,$$

$$N_r = (\text{area})_{i,r} \cdot e^{\lambda_i t_r} / \text{mass of reference material} ,$$

$$N'_s = (\text{area})_{\text{Fe},s} \cdot e^{\lambda_{\text{Fe}} t_{\text{Fe},s}} / \text{mass of iron wire around sample vial} ,$$

$$N'_r = (\text{area})_{\text{Fe},r} \cdot e^{\lambda_{\text{Fe}} t_{\text{Fe},r}} / \text{mass of iron wire around reference vial} ,$$

λ = decay constant ,

t = time that the activated material was allowed to decay before measuring its activity.

where

i, s, r , stand for isotope (Mg, Al or Ti), sample (TLD-100) and reference materials (MgO , Al_2O_3 , or TiO), respectively.

The Neutron Activation Analysis for TLD-100 has shown that the crystals contain magnesium, aluminum and titanium at concentrations of 127.0 ± 11.7 ppm, 20.8 ± 0.9 ppm and 10.4 ± 2.1 ppm, respectively.

STUDY OF THE OPTICAL ABSORPTION AND DICHROISM
OF COLOR CENTERS IN GAMMA-IRRADIATED LiF:Mg

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1977

ABSTRACT

The optical absorption from 3.0 eV to 6.0 eV of gamma-irradiated LiF:Mg was studied at 90 °K and 300 °K with unpolarized light and light polarized in the $[0\bar{1}1]$, $[010]$, $[011]$, and $[001]$ directions. The reduction of the 5.0 eV absorption band and a seeming dichroism induced in this absorption band by a room temperature bleach at 254 nm indicate that other absorption bands may be buried under the F center absorption band at 5.0 eV. The results of Neutron Activation Analysis show the existence of an aluminum impurity in LiF:Mg crystal as well as Mg and Ti and thus indicates the existence of the aluminum-related Y centers in LiF:Mg. The growth of the Y center absorption band (4.4 eV) and the reduction of the 4.0 eV absorption band explain the shift of the 4.0 eV absorption band to higher energy after optical bleach at 313 nm at 90 °K. A subsequent bleaching at 280 nm or 254 nm at 90 °K reverses this reaction and the maximum of the absorption peak shifts back to 4.0 eV.

The dichroism of the Z_2 center of LiF:Mg was studied for the first time. A gamma-irradiated LiF:Mg crystal was bleached at 313 nm at 90 °K with light polarized in one selected direction, and then with light polarized at 90 degrees from the selected direction. The dichroism is induced in the Z_2 center by bleaching with polarized light. The decrease in absorption is always greatest when measured with light polarized in the same direction as the bleaching light. There was an increase in absorption at 4.0 eV after the second bleach when the measuring light was polarized perpendicular to that of bleaching light. The results were observed in all of the four directions: $[0\bar{1}1]$, $[010]$, $[011]$ and $[001]$, indicating the existence of four symmetry axes for this center.