

THE F-ABSORPTION BAND IN LiF

A Thesis

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In Partial Fulfillment

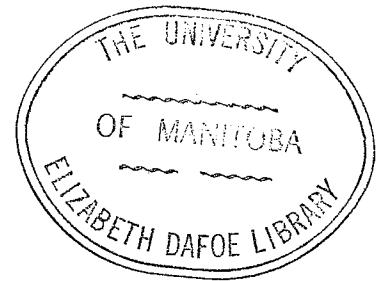
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INTRODUCTION

It has been stated that almost every field in physics possesses a few problems which merit particular attention because as a result of their inherent simplicity, they may eventually be understood in a complete fashion. The typical alkali halide crystal represents a remarkable medium for the study of crystalline imperfections. The perfect alkali halide crystal is exceedingly simple in structure, from the standpoint of both lattice and electronic systems. The crystals can be obtained with comparative ease in a state of purity and reasonable perfection. They can also be subjected to a variety of physical measurements which is almost unique among available materials. Moreover, they appear to exhibit in striking form a large number of physical and chemical properties of the type that are strongly influenced by the principal crystalline imperfections, namely, excitons, electrons and holes, vacant lattice sites, impurity atoms and dislocations. No other type of crystal has permitted so clear a vista of the imperfection-determined properties.

A region of great interest in the study of alkali halides has been in the production of colour

centers. Specimens colored by the addition of stoichiometric excess of alkali metal have occupied a special position in this study. This is principally because of the relative stability of the coloration, for it is associated with a specific chemical agent, the excess metal. Thus one may coagulate the color centers, but to bleach them out completely is extremely difficult. In contrast, crystals colored by ionizing radiations can be bleached by providing conditions where electrons and holes can annihilate one another.

Additively colored crystals possess additional virtues. One can study complexes composed of electrons and vacancies (F-centers), or of holes and vacancies (V-centers). Thus they permit the separation of effects associated with F-centers from those arising from V-centers.

On the other hand, a reasonably pure F-band can be obtained in additively colored crystals only by quenching them from temperatures well above room temperature. Unless the crystals are quenched, a fraction of the centers will appear as aggregates or precipitates. It is not known to what extent the properties of the crystals are altered as a result of the quenching procedure.

The analogy between the absorption spectra produced in alkali halides by x-irradiation or additive coloring is in most cases fairly clear. Corresponding bands in each can be classified as F, F', M, R, V, etc. In the case of lithium fluoride the correspondence is not so clear. One reason for this is that the F-band lies at 250 m μ and the first fundamental absorption band, which is due to electrons raised from the filled band to a level close to the conduction band, lies at 120 m μ . These regions of the spectrum are relatively difficult to explore. Another reason is that most of the bands of lithium fluoride are much more stable at room temperature and at higher temperatures than those of other alkali halides, and thus certain bands of an intermediate stability can be observed which in other halides may be too short-lived to be noticed.

Historically, the first observation of the coloration of alkali halides was made by Goldstein (1) late in the last century. The entire subject remained of passing interest until Pohl (2,3) and his co-workers subjected the discoloration to an extensive series of measurements. Review papers (4,5,6,7) indicate the amount of research done to create a better understanding of these phenomena.

Models for the various types of color centers, as proposed by Seitz(5), are shown in Fig. 1. These will be discussed later.

In general, the alkali halides may be colored, with the introduction of a F-band, either by the addition of a stoichiometric excess of alkali metal or by the use of ionizing radiations. Both methods can produce F-center densities as high as 10^{19} per cm^3 . These solids have atom densities of $10^{22} - 10^{23}$ per cm^3 .

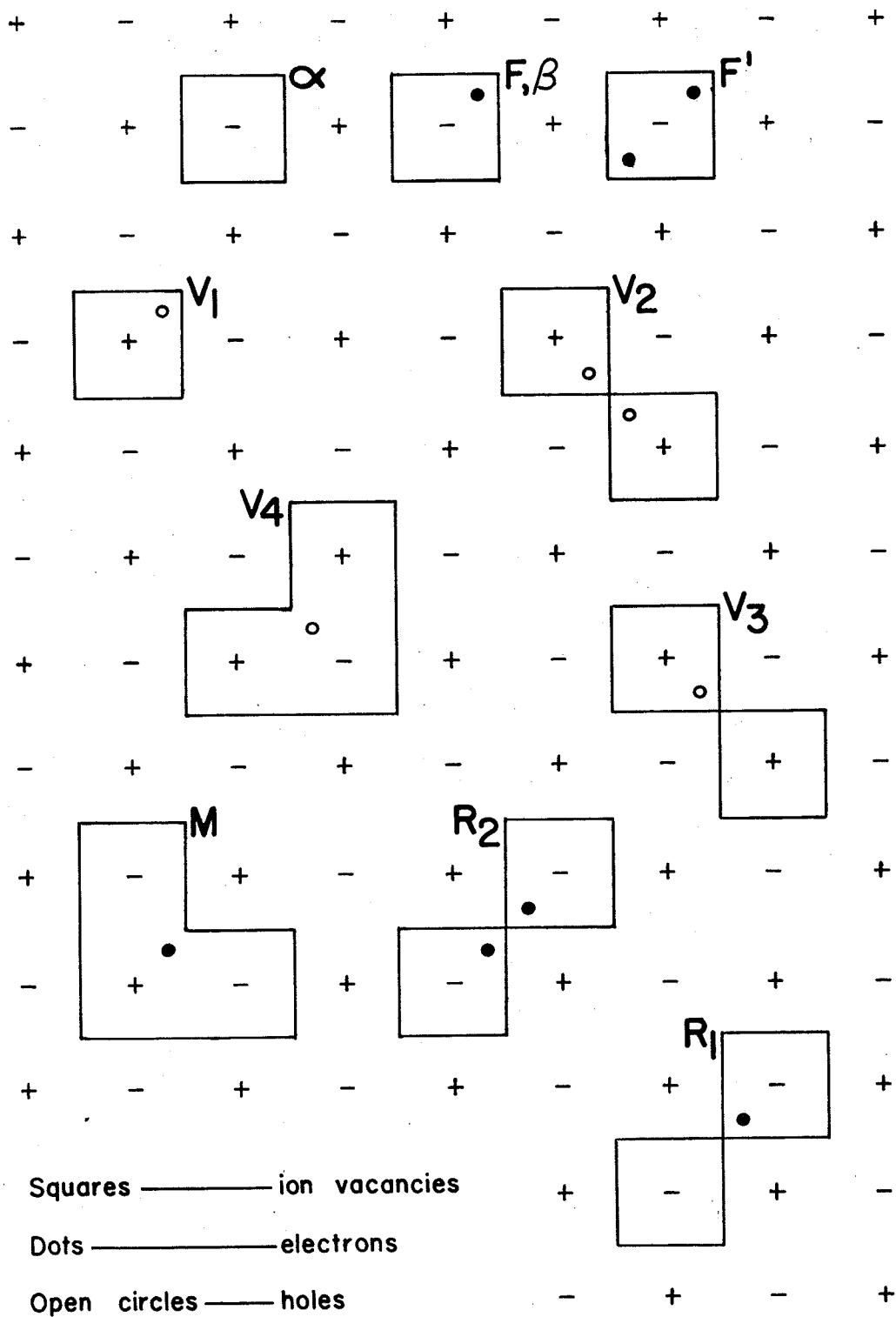
DeBoer (8) proposed that the F-center was an electron attached to a negative ion vacancy. He suggested that when the alkali halides are heated in the presence of alkali metal vapor, halide ions diffuse to the surface of the crystal and combine with the atoms of the vapor to form new layers of lattice. The valence electrons initially attached to the alkali metal atoms wander into the crystal and become attached to the negative ion vacancies. Theoretical calculations and experimental evidence have given this model considerable support.

-- COLOR CENTERS PRODUCED BY X-RAYS --

Most of the alkali halides have been colored quite readily by exposing the material to x-rays. Most crystals show the bell-shaped F-bands in the visible part of the spectrum but in lithium fluoride it is situated at 250 μm .

FIG. I

MODELS FOR COLOR CENTERS



Molar (9) first examined closely the effect of x-rays on various alkali halide crystals. He found that the darkening produced attains a saturation value which depends on the temperature and nature of the crystal as well as the intensity of the x-ray beam. Some crystals were difficult to color and lost their coloring rapidly while others darkened easily and retained their darkening. The x-rays also produced an absorption band on the short wavelength side of the F-band and one on the long wavelength side. These are designated as the V-band and the M-band, respectively. Mollwo (10) produced the V-band by exposing bromide crystals to bromine vapor and hence introducing a stoichiometric excess of bromine. He concluded that a V-center is a hole trapped in a positive ion vacancy and there is an analogy with the F-center. The model proposed by Seitz (5) for the M-center is the combination of an F-center with a pair of vacancies, i.e. a positive ion vacancy and a negative ion vacancy. Knox (11) modified this and gave as the M-center model an association of an electron with a positive ion in a region of two ion pair vacancies. Yet a third model, consisting of a pair of F-centers was proposed by Van Doorn and Haven (12). We can conclude from this that the M-center is not as well understood as the F-center.

When crystals which have been colored by x-irradiation are heated to a sufficiently high temperature, they bleach to the original colorless state. This is the result of the recombination of the electrons and holes which were produced by the x-rays and then trapped to produce F and V-centers.

--- ADDITIVE COLORING ---

The F-bands may be induced by heating the alkali halides in the presence of alkali metal vapor and cooling quickly to room temperature (i.e. quenching). The crystals absorb some of the alkali metal during the process. The coloration produced is characteristic of the crystal and not of the alkali metal used in the vapor. The V-band is not present and if the crystals are quenched sufficiently rapidly the M-band does not appear. If the crystals are cooled slowly after the heating process, the F-band is accompanied by other bands associated with the presence of colloidal aggregates of the excess alkali metal. These aggregates also appear if an attempt is made to bleach the F-centers by heat. The coloration cannot be removed by heat as was the case with crystals colored by x-rays.

Kleinshrod (13) showed that in KCl the absorption coefficient of additively colored crystals is proportional to the stoichiometric excess of the alkali metal.

Smakula (14) showed that if a medium of refractive index n' contains a number n_0 of absorbing centers per unit volume, which possesses a bell-shaped absorption peak (i.e. F-centers), the relationship between the absorption coefficient α_m at the center of the band, the concentration of centers, and the width at half maximum of the band W is

$$n_0 f = \frac{18m}{\pi e^2 h} \frac{n'}{(n'^2 + 2)^2} \quad \alpha_m W .$$

f is the oscillator strength of the absorbing centers.
 $f = 0.81$ for KCl.

Additive coloring can also be produced by electrolysis. One end of the crystal is pierced with a pointed electrode which is the cathode. The contact anode may be made by pressing a flat electrode against the opposite side of the specimen. If a current is passed through the crystal at an elevated temperature, F-centers emerge from the cathode and migrate toward the anode. Halogen gas is given off at the anode.

--- PRODUCTION OF F', α , AND β BANDS ---

If crystals are irradiated with F light, a new band (F') appears on the long wavelength side of the F-band (15). Unlike the F-band its width is relatively insensitive to temperature. Pick (13) showed that for each

light quantum absorbed in the F-band, two F-centers were destroyed. This can be explained if the photoelectron is captured by an F-center. Thus both the F-center from which the photoelectron was released and the F-center by which it is captured will be lost. It follows that the F'-center must be the result of adding an electron to a F-center. It was also found that for each light quantum absorbed in the F'-band, two F-centers were created. A restricted temperature range exists for the production of F'-centers. The temperature must be sufficiently high to thermally move the excited F-center electron into the conduction band, but it must also be low enough to prevent the two loosely bound electrons in the F'-center from being thermally excited to the conduction band.

Two new absorption bands, the α and β -bands, were discovered by Delbecq, Pringsheim and Yuster (16), and these provided a valuable tool for the study of color centers in alkali halides. In additively colored crystals the β -band was found near the edge of the fundamental absorption band. It is closely related to the F-band, and diminishes in proportion to the F-band if the crystal is F irradiated to produce F'-centers. When this happens the α -band appears just to the long wavelength side of the β -band and grows in proportion to the F'-band. The α -band is associated with halogen ion vacancies.

Both bands are associated with the excitation of electrons from the valence band to well defined higher levels not present in the perfect crystal, that is to levels produced by F-centers and negative ion vacancies.. It is reasonable to assume that an electron on the halogen ions is excited to these bound levels when absorption occurs in the α and β -bands, for both the F-centers and the negative ion vacancy can bind an electron not present initially. That is, an exciton which is trapped at the lattice imperfection is produced, the excited electron being more stable than in the perfect crystal because of the attractive potential fields occurring near the halogen-ion vacancy and the F-center. The hole associated with the exciton when the electron is bound to the lattice defect remains bound.

--- BLEACHING AND TRANSFORMATION OF CENTERS ---

Glaser and Lehfeldt (17) found that F-centers in additively colored crystals may be made to coagulate by white light irradiation at temperatures above the range in which F'-centers are formed. The same happens when additively colored crystals are cooled to room temperature slowly. The F-band can be completely destroyed in this way. In the early stages of this process the M-band forms.

In this process the halogen ions must diffuse together. The transport of vacancies must be due to neutral pairs since the negative ion vacancies are not sufficiently mobile, as was proved by diffusion measurements (4). Photoelectrons ejected from F-centers are trapped by centers from which positive ion vacancies may be released as a result of the capture of electrons. These combine with ionized F-centers and transport them to other F-centers to form aggregates. When the aggregates have captured a sufficient number of photoelectrons these positive ion vacancies will be released. According to this mechanism we should expect the centers consisting of a pair of vacancies attached to an F-center to appear very early among the products of aggregation and hence to be clearly visible. Glaser and Lehfeldt's data showed that the M-band is one of the first products of the process.

Molar (9) found that M-centers appear with F-centers when the latter are produced by x-rays. Molar irradiated the crystals with light in the F and M-bands with a low intensity and his results corresponded to a more refined study of the products formed in the initial part of Glaser and Lehfeldt's investigation. Upon irradiation he found that the F and M-band can be transformed into one another. But unlike the F to F'

transformation a fraction of the intensity of both bands is lost in each transformation. The lost absorption strength appears in a set of bands between the F and M-bands, called the R-bands. These are very stable and cannot be converted into any of the other bands by light which they absorb. These centers are the first aggregates of F-centers and this suggests they are pairs of halogen ion vacancies which have captured one and two electrons. By analogy with the facts for diatomic molecules, we may suppose that photoelectrons are not formed when these centers absorb light. Instead the vacancies separate somewhat so that the first excited state and the ground state get much closer together. The system then makes an almost adiabatic transition to the ground state and returns to its initial condition. This is the reason for the stability of the R-bands.

During the 1940's Petroff (18) irradiated additively colored crystals of potassium chloride with F light. He produced M-, R, and N-bands, the last situated on the long wavelength side of the M-band. Burstein and Oberly (19) also produced N-centers from crystals colored by x-rays. The N-center should be associated with a unit containing three halogen-ion vacancies, for the R and M-centers exhaust the possibilities obtainable with two

halogen-ion vacancies. For example it could be a neutral center consisting of three F-centers or an R_2^- -center to which a neutral pair of vacancies has been attached. Or it could be a positively charged center obtained by adding a halogen-ion vacancy to an R_2^+ -center or a neutral pair to an R_1^+ -center.

--- COLLOIDS ---

Scott (20) and co-workers have studied the changes in some alkali halides additively colored induced by both light and heat. In some cases heating and cooling produces small colloidal particles of the alkali metal in the crystal. Savostianova (21) has calculated where such a colloidal band should lie. The band position depends upon the size of the colloids.

The type of aggregation with light alone at room temperature is limited to R, M, N and similar bands. If one uses light and heat a new R' -band is seen. The R' -band is a combination of R, M, N-bands and additional aggregates. This is not a true colloid band. If a crystal containing dispersed F-centers is raised to a sufficiently high temperature, the F-band decreases and the colloid band increases.

At high temperatures the F-band never disappears. An equilibrium is set up between F-centers and colloids. At equilibrium the F-band intensity depends on the temperature and not on the amount of excess metal present. The colloid centers behave as if they constituted a liquid or solid phase of the excess alkali metal and the F-centers behave as if they constituted a monatomic vapor in equilibrium with the solid or liquid phase. Additional information on the mechanism by which F-centers coagulate show that the colloidal particles contain approximately ten atoms.

--- BLEACHING OF X-IRRADIATED CRYSTALS ---

An appreciable portion of the definitive work on bleaching of alkali halides darkened by ionizing radiation was carried out by Przibram (22) and his co-workers in the 1920's. Bleaching, or partial bleaching, may be accomplished by application of heat, by light absorbed by one of the bands, particularly the F-band, or by both agencies in combination with relatively weak irradiation with ionizing radiations.

Regardless of the temperature at which darkening has occurred, bleaching occurs rapidly at first and becomes increasingly difficult. Both the F and V-bands decrease simultaneously with bleaching. The great

difference between the high initial rate of bleaching and the slow terminal rate can be described by stating that there are "soft" F-centers easy to bleach and hard F-centers which persist. Possibly the difference is that the crystals contain both F-centers and a mixture of two or more types of V-centers which are well separated from one another but which are not necessarily distributed uniformly, or the centers may have been produced in highly localized regions and are sufficiently close to one another that some of the electrons can tunnel to holes, particularly when the electrons are raised to an excited state.

The mechanisms of bleaching are not completely understood but some understanding has been reached as to the roles of the various types of V-centers. Much of the preliminary research was done using potassium chloride crystals.

Casler, Pringsheim, and Yuster (23) studied bleaching in KCl crystals which had been x-irradiated at liquid nitrogen temperatures and warmed above -100°C. The results showed that the V_1 -centers disappear and the part of the F-band which disappears does so because the holes annihilate the electrons. The rate of bleaching decreases when the easily available holes from the V_1 -centers are exhausted. The V_4 -band also vanishes and produces some

extra holes. Some V_2 and V_3 -centers may survive as these centers are more stable.

In the study of thermal bleaching one guiding principle can be used with safety. The activation energies for freeing electrons thermally into the conduction band from F-centers are so large that this process can be disregarded as a significant contribution to bleaching at any temperature near or below room temperature.

Schneider (24) examined the rate of thermal bleaching of F-centers in KCl in the temperature range between room temperature and 160°C where no V_1 or V_4 -centers exist. Again a bleaching of soft and hard centers was observed but the mechanism is not known. Schneider also studied optical bleaching in KCl at room temperature. This depended on the light intensity and the fast process seemed to be the capture of a photoelectron by a V_2 -center which possesses a hole that can be annihilated without an activation energy. The slow process here possibly is the joining of free electrons with V_3 -centers if an activation energy is furnished by thermal quanta. The conduction electron must overcome the repulsive electrostatic field which is associated with the V_3 -center.

Casler, Pringsheim, and Yuster (21) used temperatures up to 200°C to observe V-bands obtained in KCl by x-irradiation. The V₂-band bleaches first whereas the V₃-band resists bleaching most strongly.

Another phenomenon which may contribute to the progressive increase of resistance to bleaching is the development of local space charges which prevent electrons or holes from migrating over the distance necessary to permit annihilation of carriers of opposite sign. Non-identical distributions of F and V-centers imply regions which are predominantly n and p-type and hence the presence of at least incipient p-n junctions prior to bleaching.

Wannier (25) saw the possible importance of these junctions in affecting photocurrents. The bleaching process would accentuate these junctions since carriers leave regions of opposite charge and go to regions of the same charge until the differences in potential become sufficiently great to prevent the transfer. This was shown to be the case by Oberly and Burstein (26) who examined photocurrents in KCl during bleaching of x-irradiated crystals by irradiation in F-type bands. Photocurrents associated with illumination in the F, R, M, and N-bands were observed and the magnitude of the current resulting from irradiating in the F-band drops more rapidly than the absorption

coefficient of light during bleaching. This is what one would expect if the range of the electrons were limited by the development of p-n junctions.

Alexander and Schneider (27) have investigated the absorption in the V_2 and V_3 -band region when crystals, darkened by x-rays at room temperature, are irradiated with light absorbed both by these bands and by F-centers. KCl crystals were used. The conclusions drawn were as follows:

1) The initial decrease in the F-band occurs with quantum efficiency near unity when bleaching with F light. Here the V-bands decrease relatively slowly; most of the F-band drop is due to the formation of R and M-bands. The F-band later stabilizes, the quantum efficiency for the decrease approaching .005. The rate of decrease in the F and V-bands is comparable at this stage.

2) During V-band irradiation with light, the V-bands decrease but the F-band does not. After irradiation, the V-bands recover to their original value in several days. Possibly either the V_2 or V_3 -center possesses a metastable excited state from which the system slowly returns to the ground state. The holes are not freed and

cannot annihilate electrons associated with the F-type centers as occurs when V_1 -centers decompose during warming from very low temperatures. The V_3 -center probably has the metastable state since this center predominated in the crystal specimens used.

3) Irradiating F and V-bands simultaneously greatly accelerates the bleaching of F and V-centers. The free electrons may combine readily with the metastable V-centers, so that the V_3 -centers lose their resistance to bleaching.

--- X-RAY COLORATION OF ALKALI HALIDE CRYSTALS ---

It has been well known for some time that x-rays decrease the density of alkali halide crystals by the production of vacancy pairs and as a result F-center and V-center production. Following the demonstration of Estermann, Leivo, and Stern (28) that the density of a KCl crystal decreases upon being irradiated with x-rays, the physical expansion that accompanies x-ray irradiation has been measured in the alkali halides by sensitive electronic (29) and photoelastic methods (30,31). The measurement of Estermann, Leivo, and Stern indicated that twice as many vacancy pairs were created as F-centers, while Lin observed almost perfect correspondence between F-centers and vacancy pairs. Lin (29) also observed a time delay of 20 - 30

minutes before the crystal expansion could be detected after the radiation began. No other researchers report this delay.

The observed decreases in crystal density which accompany the formation of F-centers do not alone provide a proof of deBoer's model of the F-center, for the decreases could conceivably be associated merely with an increase in the average lattice spacing of the specimens. Berry (32) found an increase in lattice dimensions but it accounted for only about 5 percent of the increase in length of a crystal upon irradiation with x-rays. Hence the greatest part of the density change is due to the production of ion vacancies.

F-center production by high intensity ionizing radiations at room temperature occurs in several stages (33-36). There is an initial rapid production of F-centers followed by a second stage of very slow F-center growth. The slow stage is then followed by a third stage in which the production becomes relatively rapid. However, the rate of production of F-centers in this stage is still much less than it was in the initial stage. The initial stage has been attributed to the trapping of electrons by the negative-ion vacancies initially present in the crystal.

The number of F-centers after the first stage is from 10^{16} to 10^{17} per cubic centimeter. The slower second and third stages have been attributed to the creation of new negative-ion vacancies by the radiation, these new vacancies are then converted to F-centers. The proposed model implies that all the negative-ion vacancies initially present in the crystal are converted to F-centers. After exhaustion of these vacancies, a slow growth of the F-band continues due to the production of new vacancies by the irradiation. The final concentration of F-centers can be in excess of 10^{18} per cubic centimeter.

The rate of production of F-centers in the first stage is independent of the x-ray intensity over a wide range. The total first stage coloration however increases with increasing intensity. The radiation produces F-centers but it also bleaches some of them. An equilibrium value is reached which depends on the intensity of the radiation. The rate of coloration in the second stage is independent of the intensity over a wide range while in the third stage it increases with increasing intensity. The intensity dependence of the third stage coloration is not due to a variation in the rate of production of new vacancies but is due to a variation in the equilibrium number of F-centers produced from the new vacancies.

New vacancies are generated at a rate proportional to the square of the intensity of irradiation and inversely proportional to the dislocation density. Deformation increases the concentration of initial vacancies near dislocations, while heat treatment increases the concentration of initial vacancies dispersed in the volume of the crystal. Impurity atoms do not sizeably alter the x-ray induced expansion of crystals.

Recently a new model was proposed (36) explaining how incident radiation produces positive and negative ion vacancies and finally V and F-centers. This model requires further theoretical and experimental verification. Consider the case of an edge dislocation in an alkali halide.

+ + + + +
- - - (1) - (1) - -
skip-----plane ground state of the
+ + (2) + + +
- - - - - -
+ + + + + +

Because of the missing positive ion, the halogen ion at (1) will be above the valence band. An exciton produced by an x-ray can ionize the halogen ion. The halogen atom now can be pushed across the slip plane to the site labelled (2). This lowers both the compression strain and the tension strain at the dislocation. Another exciton may then provide the energy to move a halogen ion from its normal lattice site to the position vacated by the halogen

atom. In this way the vacancy escapes the immediate edge of the dislocation. The halogen atom soon recaptures an electron and occupies a normal halogen site along the edge of the dislocation. After a number of halogens have climbed onto the edge their charge will attract positive ions from the nearby lattice, thus creating positive ion vacancies and maintaining the neutrality of the dislocation. The net result is the climb of the dislocation and the formation of highly concentrated negative and positive ion vacancies in the wake of the dislocation. The electrons and holes produced by the x-rays can be trapped at these vacancies producing F and V-centers.

X-ray production of F-centers at liquid helium temperatures (37) is primarily dependent on the type of alkali halide and not on the defect structure of the particular specimen in contrast to observation at room temperature. This result indicates that the low temperature production of F-centers is a bulk property of the alkali halide and occurs as a result of halide ion vacancies by the ejection of halide ions from their normal lattice sites. The energy required to form a F-center at liquid helium temperature for various alkali halide is in agreement with the interstitial space available to accept the ejected halide ion.

--- PARAMAGNETIC RESONANCE OF F-CENTERS IN LITHIUM FLUORIDE ---

Since deBoer's (8) original proposal in 1937 that the F-center was an electron trapped at a negative ion vacancy within an alkali halide crystal, and thus should exhibit paramagnetism, it has been shown through electron spin resonance experiments that the F-center is paramagnetic(38). An unusually broad resonance line has been observed with a g value slightly less than the free electron g value (39-41). g is the spectroscopic splitting factor and it determines the amount by which a degenerate energy level is split in a magnetic field. For the free electron spin g is 2.0023. The slight g shift was explained as arising from a spin-orbit interaction between the electron spin moment and the magnetic field due to its orbital motion, while the unusual breadth was attributed to a hyperfine coupling of the electron with the neighboring nuclei. Through the discovery of the electron-nuclear double resonance (ENDOR) technique, Feher (42) proved the correctness of the interpretation given to the observed resonance, and determined the hyperfine coupling of the F-electron to the neighboring nuclei for F-centers in KCl.

The F-center is paramagnetic because of its unpaired electron. In a magnetic field there is a splitting

of energy levels and upon application of the proper microwave field there will be an absorption of energy. In the ENDOR technique the electron spin resonance is almost saturated with the microwave field. This decreases the signal as the population of the energy levels become more nearly equal. Then an additional intense radio frequency field is superimposed on the sample. As the frequency of this field is varied, the microwave signal changes whenever the field stimulates nuclear spin transitions between the Zeeman hyperfine levels of the F-center electron. The change becomes appreciable as this hyperfine interaction "resonance" of the neighboring nucleus is saturated. Since the nuclear line width is approximately 20 kc/sec in comparison to 150 Mc/sec for the electron line width, this technique improved the resolution by about four orders of magnitude.

The F-center in LiF is one of the color centers in alkali halides which has been most thoroughly studied both theoretically and experimentally by magnetic resonance using ENDOR (43). The partially resolved 35-line hyperfine structure existing on the broad resonance line for the (111) crystal axis parallel to the external magnetic field, was shown to be consistent with the hyperfine splitting constants obtained from ENDOR experiments (44).

--- ABSORPTION BANDS IN LiF ---

Color-center studies have been confined mainly to the face-centered cubic NaCl-type crystals (3-6) such as KCl, KBr, etc. No systematic studies of color-center formation in the simple cubic CsCl type alkali halides such as CsCl, CsBr and CsI have been pursued. In fact, only recently have these crystals been subjected to experiments (45-48). Only small modifications of the color-centers were observed when compared to those of the NaCl-type crystals.

LiF is a face-centered cubic NaCl-type crystal which has undergone fairly extensive examination. A number of absorption bands and lines have been found in irradiated LiF (49, 50). If the exposure to x-rays takes place at room temperature, the F-band forms at 250 m μ , the M-band at 450 m μ , and the F'-band at 620 m μ . At room temperature the F'-band is not stable and disappears in a few hours leaving a greatly enhanced M-band. If the LiF crystal is exposed to x-rays at -190°C, the F-band forms and also a band at 340 m μ , which disappears if the sample is heated to -135°C. When the crystal is warmed to room temperature the F-band intensity drops, and the F'-band forms. The F'-band subsequently disappears giving way to the M-band. The M-band is very stable and unlike other alkali halides cannot be bleached with M light to produce R-bands.

Prolonged irradiation however produces low intensity R₁ and R₂-bands at 313 m μ and 380 m μ respectively. Unlike other alkali halides a new band is produced at 222 m μ when the crystal is bleached with F light. Another unique property of LiF is the production of F-centers when crystals are heated to 450° C. At liquid nitrogen temperature there is an appearance of fine structure in a band at 380 m μ and of a weak line at 523 m μ .

A greater understanding of the processes involved in the formation of color-centers in LiF would be possible if the centers formed by ionizing radiations could be compared to those formed by the additive coloration method. To date, no studies have been made on color centers in LiF formed by introducing a stoichiometric excess of alkali metal. This project was an attempt to produce an F-band in this way and thus provide additional evidence supporting the model for F-centers.

THE PROJECT--- CRYSTAL PREPARATION ---

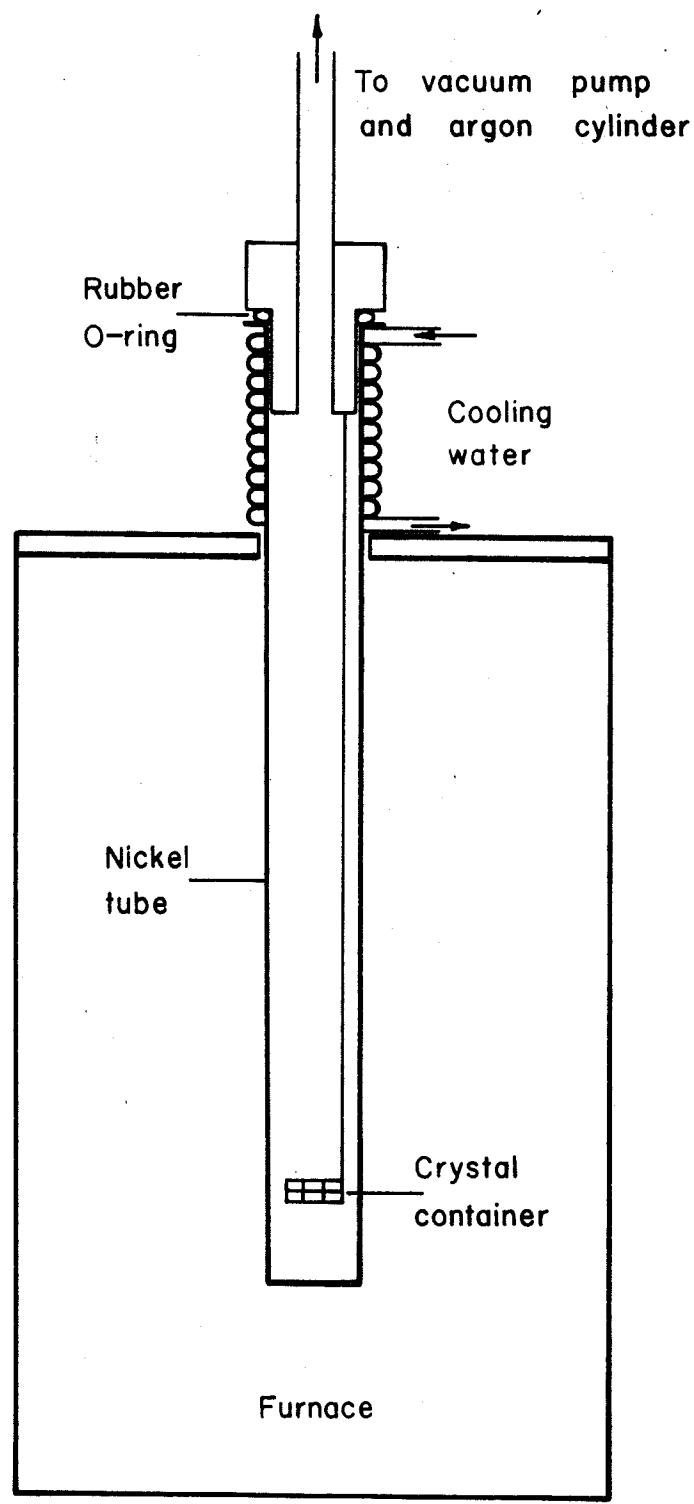
LiF blank crystals in the form of discs 1 cm in diameter and 2 mm thick were used. Several techniques were used to produce F-centers and these are outlined below:

(a) Several crystals were irradiated with x-rays using a type 32114 Norelco Fe Diffraction x-ray tube at 35 kev and 10 ma for times ranging from 1 to 15 hours. The tube dose rate was approximately 75,000 roentgens per hour.

(b) The apparatus shown in Fig. 2 was used in an attempt to color LiF crystals additively. This apparatus was similar to that used by vanDorn (51). It consists of a nickel tube (length 24 cm, diameter 2.5 cm), open at one end. It can be closed by means of a lid with rubber packing. The lid has a tube attached to it, through which it is possible to evacuate the nickel tube and admit argon to any desired pressure. The nickel container for the crystal is fastened to the lid by means of a nickel wire. The lower end of the tube can be heated in a furnace while the upper end can be cooled by water passing through copper coils.

FIG. 2

APPARATUS USED TO PRODUCE COLOR
CENTERS IN LITHIUM FLUORIDE CRYSTALS



The action within the apparatus is as follows:

If a small piece of metal (e.g. lithium) is put in the tube, the lower end of which is heated, the metal starts boiling. The vapor rises and finally condenses in the cool part of the tube. Liquid metal flows down the wall until it enters a hotter part where it vaporizes again, etc. A steady circulation of metal will be established, liquid flowing downwards along the wall and vapor upwards in the middle of the tube. This circulation zone separates pure metal vapor in the lower part from pure argon admitted to the upper part. Because pressure equilibrium exists, the pressures of the argon and the metal vapor are equal which gives a method of regulating the latter. An advantage of this technique is that since the lid is kept cool, the tube can be opened quickly which enables the crystal to be quenched in about 1 second.

The following procedure was used in attempts to color LiF crystals in Li and K vapor. About a gram of the alkali metal was put in the cold tube and the container with the crystal inserted. After evacuating completely for several minutes, argon was admitted to pressures ranging from 20 to 100 mm. VanDoorn (51) used similar pressures to obtain a high concentration of F-centers. The lower end of the tube was then heated to 700°C. Heating was

continued for about an hour, after which argon was admitted to a pressure of 1 atmosphere, the tube opened, and the crystal and its container transferred to a quenching bath of carbon tetrachloride.

(c) Blank LiF crystals were taken and thin layers of Li evaporated onto one or both sides, the operation taking place in vacuum. A layer of silver was evaporated onto the crystals over the Li to prevent oxidation of the latter. Some of the lithium probably diffused into the silver and through the silver to evaporate but it was hoped that a sufficiently high density of lithium atoms (approximately 10^{22} - 10^{23}) remained at the crystal surface. The crystals thus treated were placed in the nickel tube and heated at a temperature of 500°C for times ranging from 10 minutes to 2 hours. The heating took place in an argon atmosphere at pressures of 50 to 150 mm. After cooling in air it was observed that the Li had disappeared leaving only the Ag layer, which was subsequently removed.

(d) In an attempt to increase still further the concentration of alkali metal atoms at the LiF crystal surface, several crystals were dropped into a bath of molten lithium. Again the nickel tube was used and it was kept at a temperature of 500°C for 45 minutes. Argon was

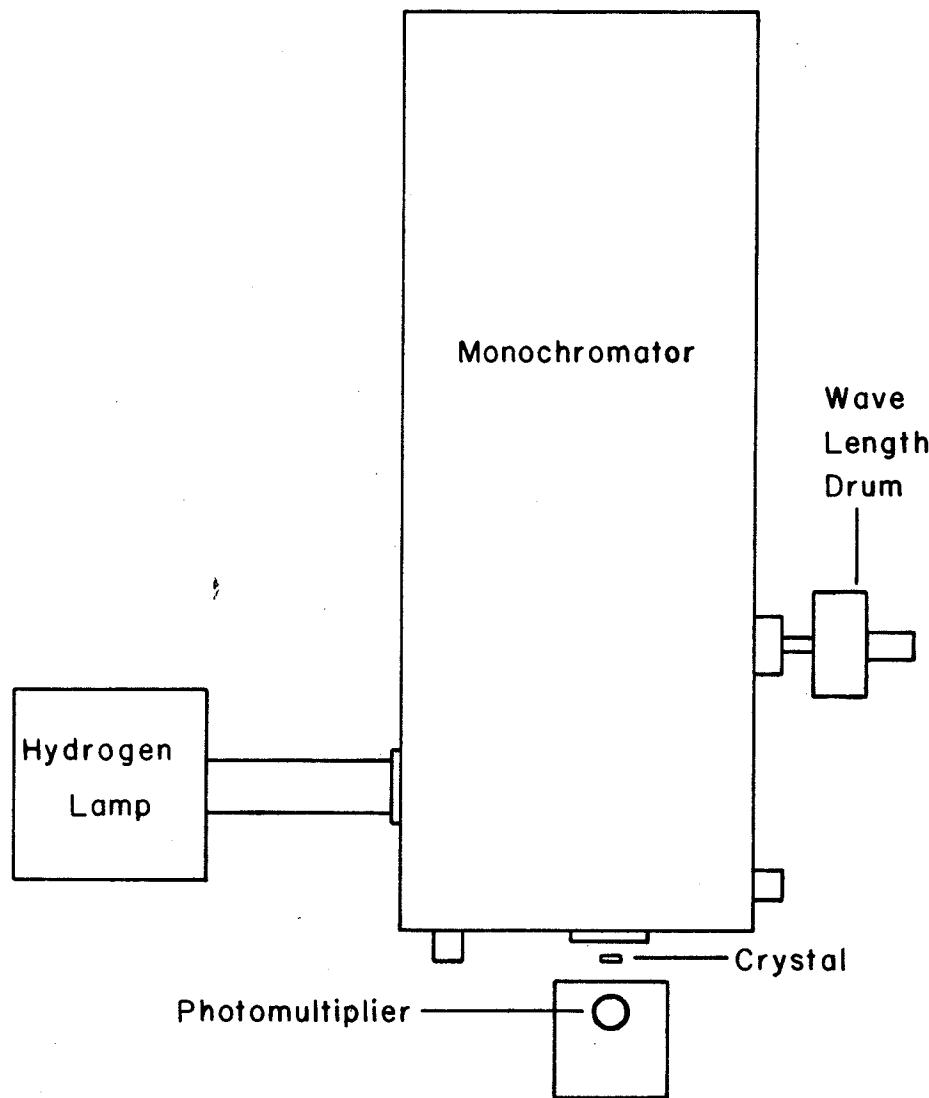
admitted into the tube at a pressure of 50 - 100 mm. After treatment the crystals were cooled in air. They were not quenched because of the lithium surrounding the crystal and the difficulty in removing the crystal from the tube quickly.

--- TRANSMISSION MEASUREMENTS ---

The transmission properties of the samples were studied with a Bausch and Lomb grating monochromator coupled to a high pressure hydrogen lamp as the source and to a RCA 1P28 photomultiplier tube and galvanometer circuit as the detector. The physical arrangement of the crystal with respect to the spectrophotometer is illustrated in Fig. 3. Light from the monochromator at any desired wavelength passes through a small circular hole and is detected using the photomultiplier and galvanometer. By means of a sliding apparatus the crystal is placed in front of the hole and the intensity of light transmitted through the crystal and observed by the photomultiplier is recorded. In this way, the percentage transmission of light through the crystal can be determined at any wavelength. Some light is also reflected at the crystal surface, the amount depending on the condition of the surfaces.

FIG. 3

APPARATUS USED TO MEASURE
SPECTRAL TRANSMISSION OF
LITHIUM FLUORIDE CRYSTALS



Measurements of LiF crystals were made at wavelengths from 200 m μ to 560 m μ . The lower limit was dictated by the diminishing intensity of the ultraviolet light source while the upper limit was due to the decrease of photomultiplier sensitivity. In this range the band width of the light emerging from the exit slit of the monochromator was approximately 5 Angstroms using a slit width of .2 mm. The observations were carried out in a dark room to eliminate stray light effects from external sources. The long wavelength part of the spectrum (400 m μ to 560 m μ) was covered using a glass filter at the exit slit in order to eliminate the second order diffraction from the grating. Before making any measurements, the calibration of the monochromator was checked in the visible regions, using the line spectrum from a mercury lamp.

DISCUSSION OF RESULTS

A total of about 70 crystal blanks were used and the transmission spectrum examined for about 15 of these. It was felt unnecessary to examine every blank in this way because of the practically exact correspondence of the spectrum from one sample to another. Typical transmission curves for the untreated crystals are shown in Figs. 4 and 5.

The transmission spectrum of several x-irradiated crystals was examined and typical results are shown in Fig. 6. In the curve shown the lithium fluoride crystal was exposed to x-rays for 2 hours and received approximately 150,000 roentgens. Longer exposure to the radiation enhances the bands already present but produces no new ones. The F-band is seen to occur at 250 m μ as observed by other workers (50). The smaller absorption band at 450 m μ has been identified as the M-band (50).

An attempt was made to introduce F-centers into the crystal samples by heating in an alkali metal vapor. Potassium chloride crystals were first used and these acquired a deep violet coloring very easily. However, no success was obtained by this method when lithium fluoride crystals were used. The nickel tube temperature was varied as was the time of heating. Lithium, sodium, and potassium metal vapors were used, all to no avail.

FIG. 4

SPECTRAL TRANSMISSION OF PURE
LITHIUM FLUORIDE CRYSTALS

TRANSMISSION (%)
100
90
80

BAND WIDTH .7m μ

WAVE LENGTH (m μ)
500
400
300
200

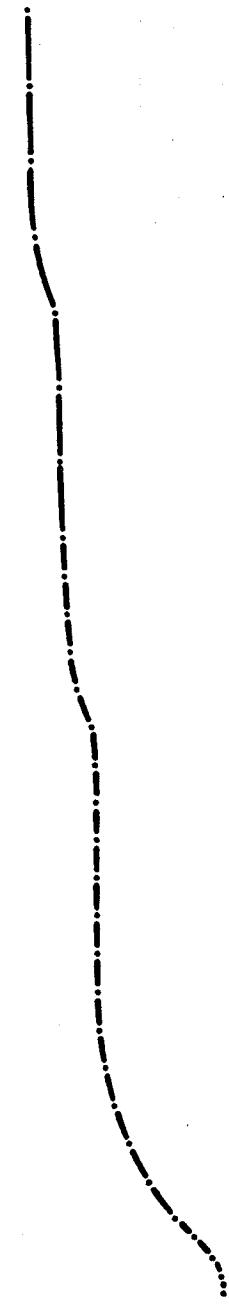


FIG. 5

SPECTRAL TRANSMISSION OF PURE
LITHIUM FLUORIDE CRYSTALS

TRANSMISSION (%)

95

90

85

200

400

500

WAVE LENGTH ($m\mu$)

BAND WIDTH .7 $m\mu$

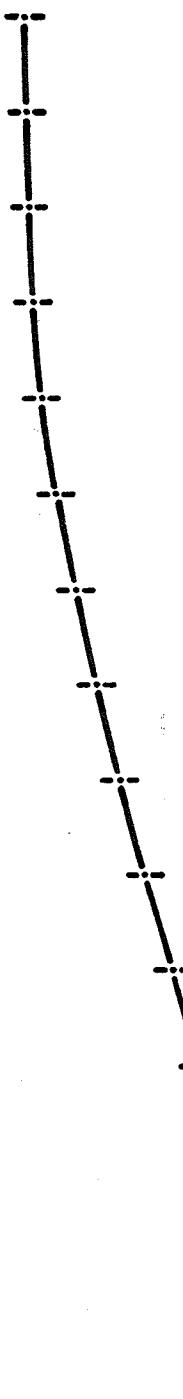
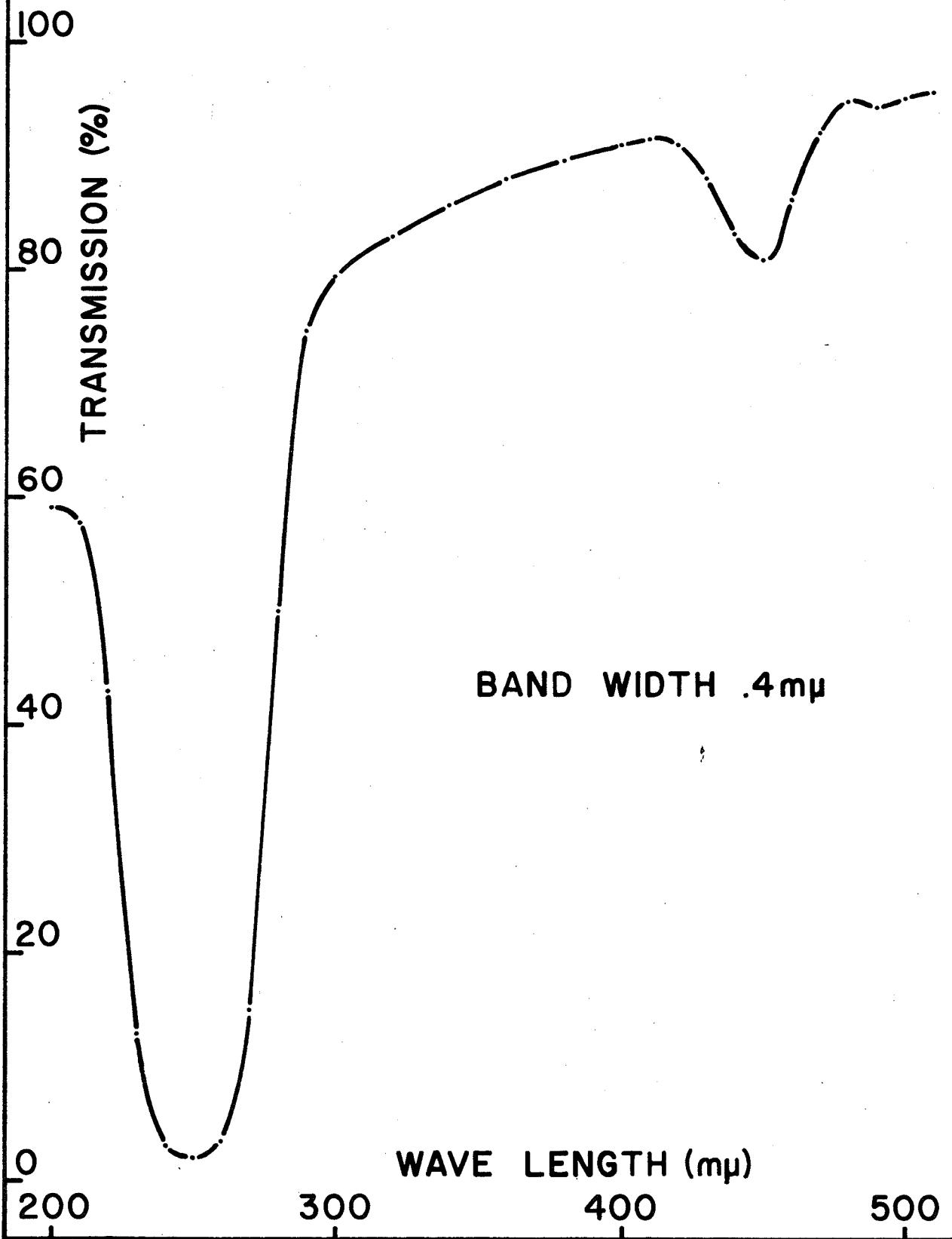


FIG. 6

SPECTRAL TRANSMISSION OF X-IRRADIATED
LITHIUM FLUORIDE CRYSTALS



Some of the difficulty in producing F-centers in lithium fluoride crystals can be attributed to the fact that these crystals are the most stable of the alkali halides. The cohesive energy of lithium fluoride is 244 k. cal/mole while that of KCl and KBr is 168 and 161 k. cal/mole respectively (57). In the generally accepted model for the formation of F-centers there is an adsorption of alkali metal atoms to the crystal surface followed by the movement of a lattice halide ion to a position next to the metal atom producing a new crystal layer. Because of the stability of lithium fluoride crystals more energy is required to move the halide ion to the surface than in other alkali halides.

The transmission curve on Fig. 7 shows the effect of an evaporated film of lithium on the surface of a lithium fluoride crystal. Many samples (about 20) were treated in this way. Not all showed the complex three component structure with two resolved components at 210 and 240 m μ , together with a third (unresolved) component producing the inflection at about 290 m μ . Those which did not, exhibited either the two peaks at 210 and 240 m μ or a single broad absorption peak in the range 200 to 300 m μ .

As mentioned before a layer of silver was evaporated over the lithium layer to prevent the latter

from oxidizing when exposed to air. Also the lithium would not have remained on the crystal surface during heating if the silver had not been deposited. That some of the lithium is incorporated into the crystal lattice is evidenced by the curve shown on Fig. 7.

The possibility that the silver diffusing into the crystal caused absorption in the ultraviolet region of the spectrum was also explored. Fig. 8 shows a comparison of the transmission properties of a blank lithium fluoride crystal, a crystal on which lithium and silver were evaporated, and a crystal on which only silver was evaporated. The two treated crystals were heated together in the nickel tube and as a result each underwent the same treatment, except for the evaporated metal films. As seen in Fig. 8 the lithium treated crystal shows some structure at 210 and 240 μ while the silver treated crystal shows only slight absorption in the same region. This slight absorption could be due to silver ions being incorporated into the crystal lattice in much the same way as lithium atoms do when F-centers are formed. In this case the silver atoms would produce some F-centers. However, when lithium and a silver layer are both applied, the density of the silver would be much lower at the crystal surface and hence the probability of silver induced F-centers would be decreased.

FIG. 7

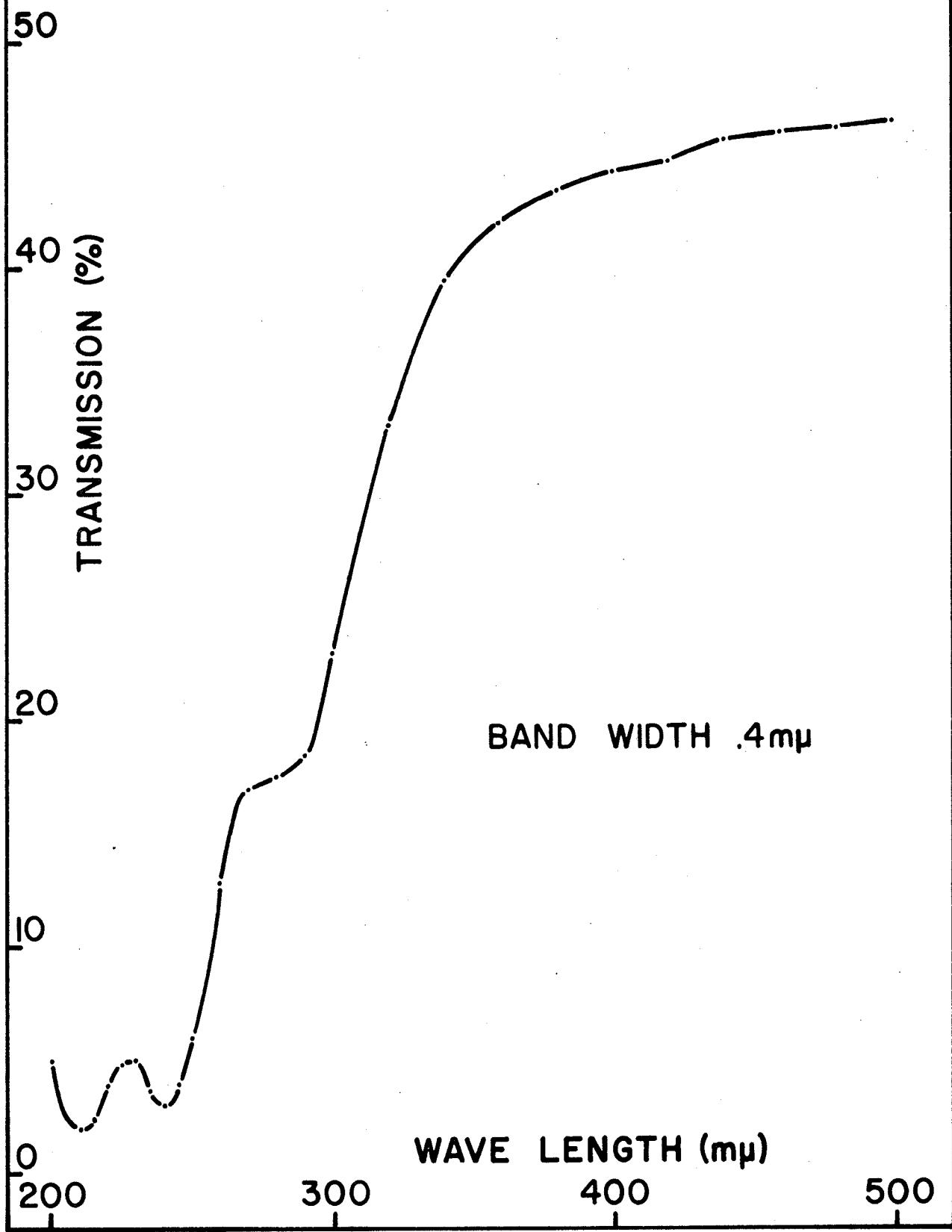
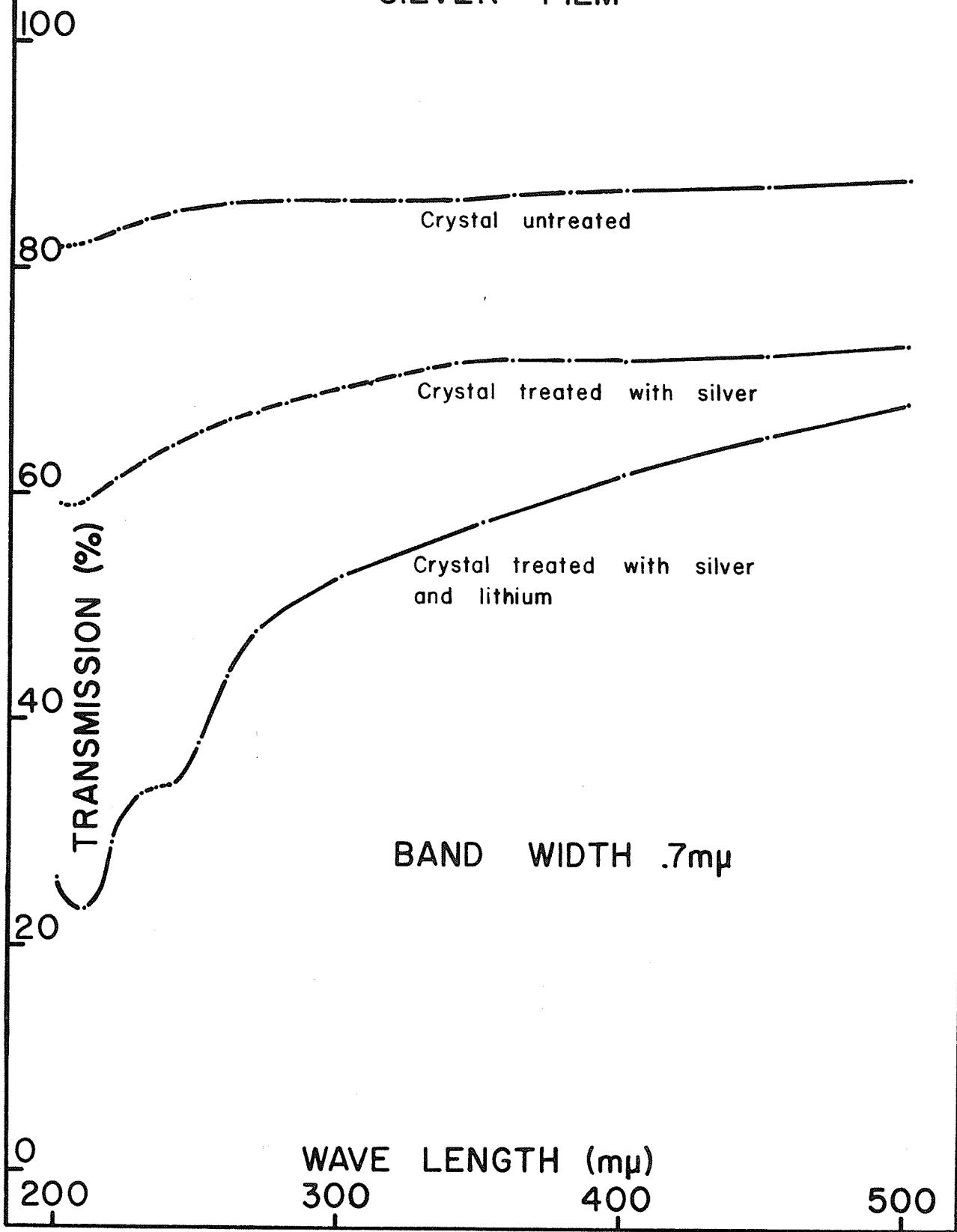
SPECTRAL TRANSMISSION OF SURFACE
TREATED LITHIUM FLUORIDE CRYSTAL

FIG. 8

EFFECT OF AN EVAPORATED
SILVER FILM



As seen in Fig. 8 some decrease in transmission is shown in the visible region of the spectrum even though it is not as pronounced as in the 250 m μ region. This decrease is due to surface reflection. The heat treatment scarred and pitted the crystal surface quite extensively. It was possible to polish the surface but as this would probably remove the F-centers at the crystal surface this was not done. The effect of polishing these lithium treated crystals will be discussed later.

As mentioned before the model for the formation of F-centers is the adsorption of an alkali metal atom on the crystal surface followed by the movement of a lattice halide ion to a position next to the metal atom producing a new crystal layer. The alkali atom is ionized and the electron is captured by a negative ion vacancy forming an F-center. The ionization energy of a potassium atom is 4.32 e.v. while that of a lithium atom is 5.36 e.v. Hence less energy is required to incorporate potassium into the crystal. This metal was deposited on the surface of a lithium fluoride crystal. When an attempt was made to deposit the silver layer, the heat from the molten metal caused the potassium on the crystal surface to melt. As a result the silver could not be deposited on top of the potassium.

Treating the lithium fluoride crystals by dropping them into a bath of molten lithium also produced an absorption band in the region from 200 m μ to 260 m μ . This is illustrated in Fig. 9. This spectrum is similar to the one on Fig. 7, but it shows less structure.

The transmission spectrum on Fig. 6 clearly shows the F absorption band at 250 m μ . Figs. 7, 8 and 9 shows absorption in this same region but no single clear band is in evidence. The structure occurring on Figs. 7 and 8 is also difficult to explain. An added proof to the existence of F-centers in our samples, a paramagnetic resonance study was undertaken. The results obtained are as shown in Fig. 10. In Fig. 10B is seen the resonance resulting from a sample of powdered lithium fluoride which had been x-irradiated for 20 hours. This resonance was clearly due to the intense F-band that had been produced by the x-rays. The absorption of microwave energy due to the F-center in LiF has been observed by other investigators (38-41). Fig. 10A shows the resonance observed using a lithium fluoride crystal which had been heated in molten lithium. The crystal surface was removed in powdered form to use as the sample in the resonance experiments. The position of the resonance in the latter case occurred at exactly the same magnetic field as that due to the F-center in the

FIG. 9

SPECTRAL TRANSMISSION OF LITHIUM
FLUORIDE CRYSTAL HEATED IN LITHIUM

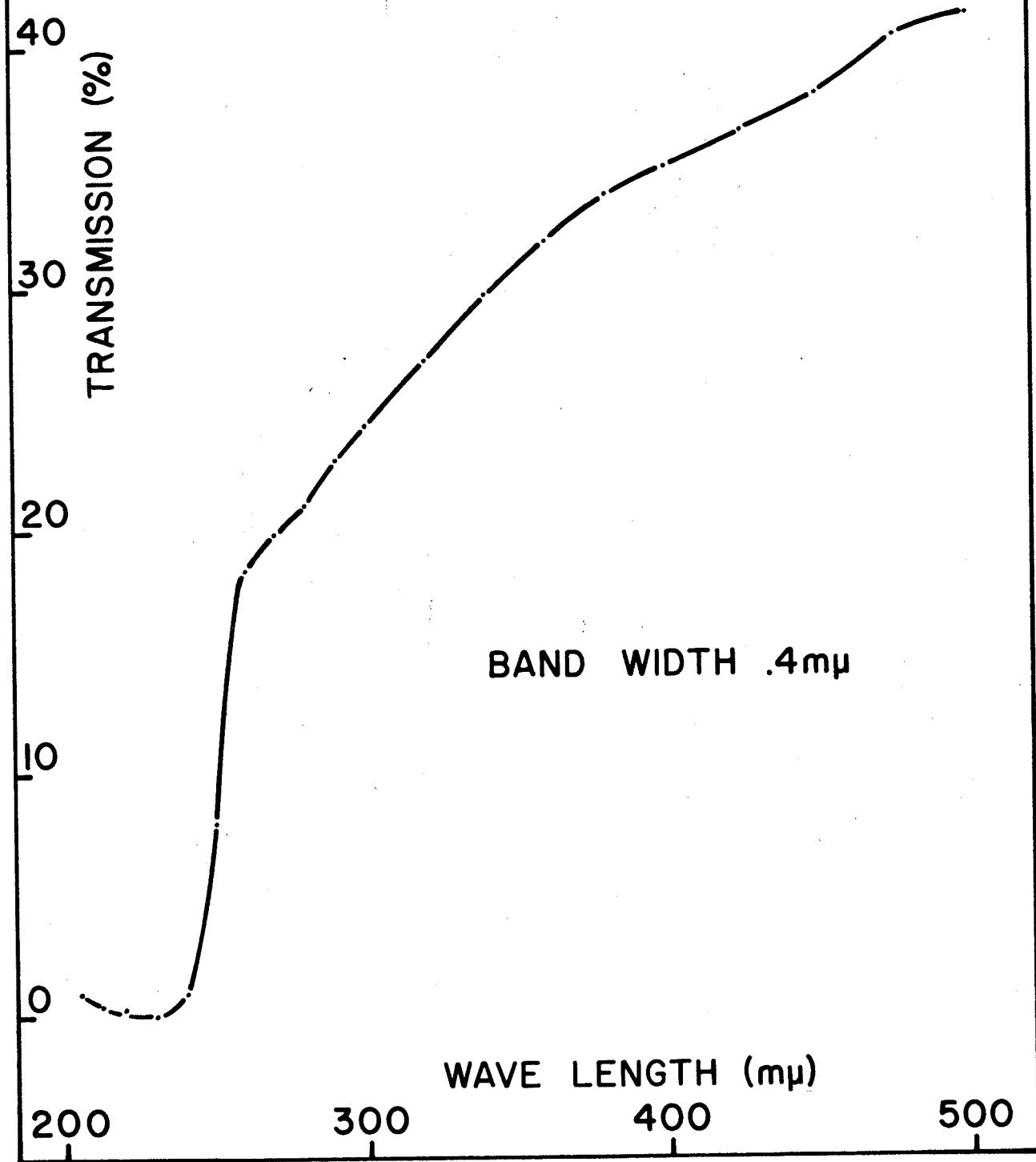


FIG. IOA

PARAMAGNETIC RESONANCE OF F-CENTERS
IN LITHIUM FLUORIDE CRYSTALS HEATED
IN MOLTEN LITHIUM FOR 45 MINUTES

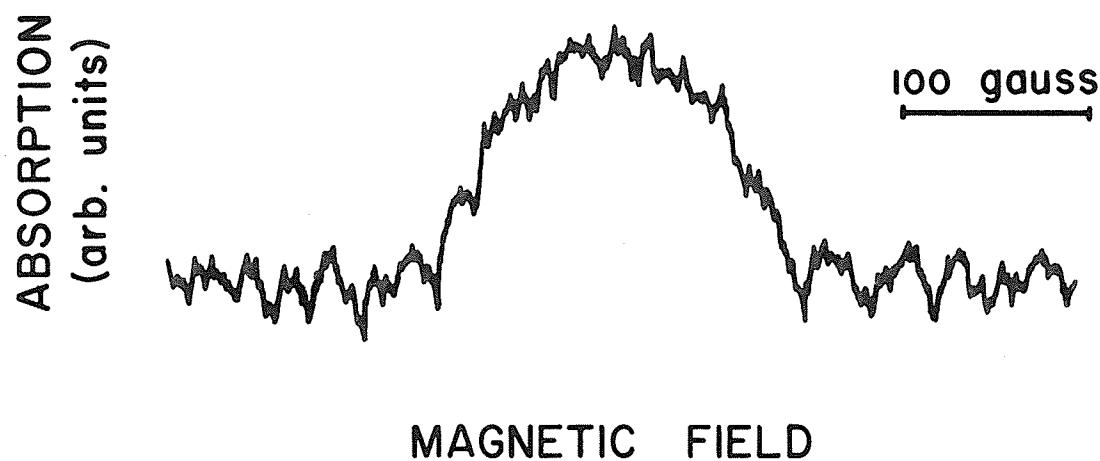
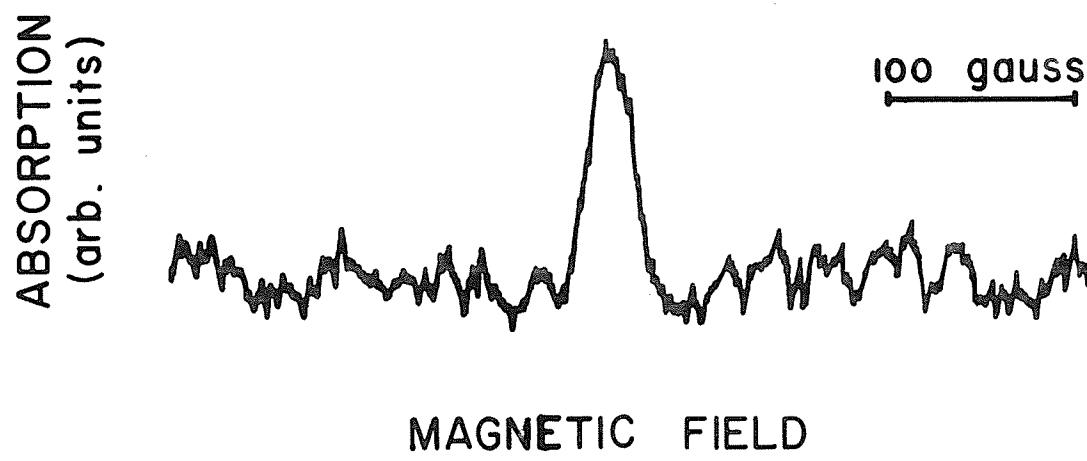


FIG. IOB

PARAMAGNETIC RESONANCE OF F-CENTERS
IN A LITHIUM FLUORIDE CRYSTAL
X-IRRADIATED FOR 18 HOURS



x-irradiated crystal. Fig. 10 shows that the width of the resonance line obtained using the crystals treated in molten lithium is greater than that obtained when the x-irradiated samples were used. This may be due to an interaction of the F-centers with one another in the lithium treated crystals. As seen on Fig. 9 the percentage transmission through these crystals is close to zero between 200 and 240 μm and since the color centers are situated near the crystal surface the density of the centers must be greater than in the x-irradiated crystals. Possibly the structure seen on Figs. 7 and 8 can also be attributed to this interaction of the centers. The fact that the F-centers occupy only a thin layer near the crystal surface was determined by removing small layers of material from the crystal and again checking the transmission spectrum. The thickness of the layer containing F-centers is approximately .002 inches.

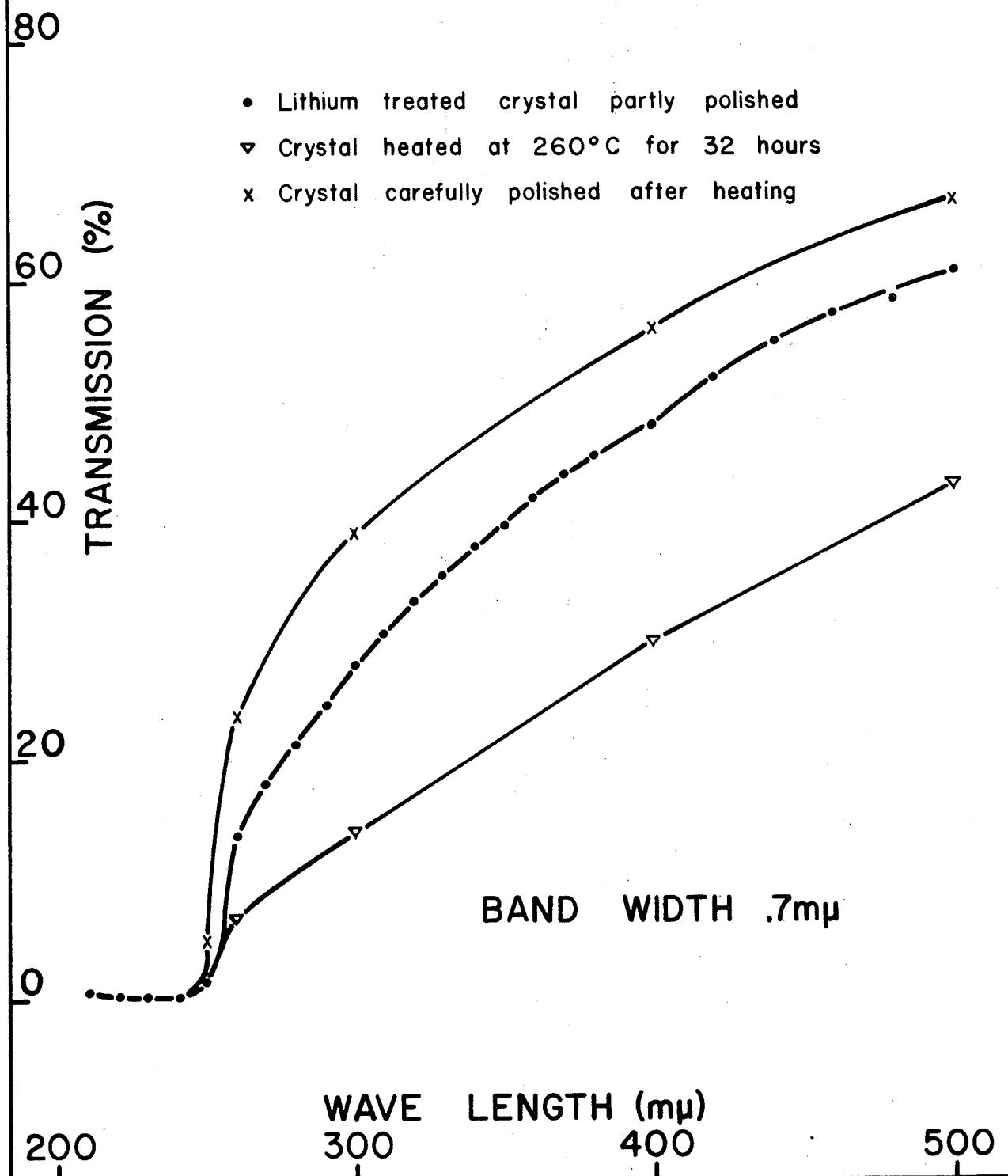
The appropriate number of F-centers in the x-irradiated LiF crystals can be determined by using Smakula's formula (14) as previously discussed. The F-center density in the crystal x-irradiated for 2 hours whose transmission spectrum is shown in Fig. 6 was found to be $3.6 \pm .6 \times 10^{17}$ per cm^3 , assuming a uniform distribution

of centers throughout the crystal volume. In actual fact the density will be higher near the surface of the crystal that was exposed to the x-ray source. It is very difficult to estimate the number of F-centers in the crystals heated in molten lithium since a well defined band is not present. However, due to the fact that the transmission is essentially zero from 200 to 240 m μ and since the F-centers are concentrated in a surface layer .002 inches thick, it can be concluded that the F-center density near the surface is substantially higher than that in the x-irradiated crystals. In crystals treated with a surface layer of lithium the number of F-centers will be less than in those heated in molten lithium. This is indicated by a higher transmission of light in the 250 m μ region. But the F-center density will probably be greater than 10^{17} per cm 3 because they occupy only a thin layer near the crystal surface.

Additively colored crystals exhibit much more resistance to bleaching than do x-irradiated crystals. The effect of heat bleaching on the F-centers in a lithium fluoride crystal heated in molten lithium is shown in Fig. 11. Heating for 32 hours at 260°C did not affect the absorption between 200 and 250 m μ . The remaining region of the spectrum is marked by a lower transmission but this was changed quite easily by polishing the crystal surface.

FIG. II

EFFECT OF HEATING ON THE TRANSMISSION
PROPERTIES OF LITHIUM FLUORIDE
CRYSTALS HEATED IN MOLTEN LITHIUM



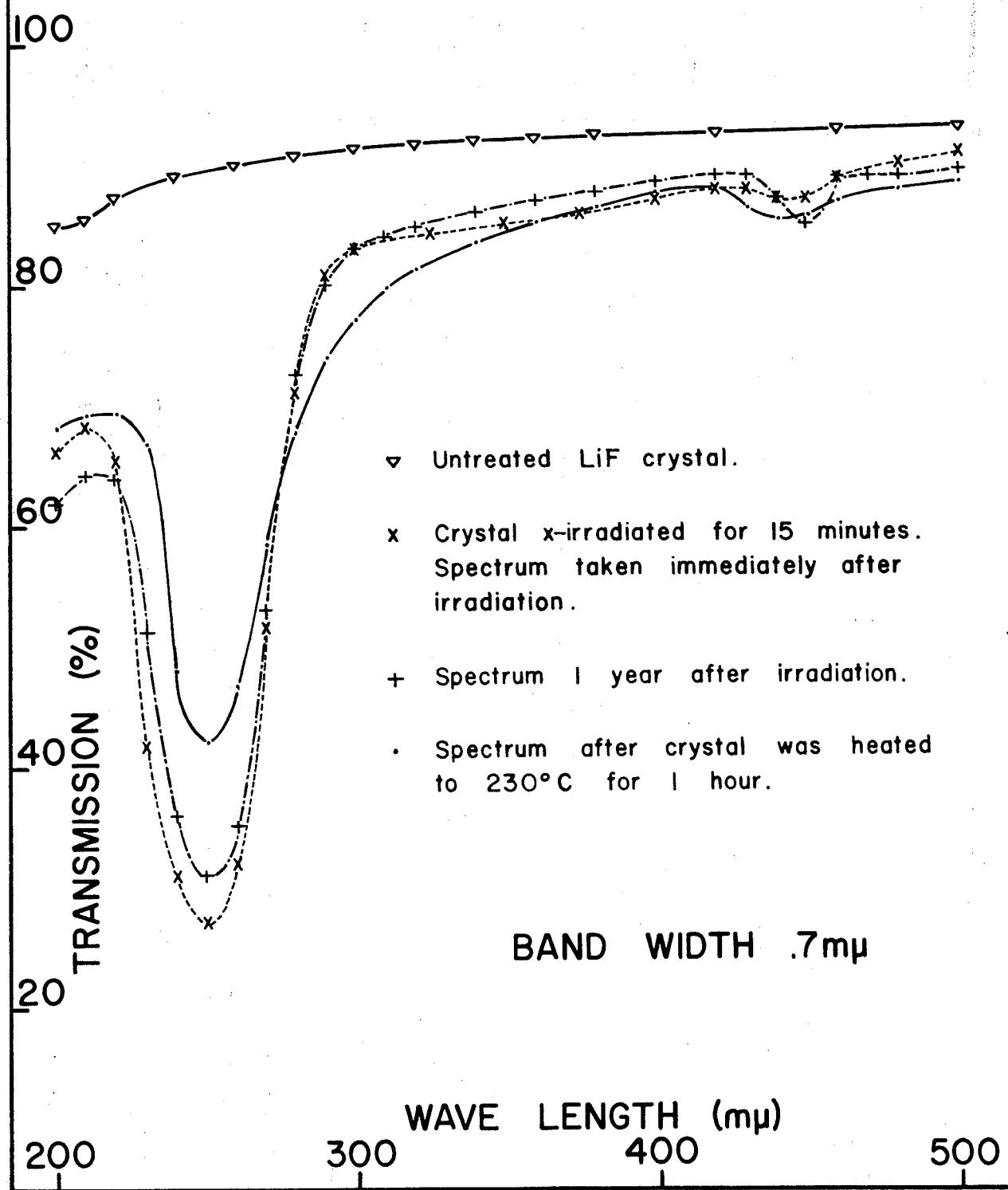
It seems that the heat has not bleached out any F-centers but has merely clouded the surface slightly. More careful polishing of the crystal after heating is the reason the transmission is higher than before the heat treatment.

On the other hand, heat bleaching x-irradiated crystals produces a marked decrease in the number of F-centers present. This is illustrated by the transmission curves shown in Fig. 12. Allowing the crystals to be exposed to sunlight during the daytime for about \sim 1 year produced an increase of 4 ± 1 percent, i.e. from 26% to 30%, in the transmission at the center of the F-band. Heating the crystal for 1 hour at 230°C produced an increase of 11 percent, i.e. from 30% to 41% at 250 m μ . As a crude approximation it can be stated that 1 hour of heating at 230°C is equivalent to allowing the crystal to stand exposed in the laboratory for 2 years. Hence heating the crystal for 32 hours would approximately be equivalent to 60 years. Applying this to the results shown on Fig. 11, it is seen that 60 years of exposure in a laboratory will probably produce no observable decrease in the F-center density of lithium fluoride crystals heated in molten lithium.

The fact that the lithium treated crystals do not bleach as easily as do x-irradiated crystals may be of some practical importance. Such crystals could be used as filters (53) in the 250 m μ region. For example one could filter out the 254 m μ line in the Hg spectrum but pass the 365 m μ line. Due to limitations in the apparatus used the transmission spectrum below 200 m μ could not be examined. Hence it is not known what properties such a filter would have in this region.

FIG. 12

EFFECT OF HEATING ON THE TRANSMISSION
PROPERTIES OF X-IRRADIATED
LITHIUM FLUORIDE CRYSTALS



CONCLUSIONS

The evidence from the absorption spectra and electron spin resonance data suggests that we have succeeded in producing the F absorption band in LiF single crystals arising from stoichiometric excess of lithium. This in turn provides additional evidence that the F absorption band arises from the presence of negative ion vacancies and associated electrons. The F-band produced in this way has been shown to be much more stable against high temperatures than that produced by x-irradiation. This is of some practical importance since it could possibly be used as a filter. The structure shown in some of the transmission spectra and the unusual width of the electron spin resonance line suggests some interaction between the F-centers in the prepared samples. This is supported by the fact that the F-center density is substantially higher in the crystals treated in molten lithium than in the x-irradiated crystal.

REFERENCES

1. E. Goldstein, Zeits. f. Instrumentkunde 16, 211 (1896).
2. R. W. Pohl, Physik Seits 39, 36 (1938).
3. R. W. Pohl, Proceedings of the Physical Society 49, 3 (1937).
4. F. Seitz, Reviews of Modern Physics 18, 384 (1946).
5. F. Seitz, Reviews of Modern Physics 26, 7 (1954).
6. N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals, (Oxford University Press, New York, 1940).
7. F. Seitz, Modern Theory of Solids (McGraw-Hill Book Company, Inc., New York, 1940).
8. J. H. deBoer, Recueil des Trav. Chim d. Pays-Bas 56, 301 (1937).
9. J. P. Molnar (unpublished work). Ph.D. Thesis, Mass. Inst. Tech., 1940.
10. E. Mollwo, Ann. d. Physik 29, 394 (1937).
11. R. S. Knox, Phys. Rev. Letters, 2, 87 (1959).
12. C. Z. VanDoorn and Y. Haven, Philips Res. Report 11, 479-488 (1956).
13. F. G. Kleinschrod, Ann. d. Physik 27, 97 (1936).
14. A. Smakula, Zeits. f. Physik 59, 603 (1930).
15. H. Pick, Ann. d. Physik 31, 365 (1938).

16. Delbecq, Pringsheim, and Yuster, J. Chem. Phys.
19, 574 (1951),
20, 746 (1952).
17. G. Glaser and W. Lehfeldt, Gottinger Nachrichten 2,
91 (1936).
G. Glaser, ibid. 3, 31 (1937).
18. S. Petroff, Z. Physik 127, 443 (1950).
19. E. Burstein and J. J. Oberly, Phys. Rev. 76, 1254 (1949),
79, 903 (1950).
20. A. B. Scott and L. P. Bupp, Phys. Rev. 79, 341 (1950).
21. M. Savostianova, Z. Physik 64, 262 (1930).
22. K. Przibram, Sitzber, Akad. Wiss. Wien 135, 202 (1926).
23. Casler, Pringsheim and Yuster, J. Chem. Phys. 18, 887,
1564 (1950).
24. E. E. Schneider, Photographic Sensitivity (Butterworth
Scientific Publication, London, 1951) p. 13.
25. G. Wannier, Phys. Rev. 76, 438 (1949).
26. J. J. Oberly and E. Burstein, Phys. Rev. 79, 217 (1950).
J. J. Oberly, Phys. Rev. 83, 228 (1951); 84, 1257 (1951).
27. J. Alexander and E. E. Schneider, Nature 164, 653
(1949).
28. Estermann, Leivo, and Stern, Phys. Rev. 75, 627 (1949).
29. L. Lin, Phys. Rev. 102, 968 (1956).
30. Primak, Delbecq, and Yuster, Phys. Rev. 98, 1708 (1955).

31. D. A. Wiegand and R. Smoluchowski, Phys. Rev. 110, 991 (1958).
32. C. R. Berry, Phys. Rev. 98, 934 (1955).
33. P. G. Harrison, J. of Chem. Phys. 37, 388 (1962).
34. R. B. Gordon and A. S. Nowick, Phys. Rev. 101, 977 (1956).
35. A. S. Nowick, Phys. Rev. 111, 16 (1959).
36. P. V. Mitchel, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. 121, 484 (1961).
37. H. Rabin and C. C. Klick, Phys. Rev. 117, 1005 (1960).
38. C. A. Hutchinson, Phys. Rev. 75, 1769 (1949).
39. C. A. Hutchinson and G. A. Noble, Phys. Rev. 87, 1125 (1952).
40. A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, Phys. Rev. 91, 1066 (1953).
41. N. W. Lord, Phys. Rev. 105, 756 (1957).
42. G. Feher, Phys. Rev. 105, 1122 (1957).
43. N. W. Lord, Phys. Rev. Letters 1, 170 (1958).
44. W. C. Holton, H. Blum, and C. P. Slichter, Phys. Rev. Letters 5, 197 (1960).
45. W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids 5, 328 (1958).
46. C. J. Rauch and C. V. Heer, Phys. Rev. 105, 914 (1957).
47. P. Avakian and A. Smakula, Phys. Rev. 120, 2007 (1960).
48. H. Rabin and J. H. Schulman, Phys. Rev. Letters 4, 280 (1960).

49. P. Pringsheim and P. H. Yuster, Phys. Rev. 78, 293 (1950).
50. C. J. Delbecq and P. Pringsheim, J. of Chem. Phys. 21, 794 (1953).
51. C. Z. vanDoorn, The Review of Scientific Instruments 32, No. 6, 755 (1961).
52. M. Born and Kun Huang, Dynamical Theory of Crystal Lattices, P. 26.
53. J. L. Weeks, S. Gordon, G.M.A.C. Meaburn, Nature 191, 1186 (1961).