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EFFECTS IN ELECTRON BOMBARDMENT OF LITHIUM ELUORIDE SINGLE CRYSTALS AT HIGH TEMPERATURES:

I. THE DEPTH DISTRIBUTION OF F CENTER DENSITY

II. THE FORMATION OF COLLOIDAL CENTERS

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Effects in Electron Bombardment of Lithium Fluoride Single Crystals at High Temperatures: I. The depth distribution of F center density II. The formation of colloidal centers

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I. The peak height of F absorption band vs. depth from the surface has been measured in LiF crystal bombarded by electrons. The depth distribution of F center density is characterized by multiple scattering of electrons in the crystal, and it agrees primarily with the depth distribution of electron energy loss calculated with the Spencer theory. With increase of the bombarding electron dosage, the F center density curve deviates from the theoretical energy loss curve due to the saturation of F center density. An additional shoulder appears beyond the electron range, which is possibly caused by the secondary photons emitted during penetration of the electrons in LiF.

II. The colloidal centers formed in electron-bombarded pure LiF crystals have been studied in heat-treatment up to 700°C. The optical absorption bands induced were the same as those by neutron-irradiation, except lack of the 550 nm (S) band; which indicates that the neutron effect in LiF amounts nearly to the ionization with localized heating. Consistent assignment of the absorption centers may be as follows: The 500 nm (E) band arises from an aggregate color center. The 430 and 480 nm bands are due to the Mie's scattering of light by metallic Li colloids. The bands at about 270 and 370 nm are caused by the resonant oscillation of plasma electrons in the metallic Li colloids, shaped in circular cylinder and sphere, respectively. The broad band at 300 nm, formed finally at temperatures above 500°C, results from the quesi-metallic zones left after the Li atoms have diffused out from the metallic colloids.

ＬｉＦ　結晶の高温電子線照射効果

Ⅰ．Ｆ中心密度の深さ分布，Ⅱ．コロイド的着色中心の形成

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Ⅰ．電子照射したＬｉＦ 中の（Ｆ吸収ｖｓ照射表面からの深さ）を測定した。このＦ中心密度の深さ分布は結晶中の電子の多重散乱により特徴ずけられ，Ｓｐｅｎｃｅｒ 理論で計算される電子エネルギー損失の深さ分布と初期においては良く一致する。照射量の増加に伴ないＦ中心密度の飽和のために理論的エネルギー損失曲線から離れ，電子飛程より奥に附加的な肩が現われる。これは電子がＬｉＦ を透通する際に放射する二次光子によるＦ中心形成の為と考えられる。

Ⅱ．高純度ＬｉＦ の高温電子線照射による光吸収は中性子照射によるものとＳ帯を除き全く同じで，ＬｉＦ における中性子効果が局所的（イオン化＋高温）であることを示す。７００℃までの熱処理によって調べた結果，コロイド的中心の同定として，５００nm 帯は複合色中心，４３０と４８０nm 帯は金属Ｌｉ によるMie光散乱，２７０と３７０nm 帯は金属Ｌｉ中のプラズマ電子振動，５００℃以上の３００nm 帯はＬｉ 拡散後の擬金属Ｌｉ 領域による光散乱によるとすれば，相互矛盾なく理解される。

目　次　な　し

I. The Depth Distribution of F Center Density

The β-rays are often treated similarly to electromagnetic radiation such as ultraviolet, x- or γ-rays, in a coloration of ionic crystals. The action of electrons in the crystal, however, is not the same as that of the photons. Because of their multiple scattering, the electrons dissipate their energy in a complex manner along the depth from the bombarded face, differing from the exponential law which the intensity of electromagnetic radiations obeys. So does the depth distribution of color center density.

Moreover, the energetic electrons also produce color centers in some other ways than in the case of electromagnetic radiation, namely, displacement collision in the lattice and ionization by the photons and electrons emitted secondarily from the lattice atoms. The depth distribution of F center density measured in electron-bombarded LiF crystal is described; and an additional F center formation by the secondary ionization process is proposed.

The specimens about 15 mm cubes cleaved from a LiF single crystal block supplied by the Institute of Applied Optics were bombarded normally by mono-energetic electron beam from a 2 MV Van de Graaff accelerator. The ambient temperature was held constant from RT to 500°C by a controlled electric heater during bombardment of the cubes.

After bombardment, the specimen was cleaved normally to the bombarded face into thin wafers. Optical absorption measurement was made in the wafer along the depth from the bombarded face, with an Olympus microspectrophotometer.

The coloration vs. depth curve obtained is evidently different from that by x-rays.[1] The shape of curve varies with dosage of the bombarding electrons. With the low dose, the shape is such as in Fig. 1, where the solid line, normalized to the maximum, represents the depth distribution of F center density in the slightly colored specimen with bombardment to 10^{14} 1.5 MeV-electrons/cm^2 at RT. The depth distribution of F center denstity is in agreement with that of energy dissipation estimated with the Spencer theory;[2] this is shown by the broken curve in the same figure, also with the normalization. The agreement clearly shows that the F center formation is due to the ionization by the electrons penetrating into the crystal.

With increase of the dosage, the crystal is colored deeper. The F center density vs. depth curve is flattened due to the saturation of F center density, then an additional shoulder appears in the curve beyond the extrapolated range for the bombarding electrons. Figure 2 shows the curves for deep-brown colored specimens bombarded to 2×10^{15} 1.5 MeV-electrons/cm^2 at various temperatures. The specimen temperature during bombardment influences the curve shape, especially near the range end of bombarding electrons, with the additional shoulder described. Two alternative processes for this appearance may be considered: first, the additional formation of F centers by either UV, x- or β-rays emitted during penetration of the energetic electrons; and second, the diffusion of F centers produced by the electrons beyond the range end. The latter may be ruled out because the shoulder is smaller at a higher temperature, as seen in Fig. 2. In the

former possibility, the most probable cause is by characteristic x-rays. The K_α lines of Li and F are emitted with 110 and 677 eV, respectively. The 677 eV x-rays, to say the least, are capable of forming F centers by excitonic process.[3,4] The UV light, reported to form the F centers in LiF crystal,[5-7] has also some possibility. Even when the radio-luminescence spectrum does not extend into such a high energy UV region,[8] the Cerenkov radiation extends to the absorption limit of LiF, including the responsible UV light. An accumulation of F centers thus formed by photons comes to the additional shoulder.

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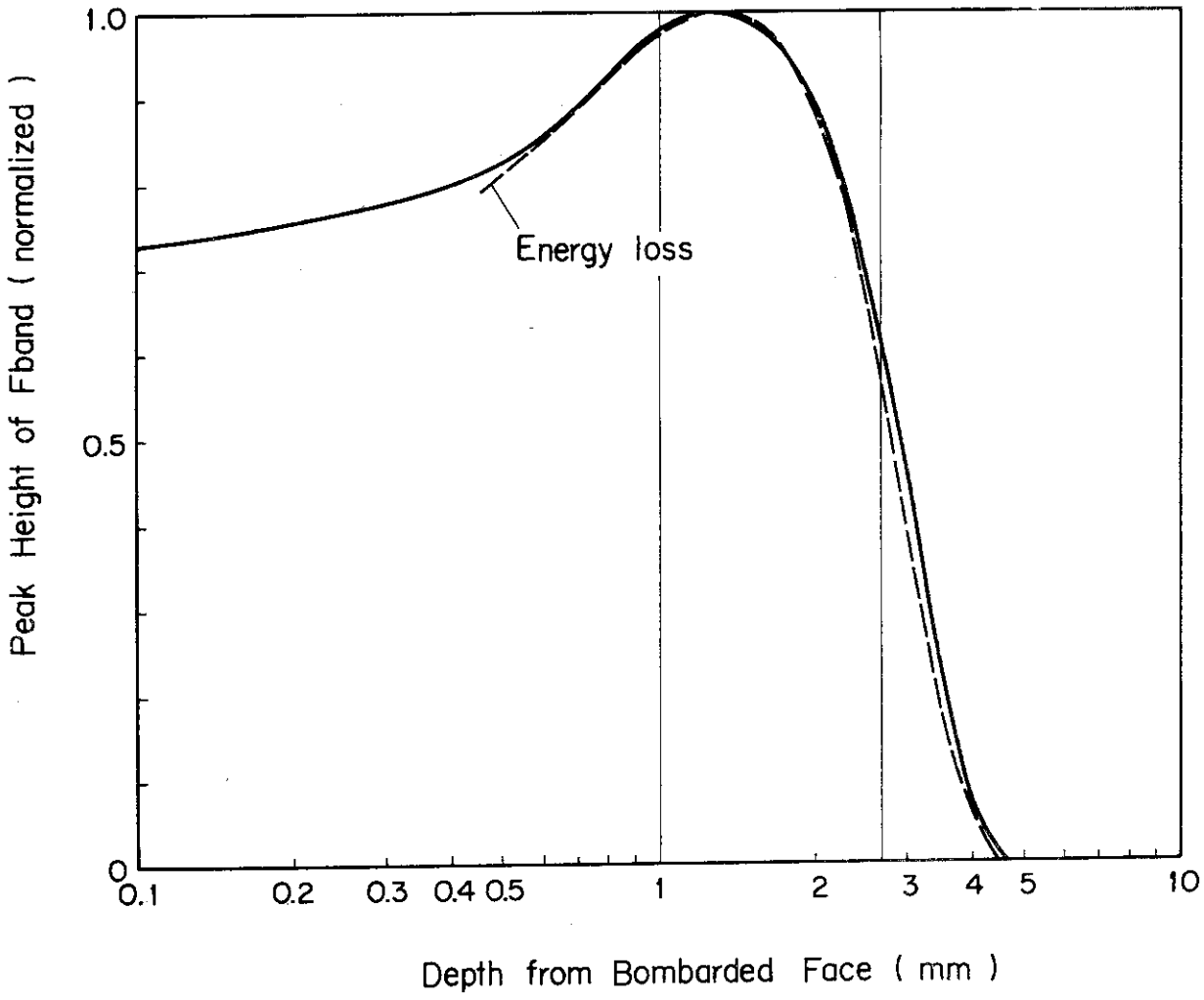

Fig. 1 Depth distributions of F center density in the slightly colored specimen with bombardment to 10^{14} 1.5 MeV-electrons/cm^2 (solid line) and theoretical energy dissipation (broken line).

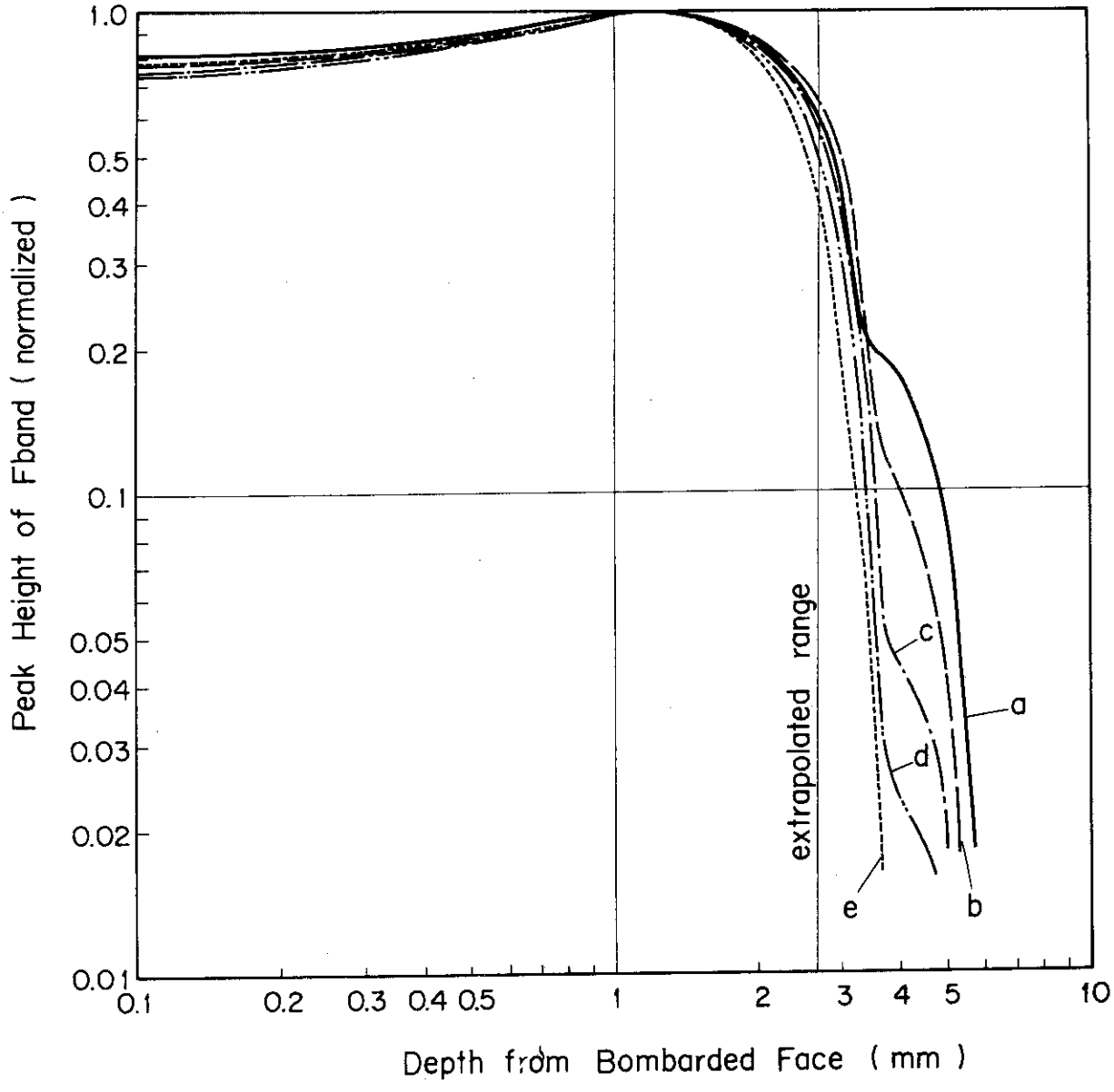

Fig. 2 Depth distributions of F center density for deep-brown colored specimens bombarded to 2×10^{15} 1.5 MeV-electrons /cm^2 at various temperatures.
(a) RT, (b) 110°C, (c) 220°C, (d) 340°C and (e) 450°C.

II. The Formation of Colloidal Centers

The complex and colloidal centers in the deeply colored LiF crystals have been studied by many workers.[1-12] These centers may group into three: aggregate color center, metallic precipitate, and quasimetallic zone. An example of the first category is the complex interstitial-Li centers accompanied by 630,[5] 550 (S)[6] and 500 (E)[7] nm bands. It is characterized by the zero-phonon transitions. The elements in the second and the third categories cause extinction of the light by both scattering and absorption; which, in the case of a metallic colloid of spherical shape, are represented by the Mie theory.[13] The extinction bands due to spherical Li-colloid in LiF were estimated in accordance with the theory;[14] the 460 nm band corresponds to the smallest radius. An example of this case is the visible broad bands at wavelengths larger than 460 nm observed in the heavily irradiated crystal after heat-treatment,[2] and the centers belong with the second category. There are, however, several colloid bands, of which the centers are indefinite though considered to be the second or third category.[1,8-12] Consistent assignment of the colloidal centers is necessary.

These works have been made mostly with neutron-irradiated crystals. A question arises that the colloid bands studied might be influenced by some impurities induced since the nuclear reaction $^{6}Li(n,\alpha)^{3}H$, producing helium and tritium nuclei, takes a part in the neutron damage of LiF. Investigation of the colloid bands was thus undertaken with the specimens free from impurities. The electron bombardment at high temperatures followed by heat-treatment was taken to attain the conditions of colloid formation.

The wafers, less than 1 mm in thickness, were cleaved from a LiF single crystal block supplied by the Institute of Applied Optics. Several in pile were bombarded normally by 1.5 MeV electrons from a 2 MV Van de Graaff accelerator, up to a dose of (1.3 $\sim$ 1.6)$\times 10^{16}$ electrons/cm^2 on the face of the first wafer. The electron dose received by each wafer was varied depending on its location during bombardment.

After the bombardment the wafers were heat-treated by the 10 min pulses, 25° higher at each stage, from 100 to 700°C. An optical absorption spectrum was taken with a Beckman DK-2 at RT after each pulse heating. Measurements at the low temperatures were made with a Cary 14R in some cases.

Results and discussion

(1) All the absorption bands in neutron-irradiated LiF were produced by electron bombardment except for the S band. This provides a solution for the problem described above; neither helium nor tritium impurity is necessary to produce the complex and colloidal centers in LiF. Only the S centers require the tritium nuclei which emit β-rays during aging process.

(2) The wafers located beyond the electron range were lightly colored by F and M bands. The F centers produced in the region where no electrons penetrated are the object of interest, which will be described elsewhere. The wafer located at the electron range end exhibited the R, N and E bands in addition. The E band at 500 nm was accompanied by zero-phonon pips, as seen in Fig.1; in which the solid, broken and dotted curves are the absorption spectra of E band measured at LHeT, LNT and RT, res-

pectively. Being accompanyed by zero-phonon pips indicates that the E center is a defect aggregate. The wafers within the electron range were so deeply colored that the respective absorption bands were hardly distinguishable. There probably existed various vacancy-clusters which caused the absorption, and their complementary interstitial clusters must be present.[15,16]

(3) In heat-treatment, the E band moved to 495 nm, surviving up to 375°C, it became a maximum at 275°C. This behavior is the same as in x-rayed LiF,[7] except the higher stability, which may be due to the larger concentration in the present work. The behavior of E center may provide support to the suggestion about the model: an electron excess color center which is larger than the N center.[7] The E band did not appear in the specimens bombarded at temperatures higher than 375°C.

(4) The F band of low optical density occurring in the wafers beyond the electron range began to bleach at 300°C, completing at about 400°C, while the F band of high optical density in the wafers within the electron range survived up to 400°C where it was replaced by a band of longer wavelength, 260 ~ 290 nm. This band and another 360 ~ 390 nm which appeared earlier at 325°C survived up to 500°C. The bands correspond to those observed in neutron-irradiated LiF, which were taken as the colloid bands.[1, 9-12] It is suggested that the two bands are due to the resonant oscillation of plasma electron in metallic Li particles, shaped in circular cylinder and sphere, respectively: The energy losses by plasma oscillation estimated with the theoretical (or experimental) value $\hbar\omega_p$ = 8.02 (or 7.12) eV[17] are 4.70 and 3.64 eV, respectively, which must give the absorption bands around 264 (or

298) and 341 (or 383) nm. The observed and the estimated wavelength regions are in good agreement, suggestively. Cylindrical and spherical Li colloids are formed in LiF at above 300°C and remain metallic up to 500°C. The assumption of cylindrical shape for the Li colloids is based on the observations that the interstitial clusters in γ-irradiated LiF are accompanied by anisotropic strains[15] and the Li precipitates in O^- ion-bombarded are shaped in needle and platelet.[18]

(5) From 375 to 500°C, the 430 nm band appeared, which is familiar in the neutron-irradiated LiF in heat treatment.[1,6] The band was also observed along the dielectric breakdown paths[19,20] and on the slip bands induced by compressing stress. 430 nm is somewhat too short for the Mie scattering, the calculated wavelengths being larger than 460 nm.[14] When ambiguities in the optical constants of actual Li and LiF are considered, this discrepancy may be neglected, and the 430 nm band is due to Mie scattering by the finest Li colloids. The 480 nm band occurring at about 400°C in some specimens should be due to the Mie scattering by larger colloids (~20 nm).

(6) A broad band in the near UV region became predominant at temperatures higher than 500°C. With increase of the temperature, the maximum of this band moved to a short wavelengths of 300 nm, the optical density also reducing, the band then was completely annealed at 675°C. This band had colloidal nature; the absorption spectrum was not influenced by temperature of the measurement, as seen in Fig. 2. The band may possibly be due to the quasimetallic zones: Though no detailed studies have yet been made on the diffusion on Li in LiF, the thermal behavior may be

known on analogy of the diffusion of T in LiF, because of their close activation enthalpies, 1.87 eV for Li and 1.75 eV for T.[21] Since the diffusion of T in LiF is most active between 500 and 600°C,[19] the change in the absorption spectrum described above should be due to the diffusion of Li. The Li atoms probably move from the colloids and dissolve into the LiF lattice, transforming the colloids from metallic to quasimetallic. With increase of the temperature, the quasimetallic zones should reduce in size, resulting in the shift of the absorption band toward shorter wavelengths, and also in number, until the crystal is recovered completely.

(7) The temperature of crystals during bombardment had influence quantitatively on the formation of color centers and colloids. The bombardment at high temperatures could induce stable defects of high concentration, or otherwise no colloids survive to the temperatures higher than 500°C. As the cause for the defects, the following argument is possible: The aggregation of like defects into some stable form is predominant over the recombination of unlike defects during bombardment at reasonably high temperatures. Thereafter, in heat-treatment the defect aggregates are re-assembled into either complex color centers or colloids. The observation of defect clusters in as-irradiated crystals, either by diffuse x-ray scattering in LiF[15] or by electron microscope in other alkali halides,[22] may support this concept.

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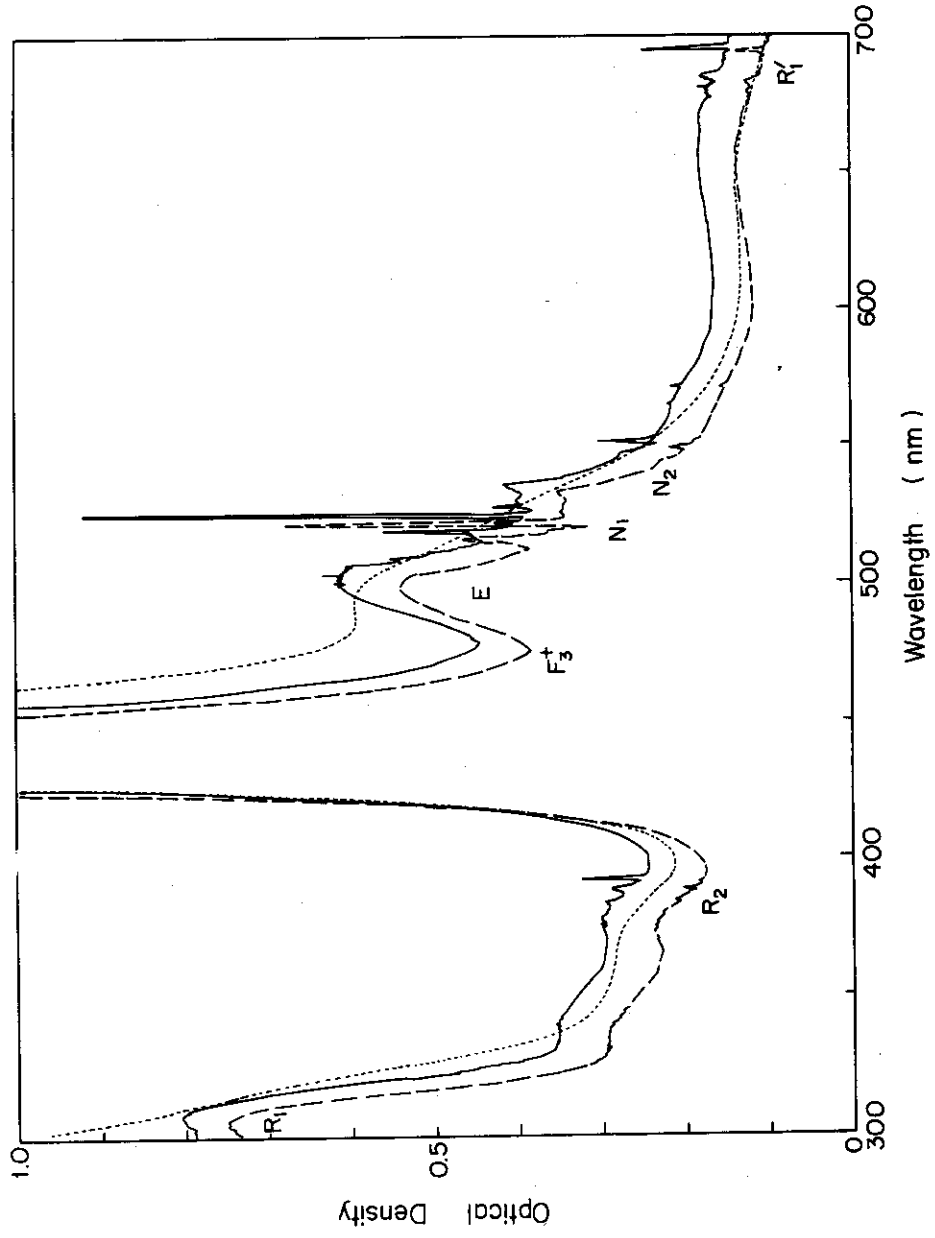

Fig. 1 The absorption spectra of E band induced by 1.5 MeV-electron bombardment at 300°C, measured at LHeT (solid curve), LNT (broken curve) and RT (dotted curve).

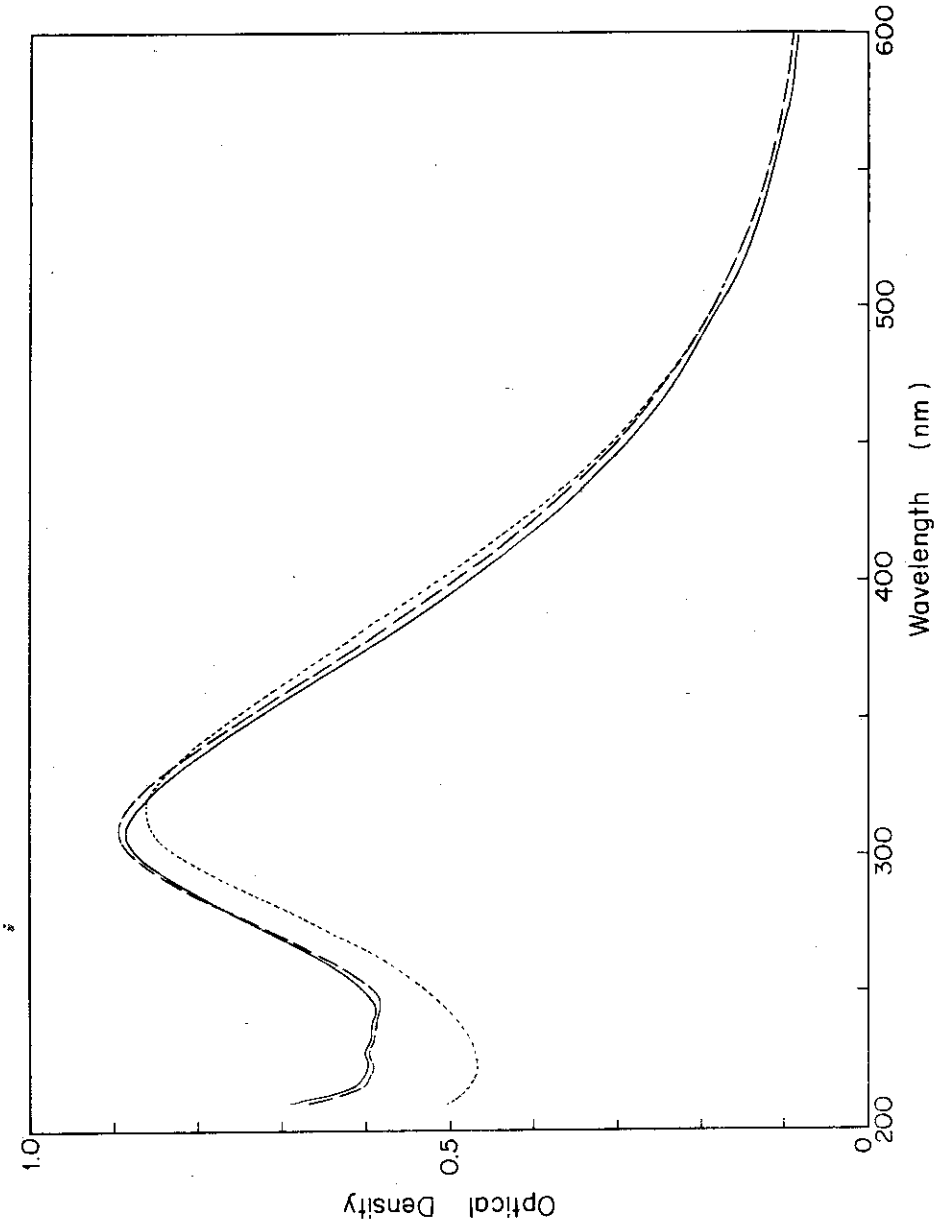

Fig. 2 The absorption spectra of 300 nm band which appeared in LiF bombarded at 400°C in heat treatment at 600°C for 10 min., measured at LHeT (solid curve), LNT (broken curve) and RT (dotted curve).