EXPERIMENTAL INVESTIGATION OF THE ADDITIVE

COLOURATION PROCESS IN LITHIUM FLUORIDE

A Thesis submitted to

the Faculty of Graduate Studies

in partial fulfilment of the

requirements for the degree of

Master of Science

By

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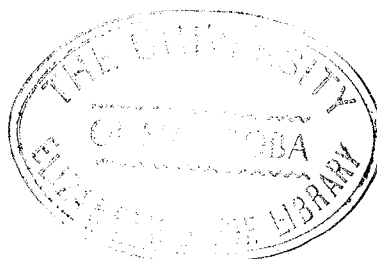

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ACKNOWLEDGEMENTS

ABSTRACT

The additive colouration process in lithium
fluoride was investigated using an evaporation technique.
The results showed that it was not possible to identify
the F band. From these experiments it must be concluded
that the activation energy for the diffusion of fluorine
ions is high enough to prohibit the bulk colouration of
lithium fluoride. Evidence indicates some absorption by
the surface of the treated crystals.

CHAPTER ONE

Introduction to the Field of Colour Centres

For over a century physicists have been interested in the phenomenon whereby colourless crystals become coloured after various treatments. Rose (1863) observed that by incorporating potassium into a crystal of potassium chloride he could produce a coloured crystal. Since that time many new ways have been found of producing such colourations, and the study of these so called "colour centres" has become a major field in solid state physics. This field, which grew out of curiosity to know what produced the coloured crystals, has now developed into a useful method for the study of basic properties of solids. Indeed, they exhibit a whole range of solid state phenomena allowing studies of such things as excitons, electrons and holes, vacant lattice sites, dislocations, impurity atoms and localised modes.

However it was only in the present century that knowledge about colour centres became quantitative rather than qualitative. The early work was conducted at Vienna under Przibram (1924) and at Göttingen under Pohl (1937). Indeed it was Pohl who introduced the term "colour centre". By a "colour centre", one means an imperfection in a crystal that produces an absorption of light due to some electronic transition associated with the centre. The basic use of such a centre is to study the interaction

between the imperfection and the pure crystal lattice in order to understand the electronic processes in solids themselves.

The basic material used in the study of colour centres is the alkali halide crystal. These crystals offer a unique medium for the study of crystalline imperfections since their structure is simple, both in their lattice configuration and in their electronic structure. The lattice structure of the alkali halides can be classified into two types. These are the so called sodium chloride structure and the cesium chloride structure.

The sodium chloride structure (Figure 1a) has each cation surrounded by six nearest-neighbour anions, and each anion is surrounded by six nearest-neighbour cations. Since the lattice is cubic this arrangement means that the lattice structure is face-centred cubic. Most of the alkali halides possess the sodium chloride structure. A few crystallise so that each cation has eight nearest-neighbour anions and conversely. This is the cesium chloride structure (Figure 1b). The lattice structure is simple cubic. For both these lattice structures the electronic structure is basically the same. The alkali metal, which is a Group I element, possesses a single s-electron outside a closed shell. Thus the binding of this electron is quite weak. The halogen is a Group VII element, and consequently posesses an outer shell of electrons which is one electron short of being completely filled. The alkali metal can be said to have a valence of + 1 and the halogen a valence of - 1. When

Fig. 1
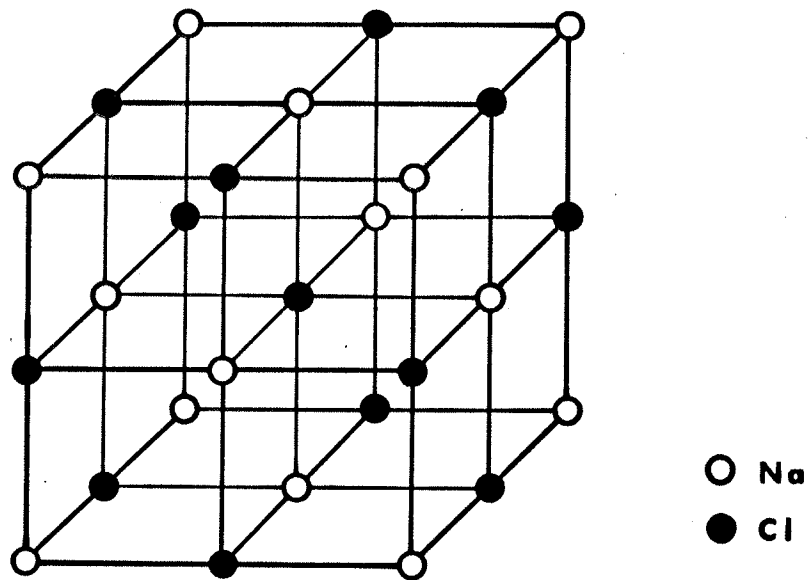
(a) Lattice Structure of NaCl type Alkali Halide

○ Na
● Cl
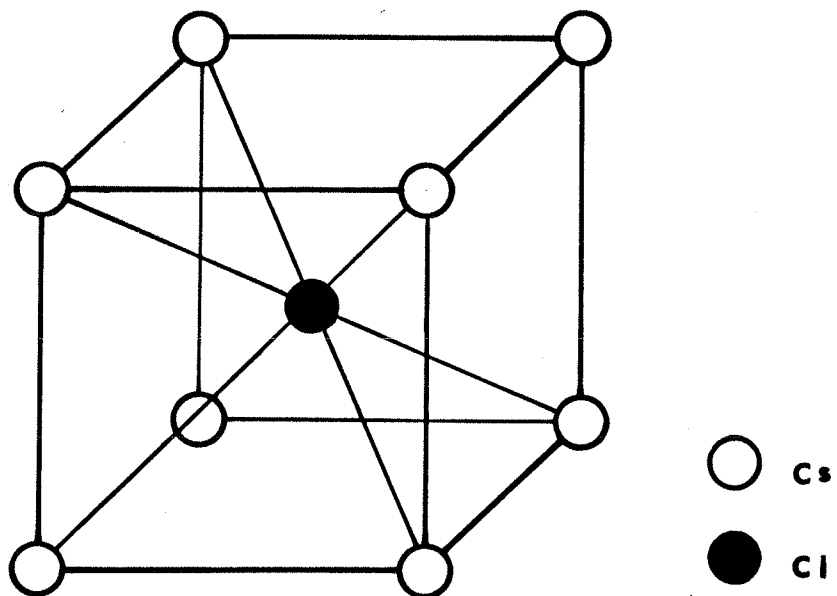
(b) Lattice Structure of CsCl type Alkali Halide

○ Cs
● Cl

the two are combined to form an alkali halide crystal the s-electron of the alkali metal is lost to the halogen so that it completes its outer shell, leaving them both with filled outer shells. The alkali ion has a net positive charge, the cation, and the halogen ion has a net negative charge, the anion. The electrostatic attraction between these ions provides the binding energy of the crystal. All electrons in the crystal are now tightly bound and thus none are present to give electronic conduction. This position may be stated by using the band theory of solids by saying the alkali halides possess a filled valence band and an empty conduction band with a large gap between the two. Because of this alkali halide crystals are insulators and transparent, with only high temperature ionic conduction. With such a structure, alkali halides offer unique opportunities for a complete understanding of their properties.

There are three main methods for producing colour centres in the alkali halides. These are :- additive colouration, the addition to the crystal of either excess alkali metal or excess halogen; electrolytic colouration, by passing an electric current through the crystal such that ionic conductivity takes place; ionising radiation, irradiating the crystal with X-rays, γ-rays, electrons etc. These methods all produce a variety of absorption bands, each one designated by a letter, e.g. F, F', M, R, N and V bands. Each of these bands is thought to be produced by separate centres. A basic problem is to produce models for these centres which will satisfy the properties of

the centres and provide information about their interaction
with the crystal lattice.

The main centre is the F centre or Farbzentren which is
the absorbing centre easiest to produce. It is produced alone
by the additive colouration process. The alkali halide crystal
is heated to a high temperature in the vapour of the alkali
metal and then rapidly quenched to room temperature. This is
illustrated in Figure 2 where the alkali metal finds a normal
cation position and anions diffuse out from the crystal to form
a new layer of the crystal. The electrons move into the crystal
and are trapped at anion vacancies to form F centres. The F
band produced in this way is a simple bell-shaped absorption
band whose spectral position and width depend upon the nature of the
alkali halide and upon the temperature. An accurate empirical
relation was proposed by Ivey (1947) for the position of the F
band at room temperature. He found

$$\lambda = 703d^{1.84}$$

where λ is the peak position measured in Ångström units and d
is the lattice constant of the particular alkali halide in
Ångström units. This relation holds true for alkali halides of
the NaCl structure and indicates that the lattice constant is
the prime factor for determining spectral position at a given
temperature. This is further verified by the fact that for a
particular alkali halide, additive colouration with any alkali
metal produces the same absorption band. One realises that the
properties of the F centre are mainly given by the lattice.
They are proper lattice imperfections.

Fig. 2
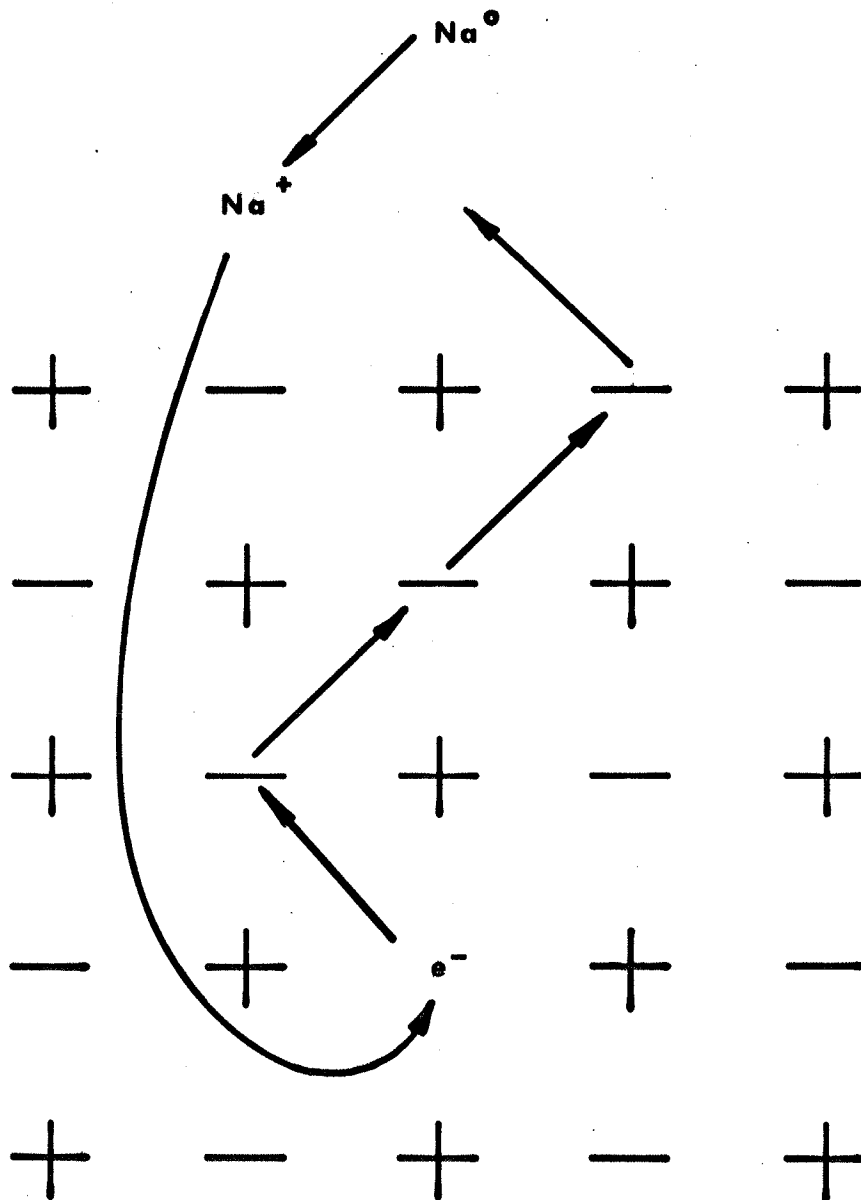
Formation of F-centres by
Additive Colouration

A model for the F centre was proposed by de Boer (1937) and this model has survived the theoretical and experimental tests and is now recognised as being correct. de Boer proposed that the F centre consists of an electron trapped at a halogen ion vacancy and is illustrated in Figure 3a. This model indicates that it is mainly the lattice around the halogen ion vacancy that will influence the behaviour of the electron, which agrees with experiment.

The physical properties of the F centre are determined by the interaction of the trapped electron with the lattice ions, and so this interaction must be theoretically known before the properties of the centre can be predicted. However a complete knowledge of the interaction involves all the ions in the crystal and is thus impossible. So theoretical approaches are characterized by the approximations made. These approximations vary from only considering long range interactions, the continuum approximations, to those only considering the interaction of the electron with the six nearest-neighbours. In the former approximation Pekar (1950, 1952) produced excellent results for NaCl, KCl, KBr and KI, while in the latter approximation Kojima (1957) made excellent calculations concerning LiF. With such good agreement from such differing theories it is obvious that theoretical problems have not been satisfactorily solved and that present theories are insensitive to experimental tests.

Fig. 3
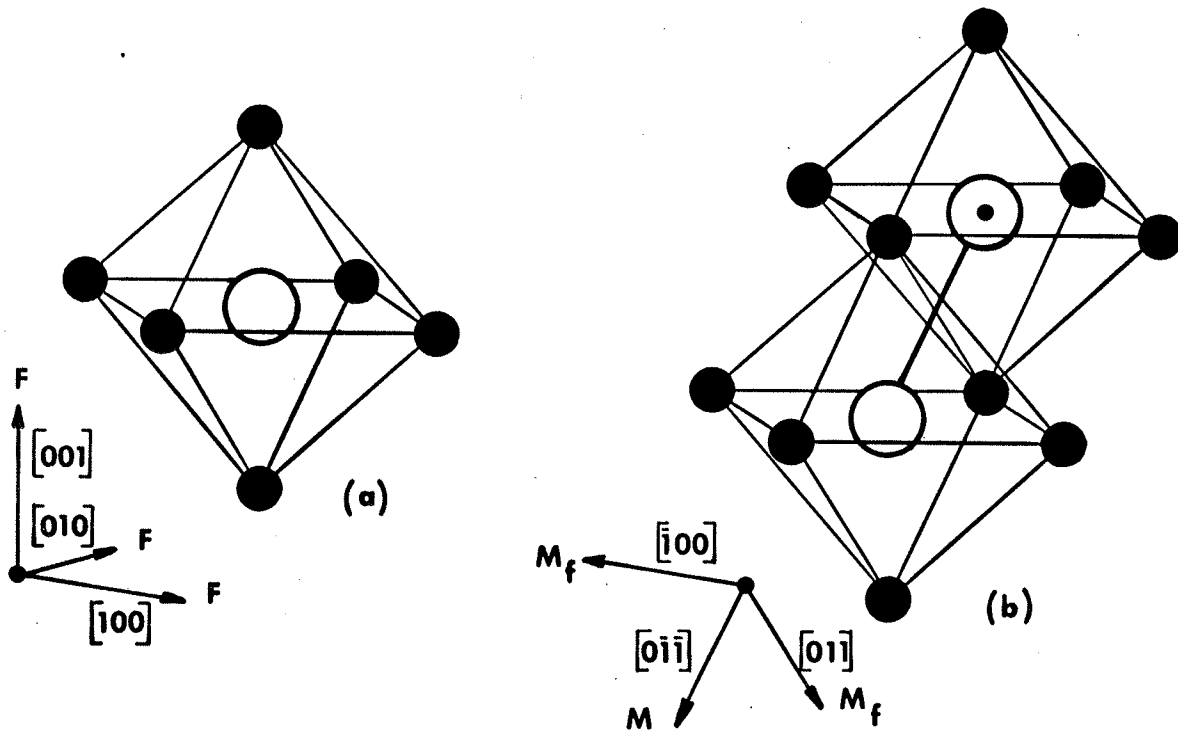
Transition moments of the electrons are shown
The centres of the coordinate axes are indicated by dots.
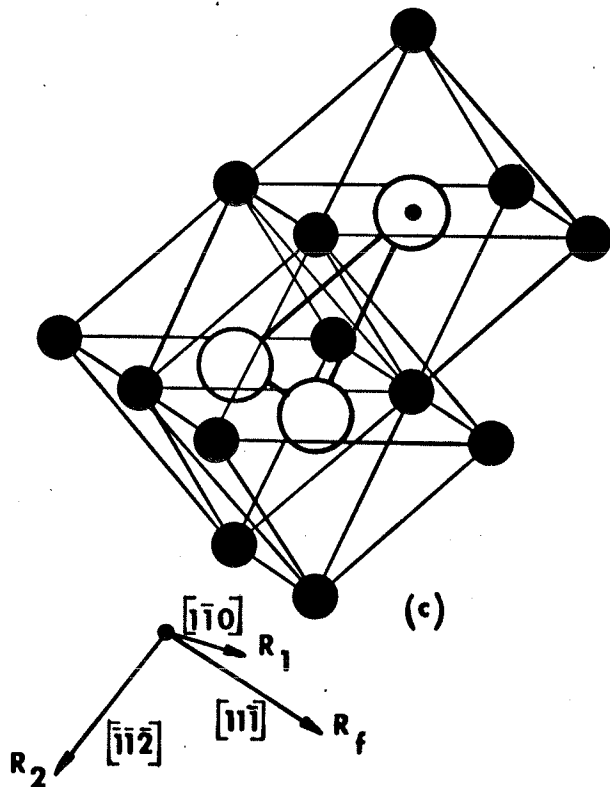
(a) The model of the F centre. A halogen ion vacancy with a trapped electron.

(b) The model of the M centre. Two adjacent halogen ion vacancies with two electrons.

(c) The model of the R centre. Three neighbouring halogen ion vacancies with three electrons.

The transition which has been characterised as the F band absorption is a 1s → 2p transition. Now from the proposed model of the F centre, it is theoretically possible that there are higher transitions that could be observed as absorption bands on the high energy side of the F band. If one studies the F band with good resolution then there is a noticeable tail at higher energies. Lüty (1960) performed a systematic study of the high energy side of the F band of face-centred cubic alkali halide crystals and established that four observable bands were indeed transitions of the F centre electron. These bands had been designated K, L_1, L_2 and L_3 bands but are all transitions of the F centre electron.

The problem of what happened to the F centre as it returned to the ground state was the source of much experimental work. Finally Botden, van Doorn and Haven (1954) showed that if crystals were additively coloured and immediately taken to low temperatures and kept in the dark, then F centre luminescence did occur. The reason that earlier work by Klick (1950, 1954) did not produce similar results was attributed to new centres being produced and acting as "poisons" for the F centre luminescence. The observation of their luminescence allowed Russell and Klick (1956) to produce very elegant models for the F centre in the form of configuration coordinate curves.

The configuration coordinate model, introduced by von Hippel (1936) and Seitz (1939), only considers the interaction of the trapped electron with the six nearest-neighbour ions.

Indeed the centre is considered to be the electron, the vacancy and the six ions and this total entity is treated quantum mechanically as a harmonic oscillator. In this system the strongest effect upon the energy of the centre will be when the six nearest-neighbour ions are moving radially in phase. The parameter that measures the displacement of the ions from equilibrium is called a configuration coordinate and since the centre is symmetrical only one coordinate is needed. For small displacements (i.e. to a first approximation) the potential energy of the system varies quadratically with the magnitude of the displacement. Thus a plot of the potential energy of the ground state as a function of the configuration coordinate is a parabola as shown in Figure 4. Absorption of a photon by the centre raises it to the excited state and the average electronic distribution alters. Thus after sufficient time the ions move to a new equilibrium position and a plot of the potential energy of this state is shown as the upper curve in Figure 4.

Now when an optical absorption takes place the Franck-Condon principle states that the electronic transition occurs in a time too short for the ions to move. Consequently an absorption can be represented in energy by a vertical change from point A to point B. While in the excited state the ions can then readjust and the centre loses energy in the form of lattice vibrations until it is at the equilibrium point C. The system can then return to the ground state by changing from point

Fig. 4

Configuration Coordinate Diagram

Excited State

Ground State

Total Energy

Configuration Coordinate

A B C D E
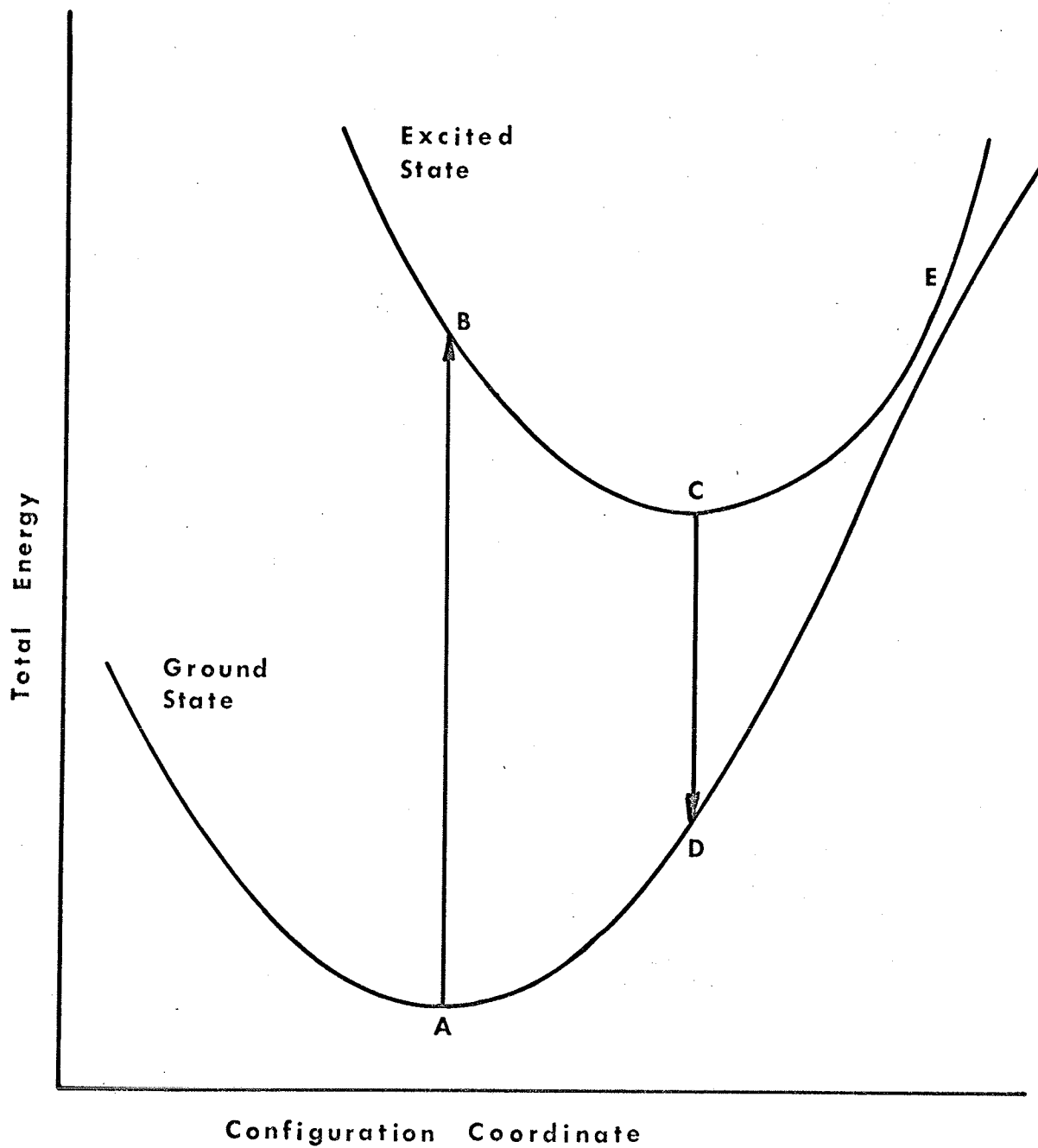
C to point D and emitting that amount of energy as a photon.
The system then loses energy as it relaxes from point D to
point A, this energy being lost in the form of heat i.e. lattice
vibrations. It can be seen that if the temperature is high
enough, the system could have sufficient energy to reach point
E in the excited state and decay to the ground state by a
radiationless transition, with the energy being lost as heat.
Experiments show that this does occur at high temperatures.
Calculations of the widths of the absorption and emission bands
using this model were made by Russell and Klick (1956) and were
found to be in reasonable agreement with experiment.

There are also two other absorption bands produced in
crystals containing F centres. Delbecq, Pringsheim and Yuster
(1951, 1952) were investigating the fundamental ultra violet
absorption bands, produced by exciton formation and electronic
transitions between valence and conduction bands, when they
found a new absorption band designated the β-band. This band
is a perturbation of the fundamental absorption of the crystal
due to the presence of an F centre, rather than a direct
transition of the F centre. Another band designated the α-band,
could be produced in additively coloured crystals by irradiating
in the F band. The same band was also produced at low temperatures
by ionising radiation and thus it was explained as a perturbation
of the lattice absorption due to negative ion vacancies. These
bands have been theoretically investigated by Bassani and
Inchauspé (1957) using normal theory of excitons.

If a crystal containing F centres is irradiated with light which is absorbed in the F band, then a broad absorption band is produced on the low energy side of the F band. The formation of this band causes a decrease in the absorption of the F band. This new band is known as the F' band and it is not thermally stable, indeed the F light irradiation must be performed at low temperatures. Even so the band fades away even in the dark and the F band is regenerated. This reversible process thus leads to an equilibrium between the two bands. From experiments by Pohl (1937) on the photoconductivity of additively coloured alkali halides, it was shown that illumination in the F band allowed the trapped electrons to move into the conduction band by thermal excitation from the excited state. These could then be trapped by a halogen ion vacancy, giving an F centre, or else be trapped by an F centre. In other words a centre was produced that consisted of two electrons trapped at a halogen ion vacancy. This is the F' centre. Pick (1958) investigated the equilibrium between F and F' centres as a function of temperature and he showed that two F centres were destroyed to form one F' centre and the destruction of one F' centre gave two F centres. This gave good evidence that the model for the F' centre is correct.

Our consideration so far has been essentially concerned with additively coloured crystals. By using ionising radiation the F band is again produced but with prolonged irradiation a multitude of other bands are also produced at lower energies than

the F band. They are also produced by prolonged irradiation
by F light in additively coloured crystals and they are denoted
M, R_1, R_2, N_1 and N_2 bands. These bands have been described
over the years in two review articles by Seitz (1946, 1954).
They were thought to be produced by centres consisting of F
centres combined with vacancies and the original models were
proposed by Seitz (1946). However van Doorn and Haven (1956,
1957) speculated that these models were essentially incorrect,
and measurements by van Doorn (1960) indicated that the
bleaching of two F centres created one M centre. Thus they
proposed that the M centre was simply two adjacent F centres,
as shown in Figure 3b. This was the model Seitz proposed for
the R_2 centre. This proposal that F centres could aggregate
together was enlarged by Pick (1960). He proposed that, besides
M centres being two adjacent F centres, R centres consist of
three F centres (Figure 3c) and N centres consist of four F
centres (Figure 5a and 5b). According to this theory the R_1
and R_2 bands are not produced by separate centres but by the
same centre which has different optical transition moments in
different directions. The two absorption bands labelled N_1 and
N_2 can be explained by the fact that there are two ways in which
four adjacent F centres can be arranged as illustrated in
Figures 5a and 5b. These two arrangements will give slightly
different absorption bands. Apart from explaining these bands,
the models indicate certain transitions in the aggregate centres
that should be like the transitions within the F centre and these

Fig. 5
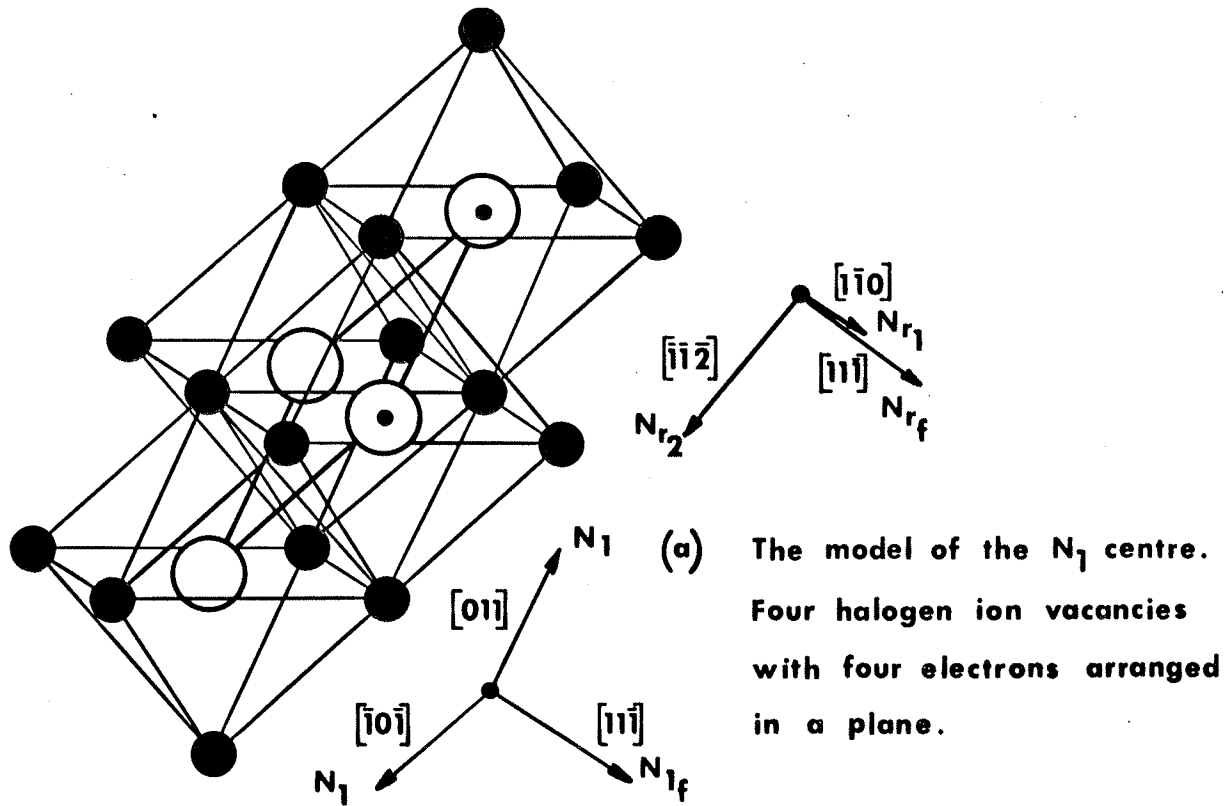
(a) The model of the N_1 centre.
Four halogen ion vacancies
with four electrons arranged
in a plane.

Transition moments of the electrons are shown
The centres of the coordinate axes are indicated by dots.

(b) The model of the N_2 centre
Four halogen ion vacancies
with four electrons arranged
in a tetrahedron.
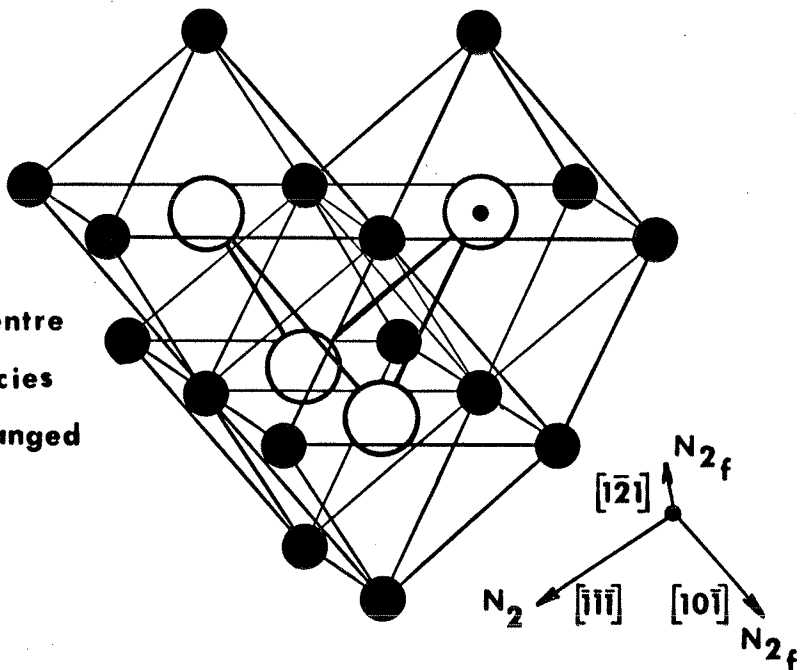
are labelled with a subscript f in Figures 3 and 5. This
explains certain problems thought to be associated with "hidden
bands" under the F band. Since these other centres, especially
the M centre, luminesce even at room temperature, then irradia-
tion in the F band also excites the aggregate centres and their
emission is the one which predominates. Thus with aggregate
centres present in a crystal most luminescence comes from these
centres rather than the F centre and they are said to act as a
"poison" for the F centre luminescence. In any case these models
are now the accepted ones for the M, R and N centres although
experimental verification is still being made in the cases of
R and N centres.

Besides these aggregates of F centres it is possible to
colour alkali halides by imperfections having much larger
dimensions. These are attributed to colloidal particles of
both alkali metal and halogens. Natural rock salt is often
found to be coloured blue. Studies of this absorption by
Gyulai (1935) indicated it was not due to F centres or aggregate
centres. In general light attenuation by colloidal particles is
due both to normal absorption and Tyndall scattering. Siedentopf
(1905) showed that colloidal centres were produced in NaCl that
had been additively coloured and then heat treated. Colloidal
particles that are of greatest interest are the "non-scattering"
colloids which are small enough to produce no Tyndall scattering
but just pure optical absorption. The main investigators of
these centres, Scott and Smith (1951, 1953), showed that it is

possible to produce the band by irradiating in the F band. Exact identification of the centre has not been possible, although the most accepted view is that they are small colloidal particles.

The centres discussed so far have been of the type known as electron-excess centres. There are other centres known as trapped hole centres. These may be introduced by additive colouration with a stoichiometric excess of halogen or by using high-energy irradiation. Mollwo (1935, 1937) performed extensive investigations using additively coloured crystals and found two bands subsequently labelled the V_2 and V_3 bands. A study of this spectral region was made with irradiated crystals and showed the V_2 and V_3 bands. Irradiation at low temperatures produced another band, known as the V_1 band, and temperature changes gave rise to another band, the V_4 band. A summary of these bands is given by Dorendorf (1950). Further investigation by Duerig and Markham (1952) indicated another band, the H band. Investigation of these bands by optical means presented a very confused picture. Models were proposed for these centres and those of Seitz (1946, 1950, 1954), based upon an analogy with the trapped electron centres, stimulated much research.

The first of these trapped hole centres to be properly understood was an entirely new band. Electron spin resonance studies by Känzig (1955) of a V centre turned out to be due to none of the previously observed bands. Delbecq, Smaller and

Yuster (1958) combining optical and resonance studies identified
it as a new band and the centre responsible was named the V_K
centre. The resonance data gave enough information for Castner,
Känzig and Woodruff (1957, 1958) to show that the V_K centre is
a halogen molecule-ion, X_2^-, orientated along the $<110>$ axes of
the crystal as shown in Figure 6. The centre is a kind of
self trapped hole, and the trapping appears to involve a
molecular bond. In other words it is formed by the loss of
an electron from a halogen ion, followed by the pulling together
of the resulting atom with an adjacent normal halogen ion.
Since the centre has a definite orientation many experiments
were performed by Delbecq et al. (1958) using polarized light
showing how the centre could be reorientated.

Reorientation experiments were performed by Compton and
Klick (1958) on the H centre and these indicated that all
previous models were incorrect. Paramagnetic resonance studies
by Känzig and Woodruff (1958) confirmed these results and
allowed them to derive a model for the H centre. Their resonance
studies showed that four halide nuclei were involved in the
centre and that all lie along a $<110>$ direction in the crystal.
These four nuclei are in the form of three ions and one neutral
atom, i.e. $X_4^{\equiv}$, all adjacent and occupying the position of three
ions as shown in Figure 6b.

Little knowledge has been gleaned from resonance and
optical studies about the nature of the other V centres. Extend-
ing the idea of halogen molecule models, Hersh (1965) used a

Fig. 6
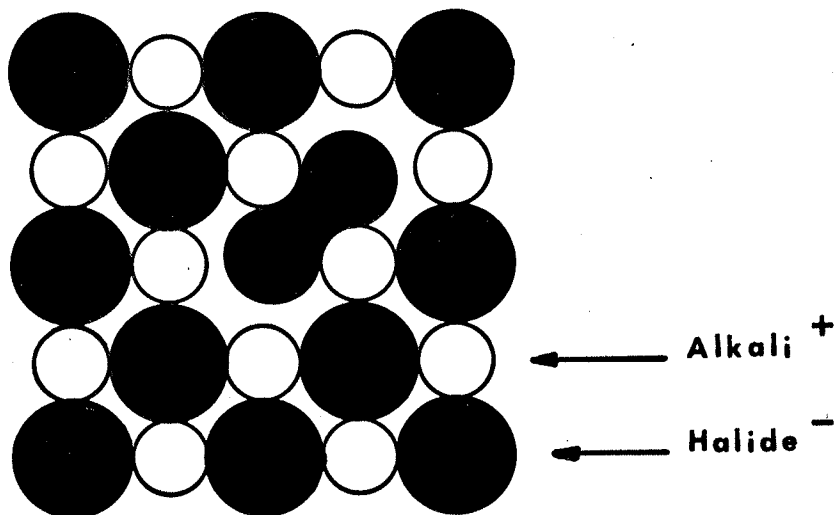
(a) Model of the V_k Centre
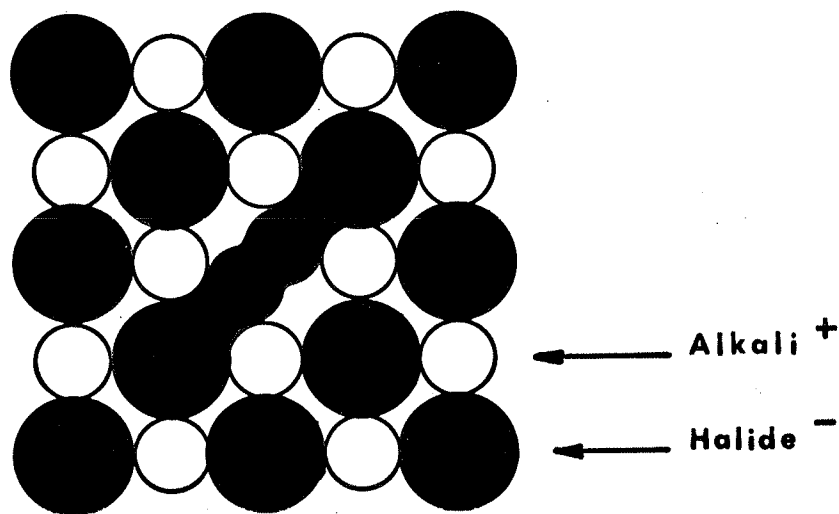
(b) Model of the H Centre

chemical approach to indicate that the V_1 centre was due to the halogen molecule X_2 in the crystal lattice and the V_2 centre was the halogen molecule-ion X_3^-. The other trapped hole bands are still caused by unidentified centres but indications are that they are due to some type of halogen molecule-ion. No centre which is analogous to the electron excess centres has so far been found.

Of all the methods used to produce colour centres, additive colouration holds a special position, especially with respect to studies of the F centre. The most important reason is that the colour centres produced in this way are much more stable than other methods since their destruction requires the transportation of material throughout the crystal. Also crystals can be produced containing only electron excess centres or only trapped hole centres. The only disadvantage is that the crystals must be quenched from a high temperature and this procedure is undoubtedly accompanied by thermal stress. The extent of the stresses produced is difficult to calculate and exact reproduction of the stresses is difficult to obtain. Since this process is a direct method of producing F centres it should be studied for all alkali halide crystals. The purpose of this project is to study the possibility of additively colouring lithium fluoride to produce F centres.

CHAPTER TWO

Introduction to the work on lithium fluoride

Lithium fluoride seems to hold a unique position with
respect to the other alkali halides. Examination of all the
alkali halides shows that the properties of lithium fluoride
are extreme. For instance the lattice constant, which has a
large effect upon the colour centre properties of the crystal,
is the smallest of all the alkali halides at 4.02 Ångström
units. Consequently the F band is situated in the ultra violet
region of the spectrum at a shorter wavelength than the F band
in the other alkali halides. Also the fundamental absorption
in the ultra violet was shown by Uchida, Kato and Matsui (1962)
to be at 12.0 eV while that for all other alkali halides was
shown to be at lower energies by Eby, Teegarden and Dutton
(1959) e.g. NaCl at 8.0 eV and KBr at 6.6 eV. A similar look
at the cohesive energies of the alkali halides as tabulated
by Seitz (1940) shows that lithium fluoride possesses the highest
cohesive energy at 220 kcal/mole with sodium chloride at
150 kcal/mole and potassium bromide 140 kcal/mole. Since it has
such a high cohesive energy, crystals of lithium fluoride are
particularly hard and resistant to corrosion. With such stable
properties and good transmission coefficient in the ultra violet,
lithium fluoride is often used in optical systems for lenses and
windows, particularly for work in the ultra violet.

With the stability of lithium fluoride and its resistance
to deterioration in air and water, it is a reasonably easy
material to handle in the laboratory. Consequently it has been
studied quite extensively. Ottmer (1928) was an early
investigator to colour lithium fluoride using X-rays and he
identified two absorption bands, one at 250 n.m. and the other
at 306 n.m. These same bands were also observed by Schneider
(1937) with crystals that had been coloured by electron
bombardment. No identification of these bands was made until
Pringsheim and Yuster (1950) identified the band at 250 n.m.
as being due to F centres in lithium fluoride. In the same
year Klick (1950) using X-rayed samples also identified the
band peaking at 250 n.m. as being the F band and he found a
band at 450 n.m. which produced luminescence and so he attributed
this band to M centres. Further experiments by Uchida and Yagi
(1952) indicated six bands which did not correspond with any
previously observed.

Thus the initial experimental situation with regard to
coloured lithium fluoride was rather confusing and exact
experimental identification of the bands did not appear to be
available. Indeed bands were identified mainly by referring
to their relative positions and by comparing these positions to
the already identified bands in other alkali halides. The
outstanding property noticed about the colouration of lithium
fluoride was that it was much more stable than in other alkali
halides. Delbecq and Pringsheim (1953) indicated that such

stability might make it possible to observe certain bands
which would be too short lived in other alkali halides to be
noticed. Their experiments identified the F band at 250 n.m.,
the F' band at 620 n.m., the M band at 450 n.m. and the R_1
and R_2 bands at 313 n.m. and 380 n.m. respectively. This
identification of these bands is still recognised as essentially
correct today. However their experiments also indicated bands
at 222, 340 and 518 n.m. and the behaviour of the observed
spectra did not agree with observations in other alkali halides.
For instance the M bands of other alkali halides are mainly
produced by irradiation with light absorbed in the F band. The
M band in lithium fluoride is produced in crystals which are
X-rayed at low temperatures to produce the 250 n.m. and the 340 n.m.
bands and the latter disappears on warming to room temperature,
finally leaving the 450 n.m. band. In this process a band at
620 n.m. is produced at temperatures between -135° C and 0° C
but it gives way to the 450 n.m. band at room temperature. Once
the M band has been formed it is very stable and not easily
bleached like the M bands of other alkali halides.

Such peculiarities led Seitz (1954) to refrain from
discussing lithium fluoride on the basis that it seemed to
exhibit properties that were unique. Pringsheim (1954) commented
that since most research workers were using the same source for
their crystals, namely Harshaw, it was possible for peculiarities
to be associated with impurities in the pure crystals themselves.
Tests showed that Optivac crystals still gave the same bands.

These experiments showed that even more bands could be observed. As before they gave the F band at 250 n.m. and the M band at 450 n.m. The band at 222 n.m. was produced by irradiating in the F band. If crystals were irradiated with X-rays for a long time such that they contained a high concentration of F centres and then they were heated for a few hours at 350° C, then the F band was destroyed and a symmetrical band at 270 n.m. was produced. By analogy to the bands studied by Scott et al. (1953, 1958) this band was attributed to colloidal particles of lithium. Irradiation of this band with ultra violet light at room temperature again gave rise to the band at 222 n.m.

Besides observing the normal absorption bands, detailed analysis showed that narrow absorption lines could be observed in lithium fluoride. Such lines were initially observed by Delbecq and Pringsheim (1953) who reported a line at 523 n.m. and showed structure on the band at 380 n.m., the largest and narrowest line being at 391 n.m. These lines were also observed by Kaplianskii (1958) who observed luminescence in the form of narrow lines as well as the normal luminescence. The origin of these lines was pointed out by Trifonov (1962) who explained them as zero phonon transitions of the colour centres in lithium fluoride. He discussed these transitions by analogy to the zero phonon transitions responsible for the Mössbauer effect. These lines were shown to occur in other alkali halides by Fitchen, Silsbee, Fulton and Wolf (1963). They showed that at low enough temperatures these so-called zero phonon lines could

always be observed in irradiated alkali halides.   Results
showed that the lines in lithium fluoride were much more stable
and maintained a smaller half width than the lines in other
alkali halides.   Each line can be associated with a zero phonon
transition of a particular colour centre and some fainter lines
can be attributed to one or two phonon transitions associated
with the absorption.   Recent experiments by Hughes and Runciman
(1965) showed that these lines can be split by uniaxial stress
and the observed splitting used to find the symmetry of the
centre responsible.   With lithium fluoride such experiments
have helped establish the well known centres but in no way
provide any information on the 250 n.m. and 222 n.m. bands.

The band at 222 n.m. was also produced in experiments
of Morehead and Daniels (1957).   Their crystals were irradiated
with electrons, γ-rays or thermal neutrons and upon heating or
irradiating with F light all produced the band at 222 n.m.   It
was found that this band could be bleached by light of wavelength
222 n.m.   Similar results were noted by Kato, Nakashima,
Nakamura and Uchida (1960) when they irradiated a lithium
fluoride crystal at 350° C with electrons.   However here they
were able to produce the 222 n.m. band and the band at 270 n.m.
which they attributed to colloidal centres.   However again no
explanation was forthcoming as to possible explanations about
the band at 222 n.m.

Another problem with lithium fluoride was that additive
colouration with excess metal did not seem practicable.   In an

attempt to additively colour lithium fluoride by heating in lithium vapour, Nadeau (1962) reported no colouration and indicated that mainly precipitates were formed near the surface. Earlier work by Pohl (1960) also reported that it was not possible to additively colour lithium fluoride.

With such apparent difficulties in dealing with the absorption spectrum of lithium fluoride, two groups performed detailed investigations to try to remove the ambiguities from the results concerning lithium fluoride. Kaufman and Clark (1963) performed a series of experiments in which they made determined attempts to colour lithium fluoride by heating in vapours of sodium, lithium and magnesium. None of these produced any absorption in lithium fluoride but always an indicator crystal of sodium chloride was coloured. Colouration was easily achieved by irradiating the crystals with electrons. With crystals showing the main absorption bands they performed polarization experiments and from these they were able to show that the 313 n.m. band and the 380 n.m. band were due to transitions from groups of three F centres. The observed orientation of these centres was such that these two bands could be identified as the R_1 and R_2 bands. By a study of the polarization of emission at 710 n.m. due to excitation by 450 n.m. light they concluded that the centre responsible had the symmetry axes of the M centre and so absorption at 450 n.m. could be identified with the M band. The work to identify the 250 n.m. band as being due to F centres was by no means conclusive. In

fact irradiation at 120° K produced a band at 200 n.m. as well as at 250 n.m. and the 200 n.m. band was the strongest at this temperature. Upon warming to room temperature the 200 n.m. absorption was almost entirely removed leaving the well known band at 250 n.m. Bleaching of this band gave the band at 222 n.m. Since these bleaching experiments seemed to show no correlation to results with other alkali halides, Kaufman and Clark (1963) admitted to having serious doubts about whether the 250 n.m. band was due to F centres.

A different approach was taken by Görlich, Karras and Kötitz (1963a) who concentrated upon determing whether impurities contributed to the unidentified bands. They grew their own crystals both by the Bridgman method, in vacuum, and by the Kyropoulos method where the crystals are exposed to the air. The two types of crystals showed different transmissions in the untreated state. However they both were identical when coloured by X-rays. They observed the usual bands and identified them by reference to earlier experiments. In addition to F, M, R_1 and R_2 bands they observed absorption at 540 n.m. and 960 n.m. which they left unidentified. After a determined attempt at additive colouration they had to report that no colouration was produced. In a series of experiments using various metals, heating tubes and temperatures they could report only that the indicator crystal was always coloured. Attempts to colour lithium fluoride by electrolytic methods also proved to be impossible. They could establish the normal ion current at

temperatures of 650° C but no current could be established which normally flows during the migration of F centres through the crystal. At a high enough voltage the crystal itself tended to break down leading to the formation of current paths between the cathode and anode. If lithium fluoride and sodium chloride were used together such that the lithium fluoride was in contact with the cathode and the sodium chloride was in contact with the anode, the two being joined by a connecting electrode, then colouration of the sodium chloride was observed as soon as the lithium fluoride broke down. Such experiments led to the conclusion that absence of colouration in lithium fluoride could not be attributed to technical shortcomings but was likely to be due to specific properties of the crystal itself. In a later experiment Görlich, Harras and Kötitz (1963b) studied the fluorescence of lithium fluoride. They observed normal M centre luminescence but could not observe any luminescence that could be attributed to F centres. The work of Botden, van Doorn and Haven (1954) indicated that observation of F centre luminescence is only possible in additively coloured crystals containing only F centres.

In some recent experiments deBlonde (1964) indicated that it was possible to produce absorption in lithium fluoride by heating the crystals with a layer of lithium on the surface, together with a layer of silver over the lithium to ensure it did not evaporate from the surface. However crystals treated in this manner did not give the 250 n.m. band alone. The

absorption spectrum consisted of three overlapping absorption

bands with peaks at 220 n.m., 250 n.m. and 270 n.m. The 270 n.m.

band was attributed to colloidal centres like those reported

by Pringsheim (1954). The present work was performed to see

if it was possible to identify the "F band" produced in the way

indicated by deBlonde and also to see if possible explanation

could be produced for the band at 222 n.m.

CHAPTER THREE

Experimental Equipment and Crystal Preparation

The lithium fluoride crystals were obtained from the
Hawshaw Chemical Company in the form of rectangular blocks,
1.5 cm. square at the ends. These were then cleaved, using
a guillotine with a razor blade cutting edge, to give samples
1.5 cm. square and 0.2 cm. thick. The crystals were then
treated in one of three ways :-

a)   A layer of lithium was evaporated onto one or both
      surfaces of the crystal, followed by a layer of silver,
      the process taking place in vacuo. The crystals were heated
      in an inert atmosphere of argon for varying lengths of
      time. After heating some crystals were quenched while
      other were allowed to cool slowly.

b)   Crystals were heated in a bath of molten lithium in an
      inert atmosphere of argon.

c)   A single crystal was x-irradiated for several hours at
      room temperature so that the 250 n.m. band was produced
      for comparison with the other crystals.

The evaporations were performed in a standard evaporator
with the normal bell-jar evaporation area. Molybdenum boats
were used to hold the metal being evaporated and the current to
heat the boats was supplied from a Variac variable transformer
through a step-up current transformer. This arrangement provided

currents in the range 100 to 400 amperes at voltages of 1 to 2 volts. The current was supplied through a porcelain insulated electrode, through the molybdenum boat to an electrode connected to the evaporator chassis. The boats were approximately 3 cm. long and were held in two brass clamps which were attached to each electrode. In order to be able to evaporate both lithium and silver the boats were constructed so that there were two separate sections to hold the two metals. As the current through the boat was increased, first the lithium melted and evaporated and at a much higher current the silver would melt and evaporate.

During evaporation the crystals were held in an aluminium frame by means of two set screws. For temperature measurements a copper-constantan thermocouple was attached to the crystal surface with a small clamp, while another was connected directly to the aluminium frame of the crystal holder. These thermocouple leads were taken out of the evaporator vacuum system through Kovar seals to a two way switch so that either the crystal temperature or the holder temperature could be measured using a calibrated galvanometer. The crystal holder was placed on two aluminium blocks which supported it above the molybdenum boat. This arrangement held the crystal surface 1.8 cm. above the evaporating metal.

The evaporations were performed in a vacuum of approximately 1 micron. A current of approximately 150 amperes at 1 volt was

sufficient to melt the lithium and allow it to evaporate onto

the crystal surface. During this process the crystal temperature

rose to about 120° C. To preserve a good layer of lithium

intact it was found necessary to open the evaporator to the

air after all the lithium had evaporated. This produced a thin

layer of oxide which protected the lithium from the silver

atoms. This was necessary since lithium melts at 186° C,

silver melts at 960° C and lithium oxide has a high melting

point. Experimentally the production of such a film was found

to be difficult to perform consistently. Best results were

obtained if the crystal temperature was in the range 30°- 45° C

when the evaporator was opened to the air. After production

of this layer the evaporator was immediately evacuated and a

layer of silver evaporated onto the crystal. This usually

required 300 amperes through the molybdenum boats.

After evaporation the crystals were allowed to cool in

vacuo and then transferred to an evacuated tube where they were

held in a nickel basket as indicated in Figure 7. This tube

was similar to the one used in the additive colouration experiments

of van Doorn (1961). It consisted of a nickel tube closed at

one end and the open end smoothed off to provide a good 'O' ring

seal. The open end was connected to a pumping system which

allowed the tube to be evacuated and then filled with various

pressures of argon gas. The pressure of the inert gas was

measured by a mercury manometer which was incorporated in the

pumping system. The closed end of the tube was placed in a

Fig. 7

Crystal Heating Apparatus

To vacuum system
and argon cylinder

Rubber
O-ring

Cooling
water

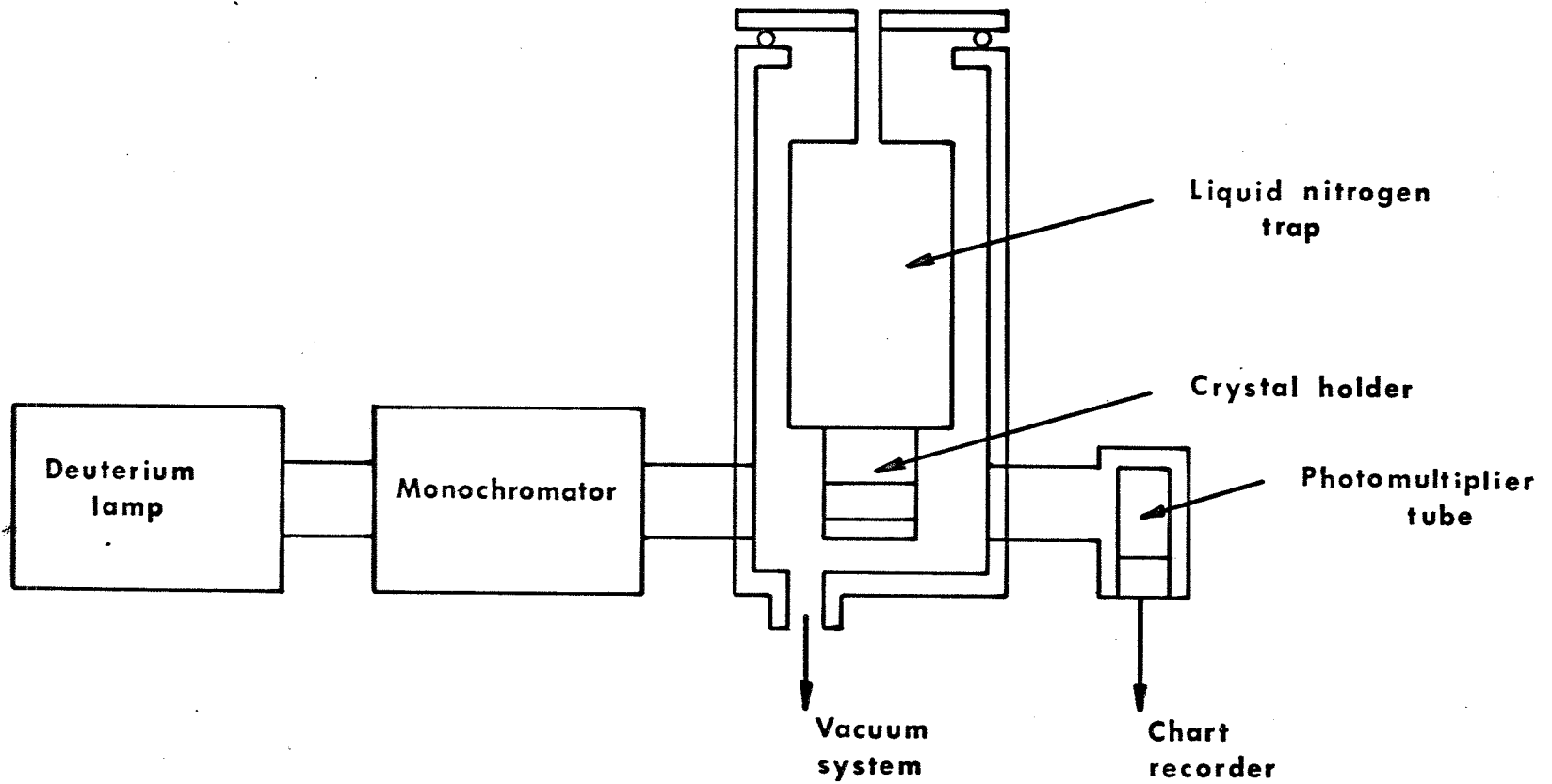Nickel
tube

Crystal
container
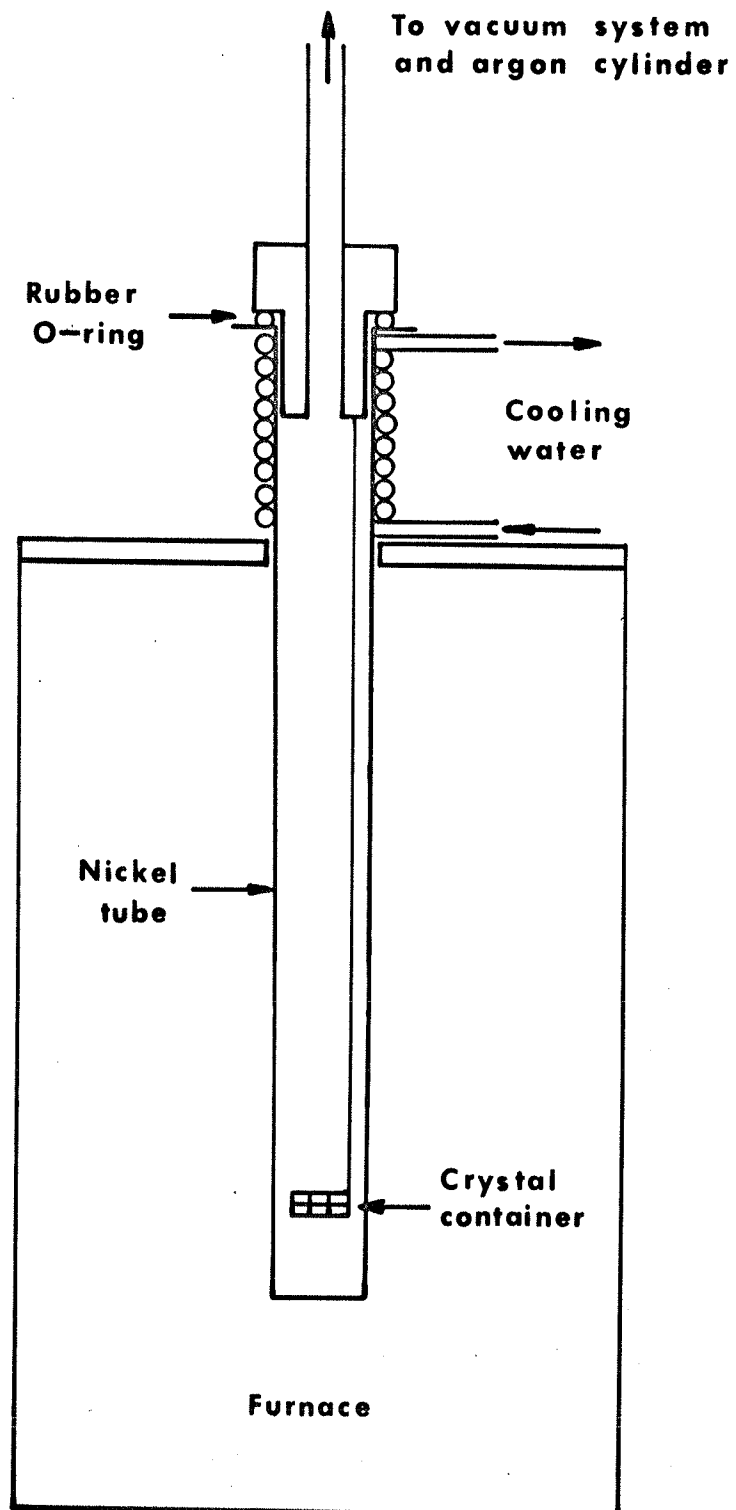
Furnace

furnace when heating the crystals and the open end was provided with a water cooling system so that the top could be removed while the crystals were still hot. The crystals were heated for times varying between 20 minutes and several hours in the argon gas at a pressure of approximately 10 cm. of mercury. Upon removal from the nickel tube the crystals were either quenched in carbon tetrachloride or liquid nitrogen, or else just allowed to cool slowly in air. The quenching process had a tendency to break the crystals. When they were cool the silver layer was removed mechanically and the optical absorption of these crystals was compared to that of a pure, untreated crystal.

With several of the crystal samples the bottom of the heating tube was filled with lithium and the crystals were heated in a bath of molten lithium. An atmosphere of argon was maintained above the molten lithium. Since it was difficult removing the crystals from the bath it was impossible to quench these crystals. When the crystals had been removed from the bath, the solidified lithium was removed by washing the crystals with water. During the heating process there was a tendency for the crystals to break due to exothermic reactions of the lithium in air when the crystals were removed. When the crystals were clean their absorption was compared with that of a pure crystal.

For the optical absorption measurements the light from a deuterium lamp was passed through a Bausch and Lomb grating monochromator as illustrated in Figure 8. The light from the

Fig. 8

Absorption Equipment

Deuterium lamp

Monochromator

Liquid nitrogen trap

Crystal holder

Photomultiplier tube

Vacuum system

Chart recorder

monochromator was passed into a vacuum box through a quartz window and the crystal was held in the light path by a brass crystal holder which was attached to a liquid nitrogen cold trap. This enabled the crystal holder to be taken down to a temperature of approximately -160° C. The temperature of the crystal holder was measured with a copper-constantan thermocouple. A graph of the warm-up of the crystal holder after all the liquid nitrogen was removed from the cold trap is shown in Figure 9 and the fastest warm-up is at most 0.5° C in a minute. The light, after passing through the crystal, left the vacuum box through a quartz window and was detected with an R.C.A.1P28 photomultiplier tube. This tube was fitted with a quartz window and was able to detect radiation down to 190 n.m. The output from the photomultiplier tube was connected to a potentiometric chart recorder. The wavelength drive on the monochromator was driven by a synchronous motor and the wave-length calibration was given by a system of microswitches which superimposed a sharp signal on the input of the chart recorder at set wavelengths. The time taken for a complete scan from 700 n.m. to 200 n.m. was 4 minutes and so temperature variation on warm-up of the crystal holder was no more than 2° C for each scan.

Comparison of the optical absorption of pure and treated crystals required the transmission spectrum of each crystal to be taken separately and then compared. The deuterium lamp source was checked and found to be stable to better than 1% over a

Fig. 9

Variation of Crystal Temperature After the Liquid Nitrogen Has Been Removed
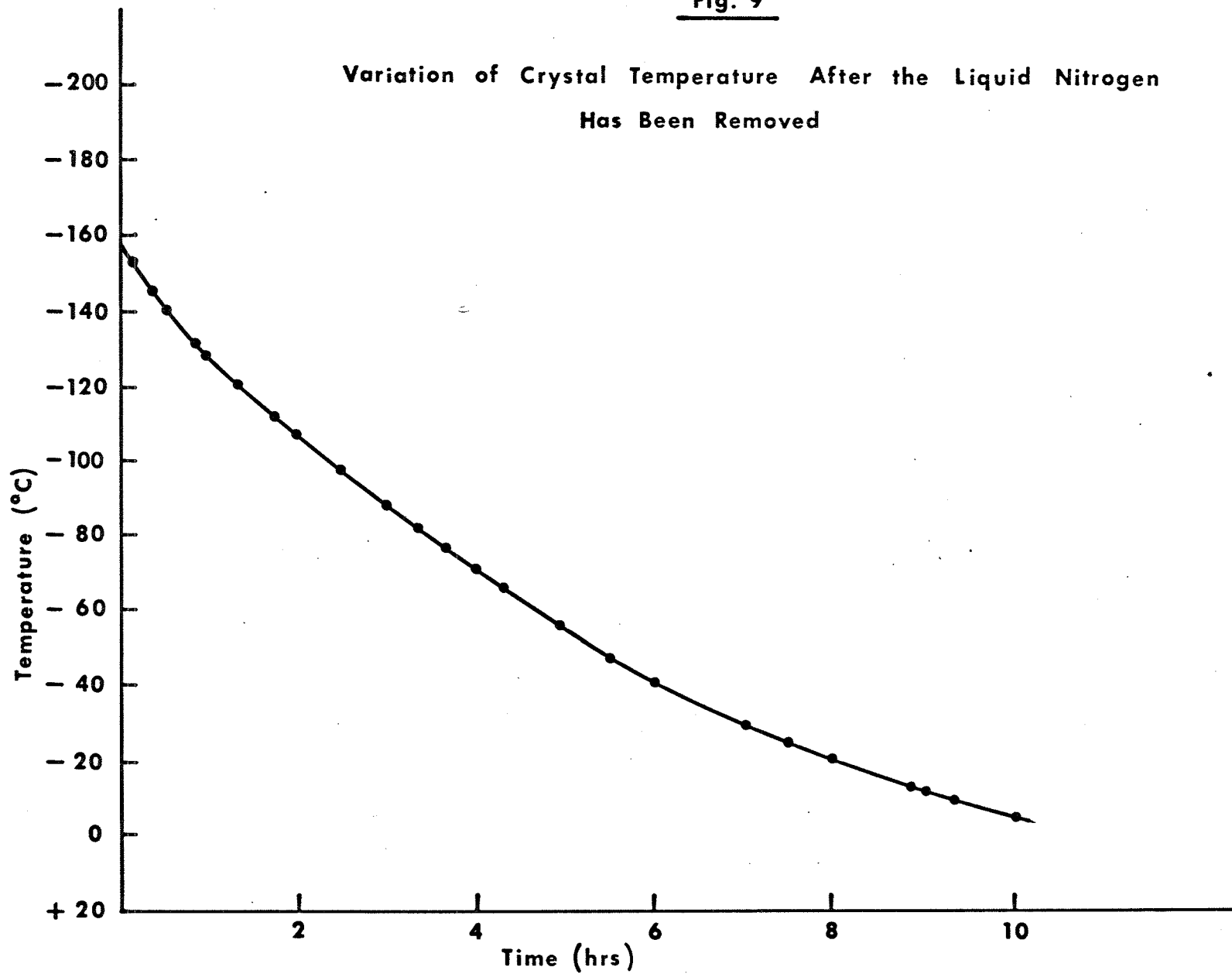
period of several hours, provided it had been allowed a

15 minute warm up period prior to taking the spectra. This

stability was adequate to allow separate spectra to be compared.

The optical absorption results were plotted as the ratio of

the light transmitted through a pure crystal to that transmitted

through a treated crystal and this method required no correction

for variation of response of the equipment at different wave-

lengths. Often the logarithm of this ratio is used and plotted

either against the wavelength of the incident light or the

energy of the light.

CHAPTER FOUR

Results of the Experiments

In this investigation approximately seventy crystals were treated by the evaporation process, twenty crystals were treated by heating in a bath of molten lithium and one crystal was x-irradiated to indicate the band produced at 250 n.m. The graph showing the optical absorption of this x-irradiated crystal, as compared with a pure, untreated crystal, is shown in Figure 10. This indicates a strong band at 250 n.m. that most of the literature, e.g. Görlich et al. (1963a), identify as the F band. The graph also shows that bands at 450 n.m. and 360 n.m. are beginning to form and these are attributed to M centres and R centres respectively.

Of the crystals treated by the evaporation process, most showed very little absorption. There was a general tendency for the process to produce some absorption in the region between 200 n.m. and 300 n.m. but it was normally very slight and did not resolve into recognisable bands. However with a few crystals the absorption produced was quite large but totally unresolved. An example of this type of absorption is shown in Figure 11. It was not known whether this absorption formed a band since the absorption equipment was only sensitive down to 200 n.m. The absorption of samples such as the one in Figure 11 was often so great that all light below 215 n.m. was absorbed. This absorption is typical of crystals treated in the melt. A few crystals
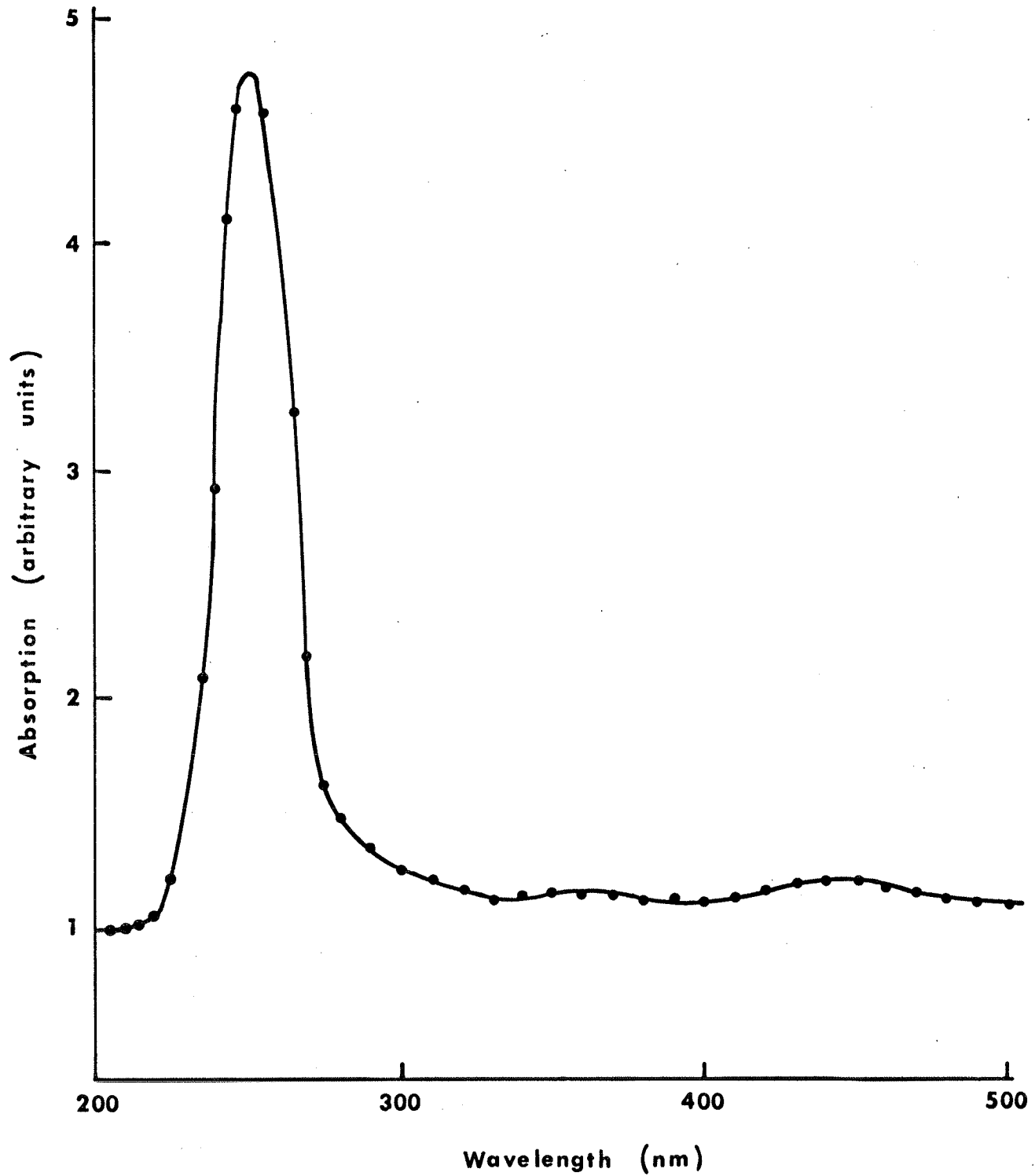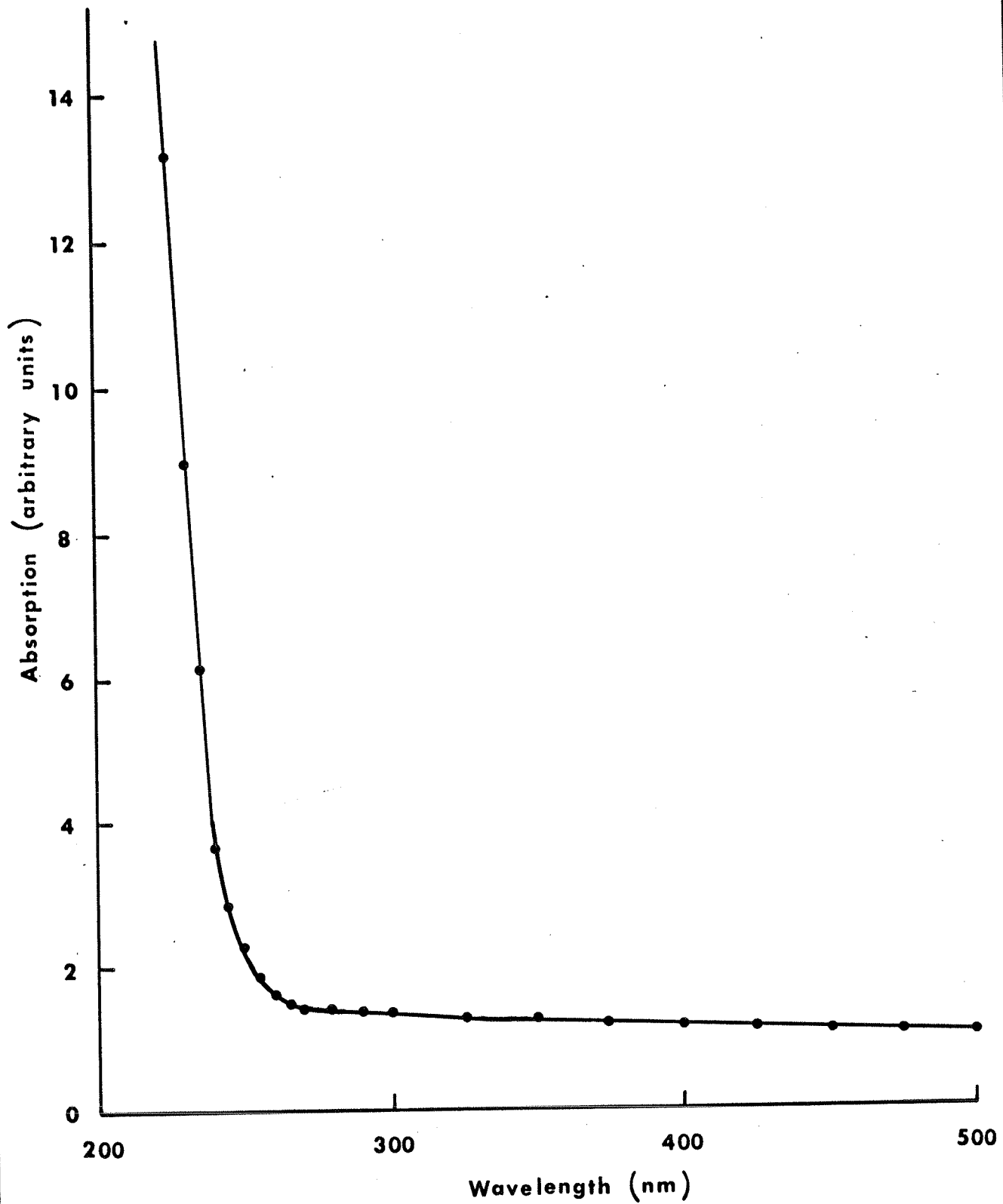
Fig. 10

X-Irradiated Lithium Fluoride Crystal

Fig. 11

Unresolved Absorption Produced by Evaporation and Melt Processes

that had been treated by the evaporation process did produce

resolvable absorption bands in the region 200 n.m. to 300 n.m.

An example of this type of absorption is illustrated in

Figure 12. This absorption is similar to that produced by

deBlonde (1964) in that the absorption spectrum indicates

three barely resolved bands at 220 n.m., 250 n.m. and 280 n.m.

approximately. The positions of these bands are inferred from

the positions of bands observed by Pringsheim (1954) in

x-irradiated lithium fluoride. The present experiments were

unable to produce crystals which showed a clearly resolved

band at 250 n.m. but always the absorption included a band at

220 n.m.

The absorption spectrum of crystals that produced a

large, unresolved absorption in the region of 200 to 250 n.m.

could be changed by reheating the crystals in the nickel tube

for short periods of time. The absorption spectrum of a crystal

after heat treatment is shown in Figure 13. This crystal originally

possessed a spectrum similar to that illustrated in Figure 11.

Here again it can be inferred that there may be three absorption

bands but the only definite one is the 220 n.m. band.

In order to try to make the absorption bands more easily

resolvable the absorption spectra of the better crystals were

examined at low temperatures. The work of Russell and Klick

(1956) indicates that as one lowers the temperature of the

crystal, then the F band half-width becomes smaller while the

Fig. 12

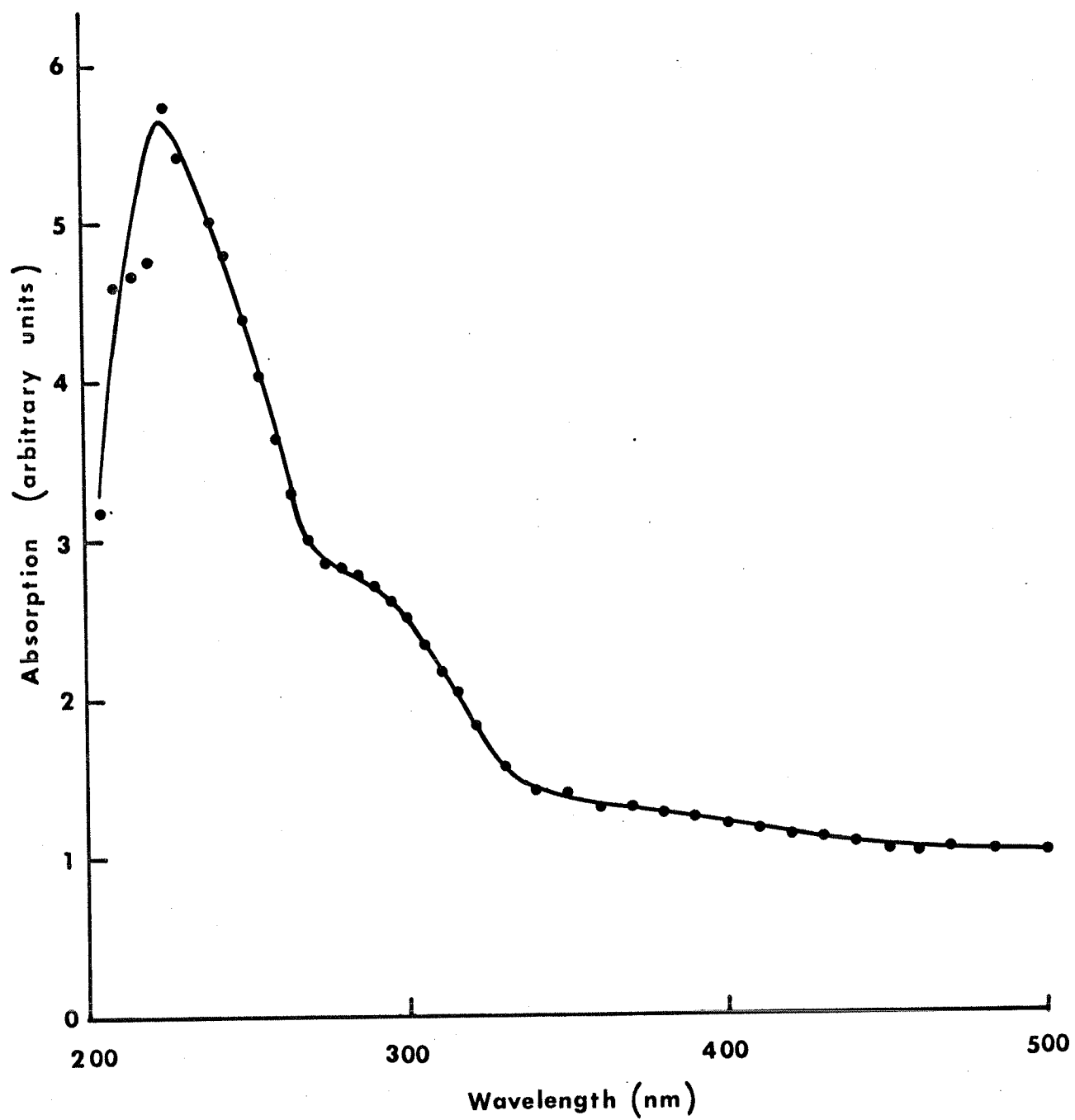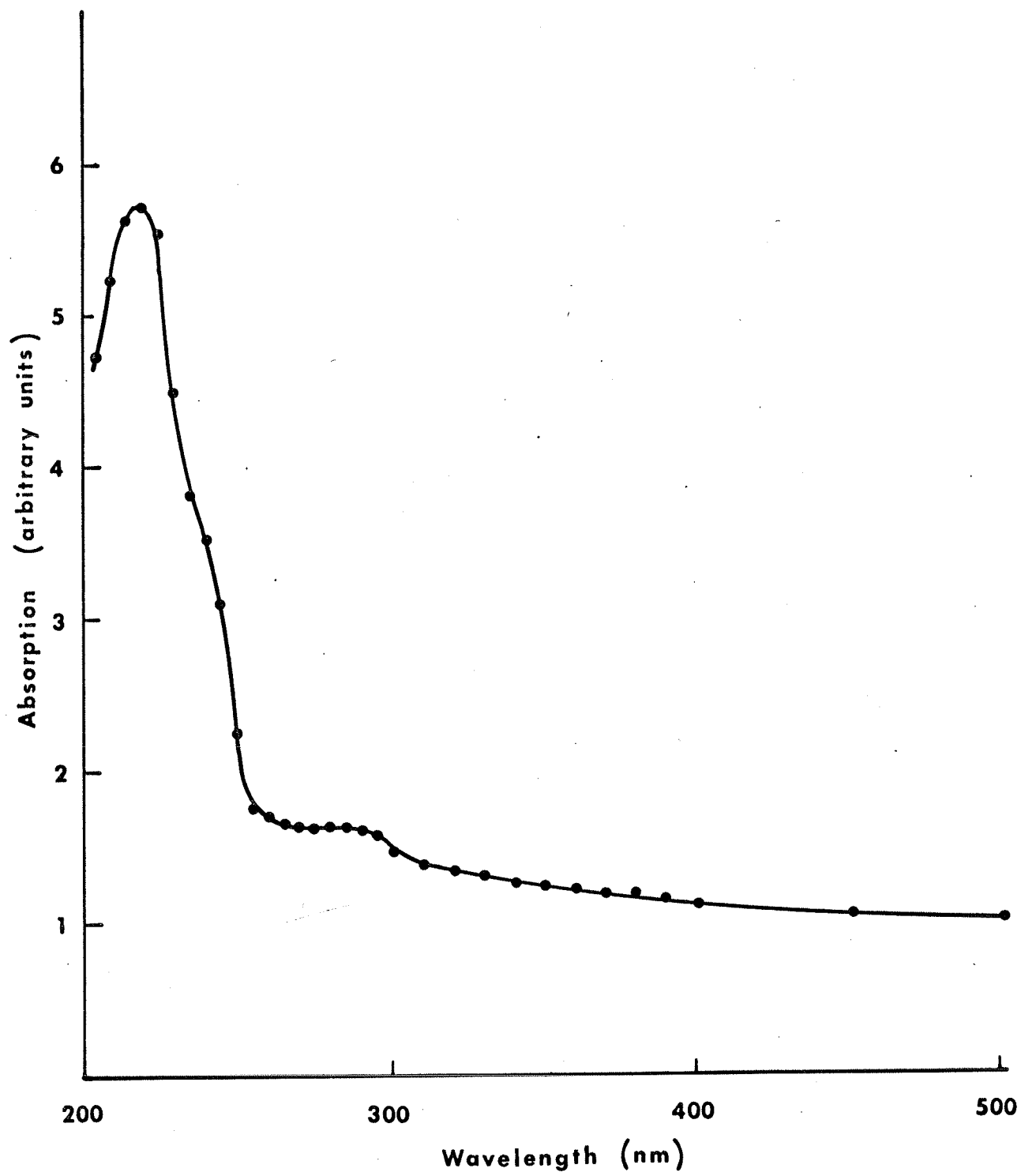Absorption of a Few of the Evaporated Crystals

Fig. 13

Absorption Spectrum

after Heat Treatment

height of the band increases. This variation was theoretically predicted from consideration of the continuum model of the F centre by O'Rourke (1953) and Lax (1952). Consideration of the configuration coordinate model by Williams and Hebb (1951) also predicted the same variation and consequently this variation does not differentiate between the two theories. However such a variation provides evidence by which F centre absorption can be identified. The work of Russell and Klick (1956) also showed that at low temperatures the position of the absorption band moved to higher energies (i.e. lower wavelengths). The work of Dexter (1956) indicated that the absorption curve for the F centre has a Gaussian distribution in energy. To make use of this information the temperature variation of the crystals examined was plotted against the energy of the incident light.

The results of a study of the absorption of a treated crystal as the crystal temperature was varied is shown in Figure 14. On this diagram the spectral region covered is from 275 n.m. to 205 n.m. but an energy scale is used to enable any possible Gaussian absorption bands to be identified. The curves show a slight variation between room temperature and $-160°$ C but there is no enhancement of any of the bands such that they could be resolved. The absorption definitely indicates a band at 5.6 eV which is 220 n.m. The point of inflection at 5.3 eV indicates that there is an unresolved band on the low energy side of the band at 5.6 eV. The position of this band

Fig. 14

Temperature Variation of Absorption Spectrum
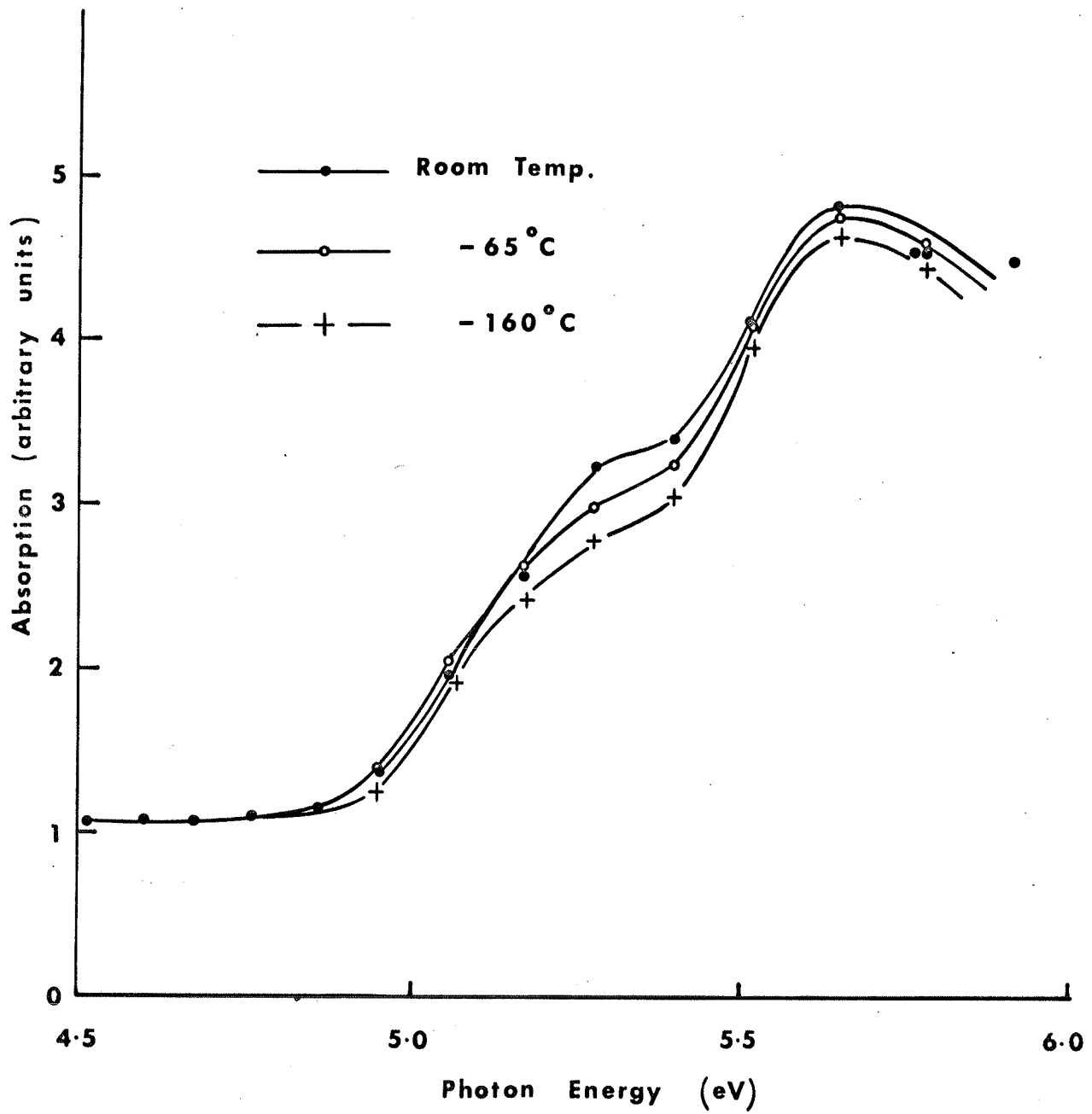
is difficult to assess, but the work of Rabin and Klick (1960) indicates that the low temperature position of the band in x-irradiated crystals is at 5.1 eV while most investigators place it at 5.0 eV at room temperature. This, however, does not allow us to identify the band producing the point of inflection with the "F band".

An investigation of the properties of the crystals producing some absorption showed that it was only the surface region that contributed to the absorption. Removal of a thin layer of the treated surface totally removed any absorption. This indicates that the lithium in some way does alter the transmission properties of the crystal but the effect is only in the surface region and not in the bulk of the crystal. Thus the observed absorption must not be taken to be characteristic of the bulk material since the regular lattice is disrupted at the surface. This could explain the band at 220 n.m. although this would seem to conflict with data from x-irradiated crystals where this band is produced by bleaching the band at 250 n.m. Consequently the only comment that can be made about this band is that it is produced by a centre that must be in the class known as electron-excess centres since it is produced in the additive colouration process.

Thus it must be concluded that the results presented here do not provide sufficient evidence to indicate that the band at 250 n.m. is due to F centres. Nor do they provide

information as to the identification of the band at 220 n.m.
They show that it seems to be impossible to additively colour
lithium fluoride with lithium, as regards to the bulk properties.
The experiments do indicate that the lithium in some way alters
the surface properties of lithium fluoride to produce slight
absorption bands.

CHAPTER FIVE

Discussion

The results of these experiments indicate that it is not
possible to produce bulk colouration of lithium fluoride by
the addition of excess lithium to the crystal. Only a surface
effect is produced by the additive colouration process. To
interpret these results it is necessary to consider the mechanism
involved in the additive colouration process. As indicated in
Figure 2, the process involves an atom of the alkali metal
attaching itself to the surface of a crystal in a normal lattice
position of a cation. The atom loses an electron which is then
free to move within the crystal. Anions then move towards the
surface where the excess cations are, so that the surface is an
additional layer of alternating ions which is identical with
the original surface. The motion of the anions leaves vacancies
in the crystal and these are able to trap the extra electrons
released by the lithium atoms upon attachment at the surface to
produce F centres. Thus the process involves the diffusion of
anions and electrons in the crystal. The diffusion of anions
requires vacancies present to allow the anions to move.

Experiments on the diffusion of fluorine ions in lithium
fluoride have not been performed, presumably because of the
difficulties of working with fluorine gas and also that fluorine
does not possess a radioactive isotope with a long lifetime.
Work was performed on the diffusion of positive ion vacancies in

the lithium halides by Haven (1950). This indicated that the
height of the potential barrier which must be surmounted by
lithium ions when moving through the crystal was 0.65 eV in
lithium fluoride and almost the same for all the other lithium
halides at 0.40 eV. The energy of formation of a pair of
vacancies was correspondingly higher in lithium fluoride, while
the percentage of vacancies produced at comparable temperatures
with respect to the melting points was lower in lithium fluoride
than in the other lithium halides. Such experimental data do
not provide any direct observations on the diffusion of
fluorine ions but indicates that it can be expected that the
activation energy for the movement of a fluorine ion would be
high.

The negative results of the present experiments have the
interpretation that the activation energy for fluorine ion
diffusion is indeed high and prohibits the mechanism of additive
colouration altogether in the bulk material. Since absorption
can be produced in the surface of the crystals it must be
assumed that the lithium atoms are in some way incorporated
into the surface. Work on semiconducting materials, e.g. Bardeen
(1947), showed that the surface region of solids possesses
different properties than the bulk material. Primarily the
regular lattice itself is disrupted and the normal bonding of
the crystal is altered. Since it was possible to produce
absorption in this layer it is possible to say that the activation
energies for diffusion were probably less than in the bulk crystal.

This should allow the lithium to be incorporated enough to produce some absorption. However since the lattice at the surface is different from that of the bulk crystal then the absorption produced would not be exactly like that of the bulk crystal. Consequently the observed bands cannot be directly identified with bands produced in the bulk material. The band observed in x-irradiated crystals at 220 n.m. may be due to surface effects and not due to the properties of the bulk crystal itself.

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