ILLINOIS INSTITUTE OF TECHNOLOGY

COLOR CENTER PHENOMENA IN SODIUM CHLORIDE

By

Alvin E. Weinstein

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Approved Theodore J. Reubert.
Adviser

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ABSTRACT

Absorption spectra of M centers in x-ray colored Harshaw NaCl crystals were measured at several temperatures between 66 and 274°K using a Cary 14 PMR Spectrophotometer. Also measured in NaCl were the absorptions of M^+ and R^+ centers at 80°K. Additively colored crystals were found to be unsuitable for studies of the absorptions of F-aggregate centers because of low concentrations of F centers and persisting colloid absorptions.

In order to examine M bands free of overlapping absorptions of F centers, an M-band anisotropy was produced by exciting M centers with appropriately polarized light. Irradiation at 0°C with [011] polarized M_1 -band light resulted in both reorientation and annihilation of M centers while irradiation at 80°K with $[0\bar{1}1]$ polarized 405 nm light resulted only in reorientation yielding a much larger anisotropy than produced at 0°C.

Between 66 and 274°K, the position of the M_1 band varies from 715 (1.734 eV) to 727 nm (1.705 eV) and the half-width varies from 0.080 to 0.144 eV. From the temperature dependence of the half-width, the phonon frequency responsible for broadening of the M_1 band was found to be $3.2 \pm 0.2 \times 10^{12} \text{ sec}^{-1}$. Asymmetry of the M_1 band was also found to be temperature dependent.

For M_2 and M_2' bands it was not possible to determine asymmetry because of the large overlap by M_3 and M_3' bands respectively. In order to determine M_2 and M_2' band parameters it was assumed that each band is Gaussian in energy. Between 66 and 197°K, the position of the M_2 band from 447 (2.773 eV) to 453 nm (2.737 eV) and the half-width

of the M_2 band varies from 0.28 to 0.35 eV. At 274°K the large overlap of the M_2 band with higher energy M bands and the low intensity of the M_2 band precludes determination of its parameters.

The ratio at 80°K of maximum absorbance of the M_2 band to that of the M_1 band is nearly four in NaCl as in NaF but different from the ca. 2.5 ratio noted in potassium halides.

A cation effect was also noted in M_2' - M_2 band splitting. The splitting was found to be 0.012 ± 0.007 eV in NaCl. Comparison with corresponding data in other alkali halides indicates a cation effect different from the anion effect already known, i.e., the larger the anion, the smaller the splitting; but the larger the cation, the larger the splitting.

A problem in the study of M-center absorptions is overlap of the M_1 and M_2 bands by the R_r^+ and R_v^+ bands in the $[011]$ - $[0\bar{1}1]$ anisotropy. R_r^+ and R_v^+ bands were eliminated from the anisotropic spectrum by storing the sample overnight at 25°C. Band position values of 692 and 402 nm for the R_r^+ and R_v^+ bands are consistent with a model of H_3^+ ion in a continuous dielectric medium.

An M^+ band was measured at 80°K with a maximum at 1020 nm and with a half-width of 0.184 eV, but it was not possible to measure a higher energy band as for the R^+ center. A model of the H_2^+ ion embedded in a dielectric predicts positions of 475, 376, 321 nm for M^+ bands associated with $1s\sigma_g \rightarrow 2p\pi_u$, $3p\sigma_u$ and $4p\sigma_u$ transitions respectively. Greater resolution, which may be obtainable at lower measuring temperature, is necessary for observation of higher energy M^+ bands.

CHAPTER I

COLOR CENTER PHENOMENA IN ALKALI HALIDES

Introduction

Color centers are lattice point defects which cause normally transparent solids to be colored. These defects have been extensively studied^{1,2,3,4*} in alkali halides because of the crystals' wide range of transparency (IR to UV) and simple face centered cubic structure.

Generation of Color Centers

Color centers may be introduced into alkali halides by x or γ irradiation or by additive coloring by the incorporation of a stoichiometric excess of either alkali metal or halogen. Radiation coloring produces both trapped electron and trapped positive hole centers. Additive coloring, on the other hand, produces only trapped electron centers if the excess is alkali metal and only trapped hole centers if the excess is halogen. Additive coloring is the preferred method of trapped electron formation because the inventory of color centers is more stable. Some salts such as KCN, LiF, NaF and NaBr do not additively color well and are thus radiation colored.^{5,6,7,8}

Trapped Electron Centers

Neutral Electron Centers. The primary trapped electron center formed in an alkali halide crystal upon exposure to ionizing radiation or upon additive coloration with excess alkali metal is the F center. The center consists of an electron trapped in an anion vacancy with an octahedral environment of cations. Such centers are considered neutral since they have the same charge pattern as the original lattice.

*Numbers in superscript refer to numbered references in Bibliography.

Simplicity and ease of formation have made the F center the most studied of defects and in fact there is a book⁹ based on this center alone. The principal absorption of the center, the F band, is associated with the lowest energy transition of the F center electron. Other bands related to the F center are the K band, appearing as a shoulder on the high energy tail of the F band and much smaller L bands (L_1 , L_2 , etc.) at even higher energies. The K band may be associated with a transition to the second electronically excited energy state. L bands appear to be linked with transitions to energy states lying in the conduction band since L-band irradiation even at low temperature produces photoconductivity.¹⁰ In addition there is a β band which is an F-center perturbation of the first exciton peak of the crystal's fundamental absorption.

The simplest model of the F center is that of a particle in an infinite square well. This particle-in-a-box model predicts that the transition energy of the F-center, E_F , is given by the relation:

$$E_F = (3/8) (h^2/md^2) \quad (1.1)$$

where d is the width of the potential well.¹¹ Using this model Mollwo¹² predicted that E_F is proportional to $1/a_o^2$ where a_o is the lattice constant. This relation agrees surprisingly well with experimental data. Ivey's¹³ empirical relation:

$$E_F = 17.7 a_o^{-1.84} \quad (1.2)$$

is in somewhat better agreement with data. In Ivey's relation E_F is in electron volts (eV) and a_o is in angstroms ($\text{\AA}$). The relation E_F

αa_0^n is now called a Mollwo-Ivey relation. Emission energies, however, are not correlated well by a Mollwo-Ivey relation.³

The particle-in-a-box model also qualitatively explains the large width of an F-absorption band and the temperature dependence of both the width and the peak position of the F-absorption band. The width arises from variation in d , caused by vibrations of neighboring cations. As the temperature is raised, the amplitude of vibration increases causing the band width to increase, and the lattice expands causing E_F to decrease.

Another simple model, that of a hydrogen atom embedded in a continuous dielectric medium, predicts that the transition energy of the F-center, E_F , is:

$$E_F = (3\pi^2/2)(e^4 m^*/K_0^2 h^2) \quad (1.3)$$

where m^* is the effective mass of the F-center electron and K_0 is the effective optical dielectric constant.³ This model agrees fairly well with emission energy data but does not work well for predicting absorption energy data.³ It does, however, predict that the F-band absorption is associated with a $1s \rightarrow 2p$ transition of the F-center.³ The K band may be associated with a $1s \rightarrow 3p$ electronic transition.¹⁰

When an alkali halide crystal is x rayed at low temperature (80°K) the F center is nearly the only trapped electron center formed. If the crystal is then heated to room temperature, F-centers aggregate into dimers called M centers. Additional M-center formation may be effected by irradiation at room temperature with F-band light. M centers are noted by the M_1 band on the low energy side of the F band. Not all F centers formed in the x irradiation take part in

aggregation, as many F centers capture positive holes to form anion vacancies or capture interstitial halogen atoms to form substitutional halide ions.

A particle-in-a-box model correctly predicts that for M centers there is an M_1 band to the low energy side of the F band, and M_2 and M_2' band underlying the F band. The M_1 -band peak position cannot be reliably predicted with this model because of electron-electron interaction.

Another simple model, an H_2 molecule embedded in a dielectric medium, is useful for labeling the M-center energy states. The model predicts that the M_1 band is associated with the lowest energy $^1\Sigma_g \rightarrow ^1\Sigma_u$ transition and that the M_2 and M_2' bands are associated with the doubly degenerate $^1\Sigma_g \rightarrow ^1\pi_u$ transition. Inequivalence of crystal fields in the x and y directions causes the $^1\Sigma_g \rightarrow ^1\pi_u$ transition to be split into two transitions of different energy $^1\Sigma_g \rightarrow ^1\Sigma_{uy}$ and $^1\Sigma_g \rightarrow ^1\pi_{ux}$, responsible for the M_2 and M_2' bands respectively. For an M center oriented in the $[011]$ direction, the $[011]$ direction is along the z-axis, the $[0\bar{1}1]$ direction is along the y-axis and the $[100]$ direction is along the x-axis.

The language of group theory can also be used in the labeling of M-center transitions. The M center has D_{2h} symmetry for which there are three allowed dipole transitions $^1A_{1g} \rightarrow ^1B_{1u}$, $^1A_{1g} \rightarrow ^1B_{2u}$ and $^1A_{1g} \rightarrow ^1B_{3u}$ responsible for the M_1 , M_2 and M_2' band respectively. Group theoretical characters such as $^1A_{1g}$ will be the predominant label for energy states in the remainder of the thesis.

Attempts to fit M_1 - and M_2 -band data with transition energies of

a hydrogen molecule in a continuous dielectric medium have been made by Herman et al.¹⁴ Potential energy vs internuclear distance curves for various energy states of this model, $E(r_{ab})$ vs r_{ab} are generated by scaling calculated published^{15,16} curves for the free hydrogen molecule, $E'(R)$ vs R , using the relations:

$$r_{ab} = K_0 R \quad (1.4)$$

$$E(r_{ab}) = (1/K_0)^2 E'(R) \quad (1.5)$$

where r_{ab} and R are the electron-electron separation in the M center and internuclear separation in the H_2 molecule, respectively, and K_0 is the high frequency dielectric constant. The best fit of experimental M_1 - and M_2 -band energies to the scaled curves of H_2 leads to an M_1 band energy which is larger and an M_2 -band energy which is smaller than experimental values. In this model the M_2 and M_2' bands are degenerate in energy.

Calculations of transition energies of the M center have been made using a rigid point ion lattice model,¹⁷ and using an extended ion model.¹⁸ Such calculations will be discussed in Chapter VI of this work.

In addition to the M_1 , M_2 and M_2' bands, other bands are evident in the spectrum of the M center. The largest of these, the M_3 and M_3' bands, appear as shoulders on the high energy sides of the M_2 and M_2' bands. These bands may be analogues of the K band related to the F center. There is also a weak absorption called the M_4 band, lying between the M_1 and M_2 bands. The low intensity of the M_4 band suggests that the M_4 band may be associated with a transition forbidden in first

order such as $g \rightarrow g$, made allowed by vibronic coupling or singlet $\rightarrow$ triplet, made allowed by spin-orbit interaction. There are also weak absorptions to the high energy side of the M_3 band. They may be L-band analogues, i.e., transitions to states within the conduction band.¹⁹

When an alkali halide crystal exhibiting F and M bands is heated above ca. 25°C or irradiated in the vicinity of 25°C with F- or M_1 -band light, two additional bands, called R_1 and R_2 , appear in the spectrum. The R_1 and R_2 bands are related to the R center, an equilateral triangular array of three adjacent F centers having C_{3v} symmetry. In addition to the R_1 and R_2 bands there are weaker bands such as R_N , R_M , R_F , and R_K lying in the N, M_1 , F and K band regions respectively and a broad R_B band between the R_1 and F bands.²⁰ Silsbee²⁰ coupled data on the effects of crystalline stresses on optical absorptions of R centers with calculations of Hirschfelder²¹ on the H_3 molecule to determine the ordering of R center states. The R_N , R_M , R_2 , R_B , R_F , and R_K bands were found to correspond to ${}^2E \rightarrow {}^2E$, 2A_1 , 2A_2 , 2E , 2A_1 , 2E , and 2A_2 transitions respectively. With group theory it may be shown that only ${}^2E \rightarrow {}^2E$ transitions, i.e., R_N , R_1 and R_F absorptions are associated with the transition dipole along the principal axis (z) while all of the transitions are associated with a transition dipole in the R-center plane. Evarestov et al.¹⁷ used the RPIL model to calculate ${}^2E \rightarrow {}^2A_1$ transition energies, which were found to be in agreement with R_2 band energies for several alkali halides. This, however, is contrary to the ${}^2E \rightarrow {}^2A_2$ assignment of Silsbee.²⁰

The R_N band mentioned above is part of a complex of bands called the N bands lying on the low energy side of the M_1 band.²⁰ At one time the N-band region was thought to contain just two bands, N_1 and

N_2 , related to different centers. It now appears that each of those N bands is a composite of bands. Pick²² suggested that a planar F_4 center of C_{2h} symmetry is responsible for the N_1 band and that a tetrahedral F_4 center is responsible for the lower energy N_2 band. Evarestov's²³ calculated transition energies, assuming the N-center models of Pick, are not inconsistent with the N_1 - and N_2 -band assignments. Some luminescence work²⁴ indicates that the N-band region is associated with rearranged F_3 centers called N_{1A} and N_{1B} . Just how much of the N-band region is due to F_3 type centers and how much is due to F_4 centers is uncertain.

Recently zero phonon lines have been observed in absorption and emission spectra of F_3 , F_4 and charged aggregate centers.²⁵ Small splittings and shifts of the narrow zero phonon lines permit direct studies of color centers under various perturbations. A zero phonon transition is one in which there is no change in vibrational state, i.e., a pure electronic transition. The presence of the line indicates that the center with which the line is related is weakly coupled to the lattice. The lack of F and M center zero phonon lines indicates that these centers are strongly coupled to the lattice. A striking feature of a zero phonon line is the very strong temperature dependence of its intensity. Fitchen³ has written an excellent review of zero phonon transitions.

Charged Electron Centers. In addition to neutral trapped electron centers mentioned above there are positively and negatively charged electron centers. The simplest positively charged center is the α center (F^+), an anion vacancy, while the simplest negatively charged center is the F' center, an F center containing an extra

electron.

Associated with α centers is an α band which, like the β band, is a perturbation of the first exciton peak of the crystal's fundamental absorption band. If an alkali halide crystal is x-irradiated at liquid helium temperature (LHeT), the α center is the predominant species formed. At liquid nitrogen temperature (LNT) α centers are also formed but in somewhat lower concentration than at LHeT.

Along with α and F centers, F' centers are formed as a result of x or γ irradiation of an alkali halide crystal, evidenced by a very broad F' band overlapping the F band. The F' center consists of an F center containing an extra electron, i.e., two electrons occupying a single anion vacancy. Brief irradiation with F'-band light at low temperature, such as 80°K, removes the F' band and causes the F band to increase. This suggests that the transition responsible for the F' band is to a state within the conduction band.

Both α and F' centers are reactants in important reactions. When a crystal which had been x rayed at low temperature is heated, α centers eventually become mobile. The mobile defects may be captured by F centers to form M^+ centers or by F' centers to form M centers. At still higher temperatures electrons are thermally released from F' centers. Some of these electrons are captured by M^+ centers to form M centers.

As may be inferred from the above, an M^+ center consists of an electron shared by neighboring anion vacancies and is thus an ionized M center. The M^+ center may, in fact, be formed by optically ionizing M centers with M_L -band irradiation at ca. 80°K. The presence of M^+ centers is noted optically by an absorption, called the M^+ band, in

the near IR spectral region. It has been found in studies of various salts that the M^+ band position moves to higher energy as the temperature is increased, contrary to the behavior of other color center bands. In other respects the M^+ band behaves as other color center bands, e.g., the band narrows but remains constant in area as the temperature is lowered. Like other color center absorptions, the M^+ band follows a Mollwo-Ivey relation.

Unfortunately it has not been possible in most salts to produce large concentrations of M^+ centers possibly due to low α -center and low electron trap concentrations. Konrad⁷ was able to produce a large M^+ -center concentration in NaF by annealing a sample which had been x rayed at 80°K. Recent calculations²⁶ indicate that the Frenkel-pair formation energy (FPFE) for an anion in NaF is lower than the corresponding value in most other alkali halides. The FPFE for an anion is the energy necessary to move an anion from a normal lattice site into a well-removed interstitial site. Low anion FPFE implies that there is a large α center concentration available for M^+ -center production in NaF.

By optical ionization of M centers at 7°K, Aegerter and Luty²⁷ recently have been able to produce large concentrations of M^+ centers in KCl crystals that were additively colored with potassium and then x rayed at LHeT. X raying at LHeT introduced extra electron traps, consisting of α , H and F centers, which shifted the pattern of the reactions occurring during M_L -band irradiation to higher concentrations of M^+ centers.

The observed M^+ -center spectral data of both NaF and KCl were found to fit well the model of an H_2^+ center in a continuous dielectric medium. This is in marked contrast to the bad fit of the M center with the model of an H_2 molecule in a dielectric medium. As with the M center though, the model fails to explain the observed²⁷ splitting of the π state into π_y and π_x states.

In addition to its importance as an H_2^+ molecular ion analogue, the M^+ center plays a significant role in M center formation and reorientation reactions. The mechanism for M-center formation will be discussed in this chapter while the mechanism for M-center reorientation will be discussed in Chapter VI.

It was found from pulse anneal experiments in LiF²⁸ and in NaCl²⁹ that the M_1 and M^+ bands make their first appearance at the same temperature. Furthermore, in NaCl the α band is known to disappear at the temperature at which the M_1 and M^+ bands appear. To explain these observations in LiF, Farge *et al.*²⁸ suggested that α centers become mobile at a certain temperature and may be captured by F centers to form M^+ centers. Many of the M^+ centers then capture electrons to form M centers. To explain their²⁸ data on photochemical conversion of F centers into M centers, optical F center ionization was added as a first step to the above mechanism.

It was found, however, that the M^+ -center mechanism does not adequately explain photochemical conversion of F centers into M centers in KBr.³⁰ Instead of capturing an α center, the F center in KBr captures an electron to form an F' center which in turn captures an α center to form the M center.³⁰

According to the data of Farge et al.²⁸ in LiF, the R^+ center plays a role in R-center formation similar to that played by the M^+ center in M-center formation. An M center thermally captures an α center to form an R^+ center which in turn captures an electron to form an R center. Like the M^+ center, the R^+ center can be formed both thermally and photochemically. The R^+ center can be formed photochemically by irradiation into any of the R bands and is stable at higher temperatures than the M^+ center. The high stability of the R^+ center is consistent with calculations of Hirschfelder²¹ on the H_3^+ molecular ion.

Calculations have been made by Evarestov's group¹⁷ of the first transition energies of the M^+ and R^+ centers in a variety of alkali halides. Their R^+ -center transition energies were in somewhat poorer agreement with experiment than were their M^+ -center transition energies.

Somewhat less studied than either the M^+ or R^+ center is the M' center, an M center containing an extra electron. M' centers have been formed by F-band irradiation at low temperature ($\leq 78^\circ K$) of an alkali halide crystal containing F and M centers.³ Associated with the negatively charged center is a weak M' band to the low energy side of the M^+ band. There is theoretical evidence³¹ that the M' center, unlike the F' center, has bound excited states both for absorption and emission.

Trapped Hole Centers

As a result of ionizing irradiation of an alkali halide crystal, different trapped hole bands appear in the UV spectral region depending

upon the temperature of irradiation. All are broad bands with half-widths ranging from 0.5 to over 1 eV. An H band is produced at ca. 4°K, V_1 , V_K and V_2 bands are produced at ca. 80°K, while V_3 and V_4 bands are produced at higher temperatures.³⁴ Of the centers responsible for these bands, models for only the H, V_1 and V_K centers have been well established.

The H center, which is stable only at low temperature (< 58°K in KCl), consists of a halogen molecular ion, X_2^- , occupying a single anion vacancy and oriented along a face diagonal direction.³² When a colored KCl crystal is warmed to 58°K the H center is converted into a V_1 or V_K center.

The V_1 center in potassium halides consists of an H center associated with a neighboring Na^+ ion. In sodium halides the V_1 center has not been characterized, but is believed to involve a K^+ ion as this is the most prevalent alkali ion impurity.³³

The V_K center has been studied somewhat more extensively than either the V_1 or H center because of its simple geometry.³⁴ It consists of a halogen molecular ion, X_2^- , occupying two adjacent anion vacancies and oriented in a face diagonal direction. Since the center is positively charged relative to the perfect lattice, presence of an electron trapping impurity such as thallium greatly enhances its production. Heating of the crystal causes the V_K band to disappear as a result of capture of electrons released from electron traps.

Impurity Centers

Another important class of color centers besides those of the trapped electron and trapped hole centers is that of the impurity

center. Included among impurity centers are cation centers such as thalium ion, Tl^+ , and anion centers such as hydride ion, H^- .

As mentioned earlier thalium impurity may be added to an alkali halide to enhance V_K center production. The Tl^+ ion has an absorption spectrum that has been extensively studied experimentally and theoretically.³

More interesting chemically are the OH_s^- , $U(H_s^-)$, $U_1(H_i^-)$, and $U_2(H_i^0)$ centers where subscripts s and i indicate substitutional and interstitial, respectively. The principal absorptions all lie in the ultraviolet region and in order of decreasing energy are the OH^- , U , U_1 and U_2 bands. An interesting feature of the centers is their photochemical interconversion.³⁵ The U centers upon photochemical excitation are converted into U_1 and α centers. The U_1 centers may in turn be photochemically converted into U_2 centers and electrons. Released electrons and α centers combine to form F centers. Thus U centers serve as a source of F centers. Kerkhoff³⁵ made an extensive study of the U , U_1 and U_2 reactions in several alkali halides including $NaCl$. Some of the photochemical experiments on $NaCl$ have been repeated and these are discussed in Chapter IV.

Summary

This chapter by no means covered the entire field of color centers. Most of the known trapped electron and trapped hole centers and a few impurity centers were described. Emphasis was placed on optical absorption since this is the tool for the present study. Absorption studies aid in the determination of a center's structure, energy states, and roles in reactions. Another important tool for structural

determination, the EPR study, was omitted for the sake of brevity.

The glossary of centers in Table 1.1 should be helpful for the chapters to follow.

Scope of Thesis

The following chapters will describe and interpret optical absorption spectroscopy experiments designed to study energy states of the M center in NaCl. Similar M-center studies have already been performed in KCl,²³ KCN,¹ KBr,¹ NaF³ and KI.³² As has already been pointed out, an anion effect has been observed in the $M_2'-M_2$ band splitting. Extension of M-center studies to NaCl means that there are now two alkali chloride salts from which cation effects can begin to be studied.

In addition to the M-center study, energy states of some other trapped electron centers in NaCl are determined. The nature of the interaction between various centers under a variety of conditions is also investigated.

Table 1.1 Glossary of Centers* in Alkali Halide Crystals and a Listing of the Bands Associated with the Centers

Center	Description of Center; Listing of Bands Associated with Center
$\alpha(F^+)^{**}$	anion vacancy; α band
F	electron trapped in an anion vacancy; β , F, K, L_1 , L_2 and L_3 bands
H	halogen molecular ion, X_2^- , occupying a single anion vacancy; H band
$M(F_2)$	two electrons occupying two adjacent anion vacancies, i.e., an F center dimer; M_1 , M_2 , M_3 , M_4 and M_L bands
$M^+(F_2^+)$	one electron shared by two adjacent anion vacancies, i.e., an ionized M center; one M^+ band in near IR and several M^+ bands at shorter wavelengths
$N_1(F_4)$	four electrons occupying four neighboring anion vacancies in a parallelogram array; N_1 band
$N_2(F_4)$	four electrons occupying four neighboring anion vacancies in a tetrahedral array; N_2 band
OH^-	an impurity hydroxide ion occupying an anion vacancy; OH^- band
$R(F_3)$	three electrons occupying an equilateral triangular array of three anion vacancies, i.e., an F center trimer; R_1 , R_2 , R_B , R_F , R_K , R_M and R_N bands

Table 1.1 (continued)

Center	Description of Center; Listing of Bands Associated with Center
$U(H_S^-)$	a substitutional hydride ion; U band
$U_1(H_i^-)$	an interstitial hydride ion; U_1 band
$U_2(H_i^\circ)$	an interstitial hydrogen atom; U_2 band
V_K	halogen molecular ion, X_2^- , occupying two adjacent anion vacancies; V_K band
V_1	H center with an alkali metal ion different from the host as nearest neighbor; V_1 band

*This is not an exhaustive listing of centers.

**In parenthesis is given the alternate name for the center.

CHAPTER II

OPTICALLY INDUCED ANISOTROPY

M-Center Anisotropy

Introduction. In the previous chapter M-center transitions responsible for various absorption bands were labeled both by molecular orbital and by group theoretical language. This chapter will describe how M-center absorption bands may be identified with particular electronic transitions by means of group theory, selection rules, and polarized light measurements. Much detail is presented on polarized light measurements to ensure a complete and logical development of the thesis. For the reader's convenience, Tables 2.2 and 2.3, "Anisotropy Glossary" and "Expected M- and R⁺-center Anisotropies", respectively, are presented at the end of this chapter.

Group Theory and Selection Rules. Application of group theory to a system having D_{2h} symmetry, such as the M center, predicts that the M center should have the following electronic energy states: A_{1g}, B_{1g}, B_{2g}, B_{3g}, A_{1u}, B_{1u}, B_{2u} and B_{3u}. Optical transitions between electronic energy states may occur by electric dipole, electric quadrupole, or magnetic dipole mechanism. Electric dipole transitions are, in general, far more intense than the other two.

The probability for an electronic transition is proportional to the square of the transition moment. For an electric dipole transition, the transition moment, r_{mk} , is given by Equation (2.1) below:

$$r_{if} = \int \psi_f^* e \bar{r} \psi_i dT \quad (2.1)$$

where ψ_i and ψ_f are the initial and final states, respectively, and

$\vec{e}r$ is the electric dipole moment vector.³⁶

In order for the transition moment to be nonzero the integrand in Equation (2.1) must transform as the completely symmetrical A_{1g} representation. The above requirement is a selection rule for determining allowed electric dipole transitions. The rule forbids $g \rightarrow g$ and $u \rightarrow u$ transitions as these would result in an integrand of u symmetry.

Another selection rule for electronic transitions is that electron spin should not change, i.e., $\Delta S = 0$. Since the M center has a $^1A_{1g}$ ground state, only singlet to singlet transitions are allowed. Application of the selection rules to an $[011]$ oriented M center (cf Fig. 2.1) leads to the following allowed electric dipole transitions:

$^1A_{1g} \rightarrow ^1B_{1u}$ associated with the $[011]$ transition dipole

$^1A_{1g} \rightarrow ^1B_{2u}$ associated with the $[0\bar{1}1]$ transition dipole

$^1A_{1g} \rightarrow ^1B_{3u}$ associated with the $[100]$ transition dipole

In what follows, (hkl) represents a plane in a crystal. The Miller indices h , k and l are the reciprocal intercepts of the plane on the x , y and z axes, respectively, reduced to the smallest integers. Planes equivalent by symmetry are denoted by curly brackets around Miller indices; the faces of a cube are $\{100\}$ planes. A direction is specified by square brackets about the Miller indices of the plane to which the line is perpendicular. Thus $[100]$ denotes the direction perpendicular to the (100) plane. A full set of equivalent planes is represented by angular brackets about Miller indices; face diagonals of a cube are $\langle 110 \rangle$ directions and are perpendicular to $\{110\}$ planes.

Figure 2.1. The Six Possible Face Diagonal Directions along which M Centers can be Oriented

There are six such $\langle 110 \rangle$ directions and the M center, for example, may be oriented in any one of the six directions.

Interaction between an electric vector of light and an optical transition dipole is proportional to $\cos^2 \theta$, where θ is the angle between the two vectors. Absorption of light, associated with a particular transition, will therefore be greatest when the electric vector of light is parallel to the transition dipole.

Terminology. In this section the terminology of anisotropy studies of M centers is defined. Consider a sample containing M centers of uniform density and completely aligned in the $[011]$ direction. If such a sample were to be measured with light moving along the negative x direction and polarized in the $[011]$ direction, only M-center absorptions associated with $[011]$ transition dipoles will appear. The band shape function for a M-center spectrum associated only with a $[011]$ transition dipole is designated $\alpha (\lambda)$ or α . The principal absorption of the α spectrum is the M_1 band associated with a ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transition.

If the measuring light is moving along the negative x-direction and is polarized in the $[0\bar{1}1]$ direction, only M-center absorptions associated with a $[0\bar{1}1]$ transition dipole will appear. The band shape function for M-center absorptions related to $[0\bar{1}1]$ dipole transitions is designated $\beta (\lambda)$ or β . The principal absorption of the β spectrum is the M_2 band associated with a ${}^1A_{1g} \rightarrow {}^1B_{2u}$ transition.

If the measuring light is moving along the negative y direction and is polarized along the $[100]$ direction, only M-center absorptions associated with a $[100]$ transition dipole will appear. The band shape

function for M-center absorptions related to [100] dipole transitions is labeled $\gamma(\lambda)$ or γ . The principal absorption of the γ spectrum is the M_2' band associated with the $^1A_{1g} \rightarrow ^1B_{3u}$ transition.

In summary, α , β , and γ are the band shape functions of [011], $[0\bar{1}1]$ and [100] dipole transitions respectively, of [011] oriented M centers. All three band shape functions may be determined on a single crystal, if the crystal has a uniform density of M centers. Uniform density of M centers may be present in an additively colored crystal.

Because of insufficient F-center concentrations in additively colored NaCl crystals, it was necessary to use x-ray colored crystals. Crystals colored by x rays are not uniformly colored along the crystal sides and cannot, therefore, be measured with light moving along the negative y direction, as is necessary to obtain the γ spectrum. Therefore a γ spectrum cannot be measured on the crystal containing [011] oriented M centers, used for the procurement of the α and β spectra. It is, therefore, necessary to combine the [010] M band dichroism from an [010] bleaching experiment with the 011 M band dichroism from an [011] bleaching experiment by Equation 2.20, presented later in this chapter. The [011] dichroism or anisotropy is the absorption spectrum measured with [011] polarized light minus the absorption spectrum measured with $[0\bar{1}1]$ light. Polarization of light in the [011] direction indicates that the electric vector of the light is in the [011] direction.

An absorption coefficient, K , is defined by the equation:

$$I = I_0 \exp (-Kx) \quad (2.2)$$

where I_0 and I are the intensities of entering and exiting beams respectively, and x is sample thickness. K is related to the measured absorbance, A , by the relation:

$$K = (2.303)(A/x) \quad (2.3)$$

The absorption coefficient unlike the absorbance is independent of sample thickness for a uniformly colored sample. A subscript on the absorption coefficient indicates the polarization of the measuring light, while a superscript gives a description of the state of the M centers in the sample. Thus $K_{[011]}^{[0\bar{1}1]M_1}(\lambda)$ is the absorption coefficient at wavelength λ , for measuring light polarized in the $[011]$ direction and for a sample which had been irradiated with $[0\bar{1}1]$ polarized M_1 -band light to produce a $[011]$ preferential distribution of M centers. The absorption coefficient, $K_{[011]}(\lambda)$ in terms of M -center concentrations is:

$$K_{[011]}(\lambda) = \alpha(\lambda) \sum_{i=1}^{i=6} m_i \cos^2 \theta_{i\alpha} + \beta(\lambda) \sum_{i=1}^{i=6} m_i \cos^2 \theta_{i\beta} + \gamma(\lambda) \sum_{i=1}^{i=6} m_i \cos^2 \theta_{i\gamma} \quad (2.4)$$

where m_i is the concentration of M centers having one of the six possible directions (cf Fig. 2.1) and $\theta_{i\beta}$ is the angle between a β transition dipole of an i -directed M center and the $[011]$ electric vector of the measuring light.

For a dichroic sample, the dichroism or optical anisotropy is equal to the difference between two spectra measured with light propagating along the same direction but polarized along mutually

perpendicular directions, e.g. $K_{[011]} = K_{[011]} - K_{[0\bar{1}1]}$. The analyses of M- and R-band anisotropies which follow are necessary for interpretations, in later chapter, of dichroic data. Analyses are similar to those of Susman,⁵ Konrad,⁷ and Gudat,³⁷ although a few improvements have been made in terminology and R^+ -center anisotropy analyses have been included. For the sake of brevity, derivations of M- and R^+ -center distributions and absorption coefficients have been omitted in the following sections and are instead included in the Appendix.

<011> Polarized Light Measurements. The M centers formed either thermally or photochemically with ordinary light are randomly oriented. There are six <011> directions in which an M center may be oriented and these directions are numbered 1 to 6 in Figure 2.1. Random orientation of M centers indicates that the concentration of M centers having a particular direction will be equal to the concentration of M centers having any other particular direction and this concentration shall be called m_0 per cm^3 . The absorption coefficients measured with [011] and with $[0\bar{1}1]$ polarized light, are:

$$K_{[011]}^{[\text{ran}]} = K_{[0\bar{1}1]}^{[\text{ran}]} = (2\alpha + 2\beta + 2\gamma)m_0 \quad (2.5)$$

Likewise the absorption coefficient measured with unpolarized light is equal to the same value. The M-band dichroism, $K_{[011]}^{[\text{ran}]} - K_{[0\bar{1}1]}^{[\text{ran}]}$, is thus zero throughout the entire spectrum.

Irradiation of a sample containing randomly oriented M centers with [011] polarized M_1 -band light moving along the negative x-direction results in the following distribution:

$$m_2 > m_3 = m_4 = m_5 = m_6 > m_1 \quad (2.6)$$

The absorption coefficients, $K_{[011]}^{[011]M_1}$ and $K_{[0\bar{1}1]}^{[011]M_1}$, and anisotropy,

$\Delta K_{[011]}^{[011]}$, are:

$$K_{[011]}^{[011]M_1} = \alpha(m_1 + m_3) + \beta(m_2 + m_3) + 2\gamma m_3 \quad (2.7)$$

$$K_{[0\bar{1}1]}^{[011]M_1} = \alpha(m_2 + m_3) + \beta(m_1 + m_3) + 2\gamma m_3 \quad (2.8)$$

$$\Delta K_{[011]}^{[011]M_1} = (\beta - \alpha)(m_2 - m_1) \quad (2.9)$$

By the above convention for dichroism, $K_{[011]} - K_{[0\bar{1}1]}$, the dichroism, of the M_2 , M_3 and all other bands of the β spectrum is positive while the dichroism of the M_1 , M_4 and all other bands of the spectrum is negative.

If all of the M centers occupying directions excited by $[011]$ polarized M_1 -band irradiation reorient to direction 2, where M centers are not excited by such irradiation, the concentration of M centers having direction 2 is $6m_0$. The absorption coefficients and anisotropy, therefore, are:

$$K_{[011]}^{[011]M_1} = 6\beta m_0 \quad (2.10)$$

$$K \frac{[011]M_1}{[0\bar{1}1]} = 6\alpha m_0 \quad (2.11)$$

$$\Delta K \frac{[011]M_1}{[011]} = (\beta - \alpha)6M_0 \quad (2.12)$$

During complete reorientation then, for an unchanging total M-center concentration, $K \frac{[011]M_1}{[011]}(M_1)$ decreases from $2\alpha m_0$ to 0 while $K \frac{[011]M_1}{[0\bar{1}1]}(M_1)$ increases from $2\alpha m_0$ to $6\alpha m_0$.

If all of the M centers occupying excited directions are instead annihilated, the population of direction 2 remains $2\alpha m_0$ and the absorption coefficients and anisotropy are:

$$K \frac{[011]M_1}{[011]} = 2\beta m_0 \quad (2.13)$$

$$K \frac{[011]M_1}{[0\bar{1}1]} = 2\alpha m_0 \quad (2.14)$$

$$\Delta K \frac{[011]M_1}{[011]} = (\beta - \alpha)(2m_0) \quad (2.15)$$

By the annihilation mechanism then, $K \frac{[011]M_1}{[011]}(M_1)$ decreases from $2\alpha m_0$ to 0 while $K \frac{[011]M_1}{[0\bar{1}1]}(M_1)$ does not change. The resultant dichroism,

$(\beta - \alpha)(2m_0)$, is one-third of the value obtained for complete reorientation.

<010> Polarized Light Measurements. For a sample containing M centers equally populating all six directions the absorption coefficients measured with [010] and [001] polarized light are the same as those measured with [011] and [0 $\bar{1}$ 1] light, and there is no [010] dichroism.

Irradiation of the sample with [010] polarized M₁-band light moving along the negative x direction results in the following distribution:

$$m_3 = m_4 > m_1 = m_2 = m_5 = m_6 \quad (2.16)$$

Irradiation with [011] polarized M₂ or M₃-band light is not effective, as M centers in all six directions are excited. The absorption coefficients, $K_{\frac{[010]M_1}{[010]}}$ and $K_{\frac{[010]M_1}{[001]}}$, and anisotropy, $\Delta K_{\frac{[010]M_1}{[010]}}$, are:

$$K_{\frac{[010]M_1}{[010]}} = (2\alpha + 2\beta)m_1 + 2\gamma m_3 \quad (2.17)$$

$$K_{\frac{[010]M_1}{[001]}} = (\alpha + \beta + 2\gamma)m_1 + (\alpha + \beta)m_3 \quad (2.18)$$

$$\Delta K_{\frac{[010]M_1}{[010]}} = (2\gamma - \alpha - \beta)(m_3 - m_1) \quad (2.19)$$

The [010] anisotropy thus contains absorptions of the α , β , and γ spectra. By combining [011] and [010] anisotropies in the following way the absorptions of the γ spectrum may be obtained free from the overlapping β spectrum:

$$\frac{(\Delta K \frac{[010]M_1}{[010]} + G\Delta K \frac{[011]M_1}{[011]})}{2} = (\gamma - \alpha)(m_3 - m_1) \quad (2.20)$$

where $G = \frac{(\Delta K \frac{[010]M_1}{[010]}(M_1)/\Delta K \frac{[011]M_1}{[011]}(M_1))}{\Delta K \frac{[011]M_1}{[011]}(M_1)}$. In such a combination spectrum

then, positive absorptions are associated with the γ spectrum while negative absorptions are associated with the α spectrum.

R⁺-Center Anisotropy

Introduction. An analysis was made of R⁺-center anisotropy since such anisotropy was observed to complicate the M-center anisotropic spectra of various polarized light experiments in NaCl. R-center anisotropy, on the other hand, was not observed in present studies. Another reason for preferring an anisotropy analysis of the R⁺ center over that of the other C_{3v} system, the R center, is that the absorption spectrum of R⁺ centers is simpler than that of R centers.

A complicating aspect of the R center absorption spectrum is that ²E → ²E transitions are allowed for transition dipoles in the R center plane (xy) as well as for z transition dipoles. Thus light associated with the ²E → ²E transition of the R center may interact with all possible R-center transition dipoles.

The R⁺-center absorption spectrum consists of ¹A₁ → ¹E transitions, allowed only for transition dipoles in the R⁺-center plane and ¹A₁ → ¹A₁ transitions, allowed only for z transition dipoles. Thus light associated with ¹A₁ → ¹A₁ transitions of the R⁺ center interacts only with z-transition dipoles (along <111> directions) of R⁺ centers.

Anisotropies of the absorption spectrum of the R⁺ center in NaF have been observed in NaF at 520 nm and 302.5 nm, associated with

${}^1A_1 \rightarrow {}^1E$ and ${}^1A_1 \rightarrow {}^1A$ transitions, respectively.⁷ The longer wavelength absorption will be called the R_r^+ band while the shorter wavelength absorption will be called the R_v^+ band. Before presenting the analysis of polarized light experiments on the R^+ center, the pertinent terminology must be introduced.

Terminology. There are eight mechanically distinct directions of the R^+ center designated a, b, c, d, a', b', c' and d' with $\langle 111 \rangle$ directions as principal axes. There are four such $\langle 111 \rangle$ directions and each of these serves as the principal axis for a pair of optically indistinguishable orientations, e.g. b and b' . Figure 2.2 on the following page shows four optically distinguishable orientations as well as orientation b' which is optically indistinguishable from orientation b . In what follows r_a will indicate the R^+ -center concentration having orientation a .

It will be considered that transition dipole vectors within the R^+ -center plane are parallel and perpendicular to the triangle edges of the R^+ center, i.e., in $\langle 011 \rangle$ and $\langle 112 \rangle$ directions. Spectra $\delta, \epsilon,$ and ζ are associated with $\langle 111 \rangle, \langle 011 \rangle,$ and $\langle 112 \rangle$ transition dipole vectors respectively of the R^+ center. The δ spectrum of the R^+ center is made up of ${}^1A_1 \rightarrow {}^1A_1$ transitions while the ϵ and ζ spectra are made up of ${}^1A_1 \rightarrow {}^1E$ transitions.

Table 2.1 presents the interactions - values of $\cos^2 \theta$ - between various electric vectors of light and all possible transition dipole vectors of the R^+ center. This table was useful for the computation of absorption coefficients of R^+ -center bands in polarized light experiments which are summarized below.

(111)

(1 $\bar{1}\bar{1}$)

(1 $\bar{1}$ 1)

(11 $\bar{1}$)

Figure 2.2. Four Optically Distinguishable Orientations, a, b, c and d and One Orientation, b', Optically Indistinguishable from b.

Table 2.1. Interactions, i.e. Values of $\cos^2\theta$, between Various Electric Vectors of Light and All Possible Transition Dipole Vectors of the R^+ Center

Dipole Direction	R^+ -center Orientations (cf Fig. 2.2)	Electric Vector Direction			
		[011]	[011]	[010]	[001]
[011]	c, d, c', d'	1	0	1/2	1/2
[0 $\bar{1}$ 1]	a, b, a', b'	0	1	1/2	1/2
[101]	b, b'	1/4	1/4	0	1/2
[10 $\bar{1}$]	a, c, d, a', c', d'	1/4	1/4	0	1/2
[110]	b, b'	1/4	1/4	1/2	0
[1 $\bar{1}$ 0]	c, d, c', d'	1/4	1/4	1/2	0
[11 $\bar{2}$]	a, a'	1/12	3/4	1/6	2/3
[1 $\bar{2}$ 1]	a, a'	1/12	3/4	2/3	1/6
[2 $\bar{1}$ 1]	a, a'	1/3	0	1/6	1/6
[1 $\bar{1}$ 2]	b, b'	1/12	3/4	1/6	2/3
[12 $\bar{1}$]	b, b'	1/12	3/4	2/3	1/6
[211]	b, b'	1/3	0	1/6	1/6
[1 $\bar{1}$ 2]	c, c'	3/4	1/12	1/6	2/3
[121]	c, c'	3/4	1/12	2/3	1/6
[21 $\bar{1}$]	c, c'	0	1/3	1/6	1/6
[112]	d, d'	3/4	1/12	1/6	2/3
[1 $\bar{2}$ 1]	d, d'	3/4	1/12	2/3	1/6
[2 $\bar{1}$ 1]	d, d'	0	1/3	1/6	1/6
[111]	a, a'	2/3	0	1/3	1/3
[1 $\bar{1}$ 1]	b, b'	2/3	0	1/3	1/3
[1 $\bar{1}$ 1]	c, c'	0	2/3	1/3	1/3
[11 $\bar{1}$]	d, d'	0	2/3	1/3	1/3

<011> Polarized Light Experiments. Consider a sample that contains R^+ centers equally populating all eight orientations with an R^+ -center concentration of r_0 per cm^3 . Absorption coefficients of the R^+ -center spectrum, $K_{[011]}^{[ran]}$ and $K_{[0\bar{1}1]}^{[ran]}$, and dichroism, $\Delta K_{[011]}^{[ran]}$, are:

$$K_{[011]}^{[ran]} = K_{[0\bar{1}1]}^{[ran]} = [(8/3)\delta + 8\epsilon + 8\zeta]r_0 \quad (2.21)$$

$$\Delta K_{[011]}^{[ran]} = 0 \quad (2.22)$$

Next consider that the sample is irradiated with R_V^+ -band light moving in the negative x-direction and polarized in the $[0\bar{1}1]$ direction. This results in the following R^+ -center distribution:

$$r_a = r_b > r_c = r_d \quad (2.23)$$

Since orientation i is optically indistinguishable from i' , the concentrations of orientations i and i' will be equal to one another regardless of the type of light used. It is shown in the Appendix that the absorption coefficients and dichroism after the above irradiation are:

$$K_{[011]}^{[0\bar{1}1]R_V^+} = r_a[(8/3)\delta + 2\epsilon + 2\zeta] + r_c[6\epsilon + 6\delta] \quad (2.24)$$

$$K_{[0\bar{1}1]}^{[011]R_V^+} = r_a[6\epsilon + 6\delta] + r_c[(8/3)\delta + 2\epsilon + 2\zeta] \quad (2.25)$$

$$\Delta K_{\begin{smallmatrix} [0\bar{1}1] \\ [011] \end{smallmatrix}} = (r_a - r_c) [(8/3)\delta - 4\epsilon - 4\zeta] \quad (2.26)$$

By the above convention for dichroism, i.e., $\Delta K_{[011]} = K_{[011]} - K_{[0\bar{1}1]}$, The R_V^+ band of the δ spectrum has positive dichroism, while the R_R^+ band of the ϵ, ζ spectra has negative dichroism.

It may be shown that the same results would be obtained as the above if the crystal were instead irradiated with R_R^+ -band light moving in the negative x-direction and polarized in the $[011]$ direction.

<010> Polarized Light Experiments. An equal distribution of R^+ centers among all of their possible orientations results in zero $[010]$ and zero $[011]$ anisotropies. R_V^+ - or R_R^+ -light moving in the negative x-direction and polarized in the $[010]$ direction interacts equally with all R^+ -center orientations resulting in no changes of the zero $[010]$ and zero $[011]$ anisotropies.

Summary

Tables 2.2 and 2.3 help to summarize the past chapter and may aid the reader in future chapters. "Anisotropy Glossary" is presented in Table 2.2 and "Expected M- and R^+ -center Anisotropies" is presented in Table 2.3.

Table 2.3 indicates that the α and β spectra of the M center may be determined from the $[011]$ anisotropy resulting from irradiation with $[011]$ polarized M_1 -band light. In order to determine the γ spectrum of the M center it is necessary to combine the $[011]$ anisotropy of an $\langle 011 \rangle$ polarized light experiment with the $[010]$ anisotropy of an $\langle 010 \rangle$ polarized light experiment.

[011] R^+ -center anisotropy may appear with [011] M-center anisotropy in an $\langle 011 \rangle$ polarized light experiment if R^+ centers are present and excited by the light. [010] R^+ -center anisotropy, however, is not expected from a $\langle 010 \rangle$ polarized light experiment.

Table 2.2 Anistropy Glossary

Symbol	Definition
1 - 6	particular $\langle 011 \rangle$ M-center orientations by Fig. 2.1
a-d, a'-d'	particular geometric orientations of R^+ centers defined by Fig. 2.2
$\begin{matrix} [011]M_1 \\ K \\ [0\bar{1}1] \end{matrix}$	absorption coefficient measured with $[0\bar{1}1]$ polarized light of a sample which had been irradiated with $[011]$ polarized M_1 -band light
$\begin{matrix} [011]M_1 \\ \Delta K \\ [011] \end{matrix}$	$\begin{matrix} [011]M_1 \\ K \\ [011] \end{matrix} - \begin{matrix} [011]M_1 \\ K \\ [0\bar{1}1] \end{matrix}$
m_1	concentration of M centers in orientation 1
r_a	concentration of R^+ centers in orientation a
R_r^+	long wavelength R^+ band associated with $^1A_1 \rightarrow ^1E$ transition of R^+ centers

Table 2.2. (continued)

Symbol	Definition
R_V^+	short wavelength R^+ band associated with $^1A_1 \rightarrow ^1A$ transition of R^+ centers (z dipole axis)
$\alpha(\lambda)$	spectrum containing M-center absorptions, associated with $[011]$ transition dipoles of $[011]$ directed M centers, e.g. M_1 band
$\beta(\lambda)$	spectrum containing M-center absorptions associated with $[0\bar{1}1]$ transition dipoles of $[011]$ directed M centers, e.g. M_2 band
$\gamma(\lambda)$	spectrum containing M-center absorptions associated with $[100]$ transition dipoles of $[011]$ directed M centers, e.g. M_2' band
$\delta(\lambda)$	spectrum containing R^+ -center absorptions associated with principal axis (z) transition dipoles along $\langle 111 \rangle$ directions, e.g. R_V^+ band

Table 2.2. (continued)

Symbol	Definition
$\epsilon(\lambda)$	spectrum containing R^+ -center absorptions associated with in-plane transition dipoles along $\langle 011 \rangle$ directions, e.g. R_r^+ band
$\zeta(\lambda)$	spectrum containing R^+ -center absorptions associated with in-plane transition dipoles along $\langle 112 \rangle$ directions, e.g. R_r^+ band

Table 2.3. Expected M- and R⁺-center Anisotropies

Anisotropy	Composition of Anisotropy
$\Delta K_{\begin{smallmatrix} [011]M_1 \\ [011] \end{smallmatrix}}, \Delta K_{\begin{smallmatrix} [\bar{0}\bar{1}1]M_2 \\ [011] \end{smallmatrix}}$	$(m_2 - m_1) [\beta - \alpha]$
$\Delta K_{[010]}$	$(m_3 - m_1) [2\gamma - \beta - \alpha]$
$(\Delta K_{\begin{smallmatrix} [010]M_1 \\ [010] \end{smallmatrix}} + G\Delta K_{\begin{smallmatrix} [011]M_1 \\ [011] \end{smallmatrix}})/2$	$(m_3 - m_1) [\gamma - \alpha]$
$\Delta K_{\begin{smallmatrix} [011]R_r^+ \\ [011] \end{smallmatrix}}, \Delta K_{\begin{smallmatrix} [\bar{0}\bar{1}1]R_v^+ \\ [011] \end{smallmatrix}}$	$(r_a - r_c) [(8/3)\delta - 4\epsilon - 4\zeta]$
$\Delta K_{\begin{smallmatrix} [010]R_r^+ \\ [010] \end{smallmatrix}}, \Delta K_{\begin{smallmatrix} [010]R_v^+ \\ [010] \end{smallmatrix}}$	0

CHAPTER III

EXPERIMENTAL DETAILS

Source of Crystals

The NaCl used in these studies was obtained as single crystals of $1/2 \times 1/2 \times 1$ in.³ size from the Harshaw Chemical Company. The NaCl crystals are transparent between 180 and 6000 nm except for an OH⁻ absorption at 185 nm with a 13 cm^{-1} absorption coefficient on a slowly rising background. The color center absorptions studied are at somewhat lower wavelength and do not overlap this band. From the intensity of the OH⁻ band it is estimated that the OH⁻ concentration is ca. 0.01 mol %. For the calculation of hydroxide concentration, half-width data of Kerkhoff³⁵ was used and it was assumed that the oscillator strength of OH⁻ in NaCl is the same as that of OH⁻ in KCl.

Cryostat

In an experiment, a platelet $1/2$ in. x $1/2$ in. x ca. 1 mm. was cleaved from a Harshaw NaCl crystal and mounted to a stainless steel cryostat. The cryostat was a Dewar type of 50 mm. o.d. x 50 cm. length with an inner coolant well of 30 mm. o.d. A crystal mounting block made of copper was attached to the bottom of the inner coolant well. The sample was clamped over a $5/16$ in. wide x $11/32$ in. high aperture of the mounting block. An o-ring seal between top and bottom halves of the cell permits rotation so that the crystal may be made to face either a Be window for x-raying or aligned with a pair of U.V. quality quartz windows for optical irradiation or measurement.

Temperature Measurement and Control

The sensing junction of a copper-constantan thermocouple was

attached, near the crystal, to the mounting block. Good thermal contact between the crystal and mounting block was assured by a sizable overlap of the two. Temperatures were monitored by measuring thermally induced voltages with a Rubicon thermocouple potentiometer.

Samples were cooled by an appropriate coolant contained in the coolant well. Table 3.1 indicates the various experimental temperatures and the methods of obtaining them. For some storage purposes a "Frigid Tip" portable cooling probe, manufactured by Blue M Electric Company, was inserted into the well, which provided a storage temperature of $245 \pm 5^\circ\text{K}$.

Sample Coloring

Initially attempts were made to color NaCl with Na vapor (additive coloring) which is described in Chapter IV. However, even after more than one full day in Na vapor at ca. 560°C , crystals were weakly colored, e.g., the maximum absorbance of the F band at 80°K was less than one unit for a crystal 1.6 mm. thick. Only a small M-center concentration could be expected from such a small F-center concentration. Because of insufficient F-center concentrations in additively colored NaCl crystals it was necessary to use x-ray colored crystals. Samples were x irradiated with a Machlett OEG-50 tungsten target x-ray tube operated at 50 Kv and 50 ma. The x rays were filtered by the Be windows of the x ray tube (1 mm.) and the cryostat (0.25 mm.). The crystals were 35 - 40 mm. from the focal point of the x-ray beam. Intense F-band absorptions could be produced with short x irradiations at 196°K .

Microscopic examination indicates that the color center density is greatest within the first 0.1 mm. depth of the crystal from the

Table 3.1. Methods of Temperature Control Used in Experiments

Sample Temperature	Substance in coolant well
$66^{\circ} \pm 0.5^{\circ}\text{K}$	liquid N_2 pumped down to triple point pressure of 94 mm., $T_{\text{TP}} = 63.3^{\circ}\text{K}$
$80^{\circ} \pm 0.5^{\circ}\text{K}$	liquid N_2 at normal boiling point of 77.4°K
$110^{\circ} \pm 0.5^{\circ}\text{K}$	liquid N_2 added to well in small increments
$197^{\circ} \pm 0.5^{\circ}\text{K}$	crushed dry ice, at sublimation point of 194.7°K , packed solidly
$274^{\circ} \pm 0.5^{\circ}\text{K}$	brass tube containing ice bath
$298^{\circ} \pm 0.5^{\circ}\text{K}$	brass tube containing water at 298°K
$>298^{\circ}\text{K}$	electric heater

x rayed face. This is confirmed by calculations which indicate that approximately one-third of the x ray energy striking a crystal is absorbed within the first 0.1 mm. depth of the crystal from the x rayed face. It is in this region that most thermally and photochemically induced F-center aggregation takes place as centers are much closer to one another than elsewhere in the crystal. Lack of uniformity of color along the direction of irradiation made it necessary to perform the [100] polarized measurements on a separate crystal.

Spectrophotometer

All optical density measurements were taken on a Cary 14 PMR recording spectrophotometer. According to Applied Physics Corporation specifications, photometric accuracy is ± 0.002 units up to one absorbance unit and ± 0.005 units up to two absorbance units. Reproducibility of optical density is within 0.002 absorbance units. Stray light is less than $10^{-4}\%$ between 240 and 500 nm and less than 0.1% below 200 nm. This makes possible accurate high absorbance measurements. The highest absorbances measured in the experiments, between 3 and 4 units, were higher than the recording range of 0 to 2 units. To record these high absorbances it was necessary to place Kodak Wratten gelatin neutral density filters into the reference beam of the spectrophotometer.

With a Hamamatsu TV Co. R 456 multiplier phototube (S-20 response, quartz envelope), it was possible to scan the M_1 band at 716 nm as well as the M_2 and higher M bands in the visible and UV regions with a single detector. Most phototubes are insensitive in the M_1 -band region and a PbS detector has to be used instead. Use of the R 456 photomultiplier

tube in place of the PbS detector results in less noise in the spectrum and greater reproducibility.

For the purpose of monitoring color center concentrations, spectra were measured at 80°K, as absorptions at this low temperature are narrow and intense.

Optical Irradiation

Optical irradiation was performed on optical benches equipped with either a G.E. AH-6 high pressure Hg arc, a G.E. AH-4 medium pressure Hg arc or G.E. 750 W tungsten projection lamp. Light of a desired wavelength was isolated by a Bausch and Lomb interference filter with back-up Corning or Jena colored glass filters to screen out unwanted light of other orders. When light of a broader wavelength region was desired, one or more colored glass filters was used without an interference filter. For isolating 300 and 318 nm light, a Bausch and Lomb grating monochromator was used.

A summary of combinations of filters and light sources and purposes for which they were used is shown in Table 3.2. In the second column of the table is listed λ/nm , the average wavelength of light in nanometers (nm) transmitted through a filter combination and $\Delta W_{0.1}$, the region in which the transmittance of a filter combination is greater than 10% of its maximum value. Both λ/nm and $\Delta W_{0.1}$ were determined from a spectrum of the filter combination measured on a Cary 14 PMR spectrophotometer.

Polarized Light Experiments

Polarizer Assembly. Polarized light experiments were made using a Glan Type A polarizing prism manufactured by Karl Lambrecht. This

Table 3.2. Combinations of Filters and Light Sources and Their Purposes in Optical Irradiation Experiments

Combination of Filters and Light Source	λ/nm $\Delta W_{0.1}$	Purpose
Corning 3-69 + 7-69 + Jena RG 715 + G.E. 750 W tungsten lamp	880 $\Delta W_{0.1} = 340 \text{ nm}$	M ₁ -band excitation to effect M-center alignment
Corning 3-69 + 4-76 + heat abs 4072 + G.E. 750 W tungsten lamp	570 $\Delta W_{0.1} = 137 \text{ nm}$	R ₁ -band excitation
560 nm Int filter + Corning 1-69 + 3-69 + heat abs 4072 + G.E. 750 W tungsten lamp	566 $\Delta W_{0.1} = 31 \text{ nm}$	F'-band bleaching
530 nm Int Filter + Corning 1-69 + 3-72 + heat abs. 4072 + G.E. 750 W tungsten lamp	527 $\Delta W_{0.1} = 27 \text{ nm}$	F-band excitation for M-band formation
500 nm Int filter + Corning 1-69 + 3-72 + heat abs. 4072 + G.E. 750 W tungsten lamp	503 $\Delta W_{0.1} = 22 \text{ nm}$	F- and M ₂ -band excitation for simultaneous M-center formation & alignment
Hg-405 Int Filter + Corning 4-97 + G.E. AH-4 Hg arc	405 $\Delta W_{0.1} = 34 \text{ nm}$	M ₃ -band irradiation for purpose of aligning M centers at low temp. (80°K)
Bausch and Lomb Grating Monochromator set at 300 or 318 nm + G.E. AH-6 Hg arc	300 or 318 $\Delta W_{0.1} = 6 \text{ nm}$	M _L -band excitation to ionize M centers

polarizer was selected because it has good transmitting and polarizing capability in the UV region (down to 215 nm), as well as in the visible and near IR regions. The polarizer was mounted on a rotatable brass ring. The ring was notched every 45° so that it could be accurately positioned with a spring detent mechanism. The polarizer assembly was attached by a brass collar to the cryostat in such a way that the polarizer faces are perpendicular to the beams of measuring or exciting light. The alignment of the polarizer with respect to the crystal was checked with a low power telescope. For spectral measurements another Glan Type A prism was inserted in the reference beam of the Cary 14 PMR spectrophotometer to compensate for the attenuation of the sample beam by the polarizer.

Spectral Data. Before coloring a crystal in an $\langle 011 \rangle$ polarized light experiment, spectra were taken at appropriate temperatures with $[011]$ and with $[0\bar{1}1]$ polarized light. Such a spectrum served as a baseline (B) and was subtracted from a subsequent spectral curve (C) to obtain the absorption spectrum (A), i.e., $A = C - B$. The $\langle 011 \rangle$ anisotropy $\Delta A_{[011]}$, then in terms of experimental data is:

$$\Delta A_{[011]} = (C_{[011]} - B_{[011]}) - (C_{[0\bar{1}1]} - B_{[0\bar{1}1]}) \quad (3.1)$$

Similar steps were taken in the procurement of the $\langle 010 \rangle$ anisotropy, $\Delta A_{[010]}$.

There apparently are wavelength independent shifts of up to 0.015 absorbance units in the dichroic spectra measured at various temperatures. Anisotropies shown in the figures have been compensated for these shifts. In order to confirm the +0.015 absorbance unit shift of

the 80°K anisotropy obtained in Experiment 14, 0.015 absorbance unit was subtracted from the anisotropy, and the compensated anisotropy was normalized to an M_1 -band absorbance of 1.00 absorbance unit. The normalized spectrum was almost exactly superimposable with a normalized M-band spectrum at 80°K obtained from the somewhat larger and unshifted dichroism produced by photochemical realignment at 80°K (Experiment 16). This confirmed the correctness of the constant +0.015 absorbance unit shift for the spectrum of Experiment 14.

Shifts may be due to small changes in the polarizer, crystal positions or the Cary 14 PMR spectrophotometer occurring after the baseline spectra were taken. Another possibility is that at 1700 nm, where the optical density for each polarized spectrum was zeroed, changes occurred in the dichroism of a broad band. It is unlikely that the shifts are due to crystal surface contamination as light scattering effects are not wavelength independent.

CHAPTER IV

EXPERIMENTAL RESULTS ON DEFECTS OTHER THAN THE M CENTER

Introduction

Before studying the M-center absorption spectrum of sodium chloride, it was necessary to perform experiments in order to develop techniques of sample preparation. It was important to investigate possible methods of F-center coloration, e.g., x-ray or additive coloration or U-band irradiation,³⁵ for efficient M-center production.

As a check of the literature⁹ on NaCl, the absorption band of the F-center was examined.

The M^+ band at 1020 nm was likewise examined as a check on results reported in the literature.²⁹ Even more important, a higher energy M^+ band was sought to enable comparison of the spectrum of the M^+ center with that of the H_2^+ molecular ion in the manner of Herman et al.¹⁴ (see Chapter I).

Another ionized center absorption, the R^+ band, was also examined. The R^+ center is important because it is an analogue of triangular H_3^+ ion, studied theoretically by Hirschfelder²¹ and because the spectrum of R^+ centers greatly overlaps the spectrum of M centers.²⁹ In order to study the spectrum of M centers, it was necessary to develop techniques for minimizing absorptions of R^+ centers in optical anisotropy studies.

Experiments in Additively Colored Crystals

Sample Preparation. Crystals of NaCl were heated at 560°C in the vapor of triply distilled sodium in sealed pyrex ampoules for 24 hours. The sealed pyrex ampoules, containing NaCl crystals, were

then quenched in petroleum oil. At the end of this treatment the crystals were blue, being more colored near the exterior than in the interior of the crystal.

A spectrum, shown in Figure 4.1, was then taken at 25°C of a typical 1.6 mm. thick plate cleaved from the interior of an additively colored crystal. The spectrum indicates that the blue color is primarily due to a complex of bands with a maximum absorbance of 0.45 units at ca. 600 nm. It has been shown^{38,39} that bands in the 600 nm spectral region of additively colored NaCl are associated with colloidal sodium. As Figure 4.1 shows, there is also an F band with a maximum absorbance of 0.20 units at 465 nm. Measurements of the F band will be described more fully later in this chapter.

The additively colored NaCl crystal was then held in a 600°C furnace for two minutes and quenched in CCl₄. Annealing and quenching resulted in removal of the 600 nm band complex and an increase in the F-band absorbance maximum from 0.20 to 0.65 units. Colloidal sodium had been converted into F centers. There was also a small (0.03 units) band lying at 700 nm (see Fig. 4.1). The band position appears to be independent of temperature. Independence of band position with temperature is a property of colloid absorptions,³⁸ but not of dispersed center absorptions. After longer periods in the furnace and quenching, the F band decreased, but the 700 nm band remained at about the same intensity. The inability to remove the 700 nm band, which would overlap the M₁ band if the latter were present, makes the additively colored NaCl crystals unsuitable for M-center studies.

F Band in Additively and in X-ray Colored NaCl. A spectrum of

the annealed additively colored crystal shown in Figure 4.1 was also taken at 80°K between 1500 and 190 nm. The most intense bands in the spectrum are the U band with a maximum absorbance of 3.1 units at 191 nm and the F band with a maximum absorbance of 0.89 units at 450 nm. Experiments on the U band, which is associated with substitutional hydride ion, will be discussed in the next section. There are also less intense absorptions at 225, 290 and 700 nm. The origin of the bands at 225 and 290 nm, labeled O_I and O_{II} bands, respectively, by Etzel,³⁸ is not known.

In order to determine parameters for the F band, the baseline was "compensated" for light scattering in the manner of Markham and Konitzer.⁴¹ The method of baseline compensation consists of drawing a straight line between the lowest points on either side. Band position and half-width values at 80°K of 450.0 ± 0.5 nm (2.755 ± 0.003 eV) and 0.290 ± 0.006 eV, respectively, were slightly different from the corresponding values of Markham and Konitzer⁴¹ of 449.5 nm (2.758 eV) and 0.278 ± 0.004 eV. High half-width has been noted previously for the F band in additively colored alkali halides and is thought to be a result of not quenching rapidly enough after coloration.⁴² No account could be taken of the unresolved K band on the high energy tail of the F band, either in the present studies or in those of Markham and Konitzer.⁴¹ Jacobs and Parsons⁴³ have shown that K-band subtraction does not affect the F-band half-width value at 80°K, but does alter half-width values at higher temperatures.

The F-center concentration in additively colored NaCl was calculated with the Dexter modification of Smakula's equation² using

Figure 4.1. Absorption Spectra of NaCl at 25°C: (a) After Additive Coloration with Sodium and (b) After a Subsequent Annealing in a 600°C Furnace and a Quenching in CCl_4

observed F-band parameters at 80°K. For the calculation it was assumed that the F band has unit oscillator strength and is Gaussian in shape. A value of 2×10^{16} F centers per cm^3 was obtained for the concentration. While adequate for absorption studies of F centers, the concentration appeared to be too low for the large M-center formation necessary for absorption studies of M centers.

The F band was also measured in a NaCl crystal which was x ray colored at 80°K. As a result of 25 minutes of x-irradiation, an F-band was produced with a maximum absorbance of 1.42 units at 450.0 ± 0.5 nm. There were no absorptions between 1800 and 550 nm indicating the absence of neutral and charged F-aggregate centers. There are, however, broad unresolved V_k and V_l bands in the UV region which keep the high energy tail of the F band above an absorbance of 0.10 unit. The reader may refer to Table 1.1 for a description of the centers responsible for the V bands. Overlap of the V bands with the F band makes the baseline for the F band uncertain. In order to correct for overlap, the baseline was "compensated" in the same manner used for spectra of additively colored NaCl and described above. Half-width values of the F band at 80°K of 0.283 ± 0.007 and 0.277 ± 0.007 eV were obtained from uncompensated and compensated spectra, respectively. Both half-width values are in excellent agreement with literature values,^{41,43} but the value from the compensated spectrum is in better agreement with literature values than is the value from the uncompensated spectrum.

Half-widths of the F band were also measured at 66 and 197°K. Without baseline compensation 0.276 and 0.390 eV were obtained while

with baseline compensation 0.271 and 0.378 eV were obtained for the F band half-widths at 66 and 197°K, respectively. The temperature dependence of only the "compensated" data is consistent with ν_g values of $4.40 \times 10^{12} \text{ sec}^{-1}$ and $4.46 \times 10^{12} \text{ sec}^{-1}$ determined by Markham and Konitzer⁴¹ and by Jacobs and Parsons,⁴³ respectively. This provides further justification of the method of baseline compensation used for crystals, x-ray colored at 80°K.

Jacobs and Parsons⁴³ also discovered in their study that K-band subtraction has a great effect in the determination of ν_g . Without K-band subtraction, a ν_g value of $4.46 \times 10^{12} \text{ sec}^{-1}$ was obtained while with K-band subtraction, a ν_g value of $4.80 \times 10^{12} \text{ sec}^{-1}$ was obtained.

U-band Irradiation Experiments. As pointed out earlier, an absorption spectrum of additively colored NaCl reveals, in addition to the F band, a much more intense U band at 191 nm, associated with substitutional hydride ion.⁴⁰ Before additive coloration, the crystal exhibited only a weak but broad band at 185 nm associated with substitutional hydroxide ion.⁴⁰ Calculations using the Dexter modification of Smakula's equation² were made of hydroxide and hydride concentrations in uncolored and colored NaCl crystals, respectively. For these calculations it was assumed that U and OH⁻ bands are Gaussian and that their oscillator strengths are the same as corresponding values in KCl.⁴⁴ The hydroxide concentration in uncolored crystals is found to be ca. $4 \times 10^{17} \text{ per cm}^3$ which is about three times the hydride concentration in additively colored crystals. This is consistent with the finding of Etzel and Patterson⁴⁰ that hydroxide ions in uncolored crystals are the source of hydride ions present in additively colored

crystals.

Etzel and Patterson⁴⁰ had also shown that the concentration of F centers, produced by either ionizing radiation at room temperature or additive coloration, is proportional to the initial hydroxide ion concentration. Removal of hydroxide ions would thus lead to a less colorable crystal.

Additional confirmation that the 191 nm band is the U band was provided by two experiments on additively colored NaCl crystals similar to those first performed by Kerkhoff³⁵ in hydride ion doped NaCl, KCl and KBr crystals. The NaCl plates used for the two experiments were cleaved from the same additively colored crystal.

In one experiment, an additively colored plate was baked at a temperature of 600°C at a pressure of 10^{-5} mm. Hg in order to remove all but impurity centers. After baking, an F band is barely visible in a spectrum at 80°K which contains a U band of 1.9 unit maximum absorbance and weak O_I and O_{II} bands³⁸ at 222 and 290 nm, respectively. The O_{II} band may contain a contribution from the U_2 band,³⁵ associated with interstitial hydrogen atoms.

The baked NaCl crystal was then irradiated for one hour at 80°K with the full output of an Osram Hg/4 lamp in order to excite the U band. To minimize attenuation of the Hg 185 nm light by oxygen, the path between light source and cryostat was purged with a stream of nitrogen gas. As a result of irradiation, the U band decreased by 50% and there were increases in both the F and U_2 bands. Kerkhoff³⁵ had obtained similar results by U-band irradiation at low temperature which were explained by the following reaction scheme:

where the subscript i stands for interstitial and the subscript s stands for substitutional.

In another experiment, a plate of additively colored NaCl was irradiated at 25°C with the full output of an Osram Hg/4 lamp in order to excite the U band. As a result of a 15 minute irradiation, the absorbance of the F band increased from 0.8 to 2.4 units while the U band absorbance decreased from 3.16 to 2.05 units. There was also a decrease in the absorbance of the band at 222 nm (U_2 band). Similar results were obtained by Kerkhoff³⁵ in U-center doped KCl, KBr and NaCl crystals. According to Kerkhoff,³⁵ the decrease in the U_2 band is a result of thermally induced reactions between hydrogen atoms to form hydrogen molecules. Depletion of hydrogen atoms and increased α -center mobility favor F-center production (reactions 4.2 and 4.3) at higher temperatures.

In addition to the large F-band increase, M, R, and N bands appeared as a result of F-band bleaching from visible light necessarily present in the Osram Hg/4 lamp output. Formation of R and N bands limits the usefulness of U-band bleaching as a means of sample preparation for M-center absorption studies. It would be desirable to excite U and U_1 centers without also exciting F and M centers, but

there are no filters which could be used to accomplish this. Another limitation of U-band irradiated samples for M-band study is the thermal instability of M centers in the presence of hydrogen molecules.⁴⁶ In view of the limitations of additively colored (a.c.) and U-band irradiated a.c. NaCl crystals, studies of F-aggregate bands were performed on x-ray colored crystals.

M⁺-Center Studies

M⁺-Center Formation. Before studying M-center absorptions, experiments were conducted to learn more about M⁺-center absorptions. Jun²⁹ had earlier performed pulse anneal experiments on NaCl crystals which were x-ray colored at 80°K. The experiments indicated that the M⁺ band was at its maximum absorbance (0.12 units) at 265°K. The present experiment was performed to determine if a large M⁺-center concentration would be produced if a NaCl crystal, containing F and α centers, is kept at 265°K for an extended period.

A plate of NaCl, 13 x 13 x 0.6 mm³, was x rayed at 80°K for 46 hours. Figure 4.2a shows the spectrum, between 1600 and 450 nm, of the x ray colored NaCl crystal measured at 80°K. Not shown in the figure is a V₂ band at 224 nm with a maximum absorbance of 3.3 units. Between 500 and 385 nm, the absorbance is greater than 2 units due to an intense F, F' band composite. Intensities of the F and F' bands were estimated to be ca. 9 and 2.0 absorbance units, respectively, from F and F' band data in the literature.^{41,45} There are, however, no observable M-, R-, M⁺- or R⁺-center absorptions noted on the long wavelength side of the F band which peaks at 450 nm.

After irradiation, the crystal was warmed to 266°K and maintained

Figure 4.2. Absorption Spectra of an X Ray Colored NaCl Crystal at 80°K: (a) Solid Curve is the Spectrum Taken Immediately After 46 Hours of X Irradiation, (b) Dashed Curve is the Spectrum Taken After Annealing the Crystal at 266°K for 30 Minutes and (c) Dot-Dashed Curve is the Spectrum Taken After a Subsequent X Irradiation at 80°K for Five Minutes

Figure 4.3. Difference Spectra at 80°K of the X Ray Colored NaCl Crystal of Figure 4.2: (b-a) Solid Curve Shows the M⁺-Band Formation which Resulted from a 30 Minute Annealing at 266°K and (c-b) Dashed Curve Shows the M⁺-Band Annihilation as a Result of a Five Minute X Irradiation at 80°K where a, b, and c Refer to the Spectral Curves of Figure 4.2

at this temperature for 30 minutes in order to produce M^+ centers thermally, i.e., by α -center capture by F centers. The temperature was then quickly lowered to 80°K and a spectrum was measured, which is shown in Figure 4.2b. A difference spectrum showing the effect of the warm-up and 266°K anneal is shown in Figure 4.3a. Besides the appearance of a small (0.07 units) M^+ band at 1020 nm, there were appearances of M_1 and R^+ bands with estimated maximum absorbances of 0.055 and 0.014 units respectively. In addition, it is estimated that the F' band decreased by 1.8 units while the F band increased by an amount which could not be estimated because of its very high optical density. The V_2 band appeared to have decreased.

Analysis of the spectral changes makes it possible to understand the low M^+ -band intensity realized. The large absorbance of the M_1 band relative to the M^+ band indicates that many M^+ centers which are formed capture electrons to form M centers. The decrease in the F' band and increase in the F band are probably a result of thermal release of electrons by F' centers and the subsequent capture of electrons by α centers to form F centers. Thus many of the α centers formed during x irradiation are not available for M^+ center formation. The appearance of an R^+ band at 690 nm indicates that some α centers are captured by M centers forming R^+ centers. Capture of α centers by M centers also limits M^+ -center production.

M^+ -Center Annihilation. After standing for half an hour at 266°K, the crystal was x irradiated at 80°K for five minutes in order to annihilate the M^+ centers, Figure 4.3b is a difference spectrum showing the effect of the brief x irradiation. In addition to removal

of the M^+ band, it is estimated that M and F' bands increased by 0.18 and 1.23 absorbance units, respectively, and the R^+ band has decreased by 0.08 unit. There was also an appearance of R bands. It is estimated that the absorbance at the maximum of the R_2 band is 0.08 units. It was not possible to determine exactly the maximum absorbance of any of the bands because of overlap with bands of other centers.

The above spectral changes may be explained by the following reactions. Interaction of x rays with chloride ions and other electron sources makes available a large supply of free electrons. Some of the electrons are captured by M^+ centers to form M centers, some are captured by R^+ centers to form R centers, and some are captured by F centers to form F' centers.

M^+ -Center Absorption Spectrum. It was not possible to locate an M^+ band in the ultraviolet region of absorption or difference spectra as the band is masked by larger F, F' and V bands. Parameters of the M^+ band in the near infrared region were measured, however, from difference spectra of Figure 4.3. The peak position of the M^+ band at 80°K was found to be 1020 ± 1 nm in both difference spectra. Jun,²⁹ at faster scanning speeds, had obtained a corresponding value of 1015 nm at the same temperature. Half-width values of 0.186 ± 0.003 and 0.183 ± 0.003 eV were obtained from the M^+ -band appearance and disappearance difference spectra (cf Fig. 4.3), respectively. The average value of the M^+ -band half-width, 0.184 ± 0.003 eV, is in excellent agreement with the value of 0.184 ± 0.003 eV estimated from the data of Jun et al.²⁹

Schneider and Bailey⁴⁷ had measured the M^+ band at 4°K and report a peak position value of 1033 nm. The shift of peak position to longer wavelength for a decrease in temperature appears to be a property peculiar to ionized aggregate absorptions. The reason for this type of behavior is not presently known. A half-width of 0.145 ± 0.004 eV is estimated for the half-width of the M^+ band at 4°K.⁴⁷ Narrowing of a band for a decrease in temperature is a general property of electronic absorptions including those of ionized centers.³⁶

R^+ -Center Studies

Following spectral investigations of the M^+ center, preliminary polarized light studies were conducted in order to determine the nature of the M-center spectrum. Details of final M-center studies will be presented and discussed in the next chapter. In this section the spectrum of the R^+ center will be discussed as R^+ bands overlap M bands.

It was learned in the early experiments in NaCl that the M_1 band formed either thermally or optically had a broadened high energy tail due to a band located at 690 nm. Schneider and Bailey⁴⁷ had earlier noted an R^+ band with peak position of 700 nm at 4°K as a result of irradiation with R_1 -band light at 4°K. Upon irradiation at 4°K with 820 nm light, the 700 nm band decreased and the R bands increased. The same behavior was noted for the 690 nm band when the above irradiations were carried out at 80°K. It appeared therefore that the 690 nm band is the R_r^+ -band. Calculations by Evarestov's group¹⁷ indicate identification of the R_r^+ band with the $^1A_1 \rightarrow ^1E$

transition of the R^+ center.

Overlap of the R_r^+ band with the M_1 band meant that irradiation with M_1 -band light excited R^+ centers as well as M centers. Thus irradiation of NaCl containing M and R^+ centers with [011] polarized M_1 -band light at 0°C, results in M-center dichroism overlapped by weaker R^+ -center dichroism. The various spectra and anisotropies mentioned here and below appear in Chapter V, along with further details of the experiments of which they are part.

Following irradiation with [011] M_1 -band light, the crystal was annealed at 25°C for 10 hours in the dark in order to remove R^+ -center dichroism. The R_r^+ band and a pronounced shoulder at 405 nm were, as desired, removed from the [011] anisotropy. The shoulder is assigned to the R_v^+ band which is related to the $^1A_1 \rightarrow ^1A_1$ transition of the R^+ center. Further support that the 405 nm shoulder is due to an R^+ band is its absence, along with the R_r^+ band, in the [010] anisotropy resulting from [010] M_1 -band irradiation.

The R^+ -center spectrum was obtained by subtracting the [011] anisotropy, measured after annealing at 25°C, from that with the R^+ band, measured before annealing. The spectrum of R^+ centers consists of an R_r^+ band at 692 ± 2 nm with a half-width of 0.13 ± 0.01 eV and an R_v^+ band at 402 ± 2 nm with a half-width of ca. 0.2 eV. The half-width of the R_r^+ band is the same as that observed by Schneider and Bailey⁴⁷ in NaCl at 4°K. Their spectra, however, do not provide data below 500 nm possibly because necessarily high optical densities in the spectra of the crystal greatly limit the precision of the spectra.

Konrad⁷ had found in NaF at 80°K, R_r^+ and R_v^+ bands located at 520 and 302.5 nm. The bands have strikingly similar properties to the corresponding bands in NaCl. As in NaCl, absorbances of the R_r^+ and R_v^+ bands are about equal to one another. Furthermore, the ratio $E_{\max}(R_v^+)/E_{\max}(R_r^+)$ is 1.72 in both salts. As far as is known, observations of the R_v^+ band in NaF⁷ and NaCl are the only ones reported to date in any alkali halide crystal although there have been several observations of the R_r^+ band.

The maximum absorbances at M_1 and R_r^+ bands, which overlap one another, may be determined with the knowledge of the shapes of the M_1 and R_r^+ bands. The absorbance of the M_1 band at 692 nm (R_r^+ -band peak) is 0.25 of its maximum value while the absorbance of the R^+ band at 716 nm (M_1 -band peak) is 0.44 of its maximum value. A simpler but less precise method of determining the R_r^+ -band maximum absorbance is by subtracting 25% of the composite maximum absorbance from the absorbance at 692 nm since the height of the R^+ band relative to that of the M_1 band is usually small. Ignored in the simple method is the overlap of the R^+ band with the M_1 -band peak. The R_r^+ -band intensity so determined is about 10% lower than the value obtained by assuming R_r^+ -band overlap with the M_1 -band peak. Calculations of R_r^+ - and M_1 -band intensities in the present studies were made with the more rigorous method, i.e., accounting for R_r^+ -band overlap with the M_1 -band peak.

N_1 -Region Studies

An attempt was made to produce an N_{1B} band in NaCl in the manner

of Schneider and Kabler⁴⁹ in KCl. The N_{1B} band in KCl is an absorption peaking at 960 nm (N_1 region), having a $\langle 100 \rangle$ - type transition moment. The 960 nm band was noted in the excitation spectrum measured after irradiation with N light of a sample rich in R centers. The center responsible for the band, according to the above authors,⁴⁹ may be an F_3 center, in which each F center lies at the corner of the smallest right isocoles triangle in a (100) lattice plane.

A crystal of NaCl was irradiated at 25°C for 100 minutes with 508 nm light in order to produce a large R-center concentration. At the end of the irradiation the height of the R bands was about the same as that of the M_1 and F bands (0.6 absorbance units). An N_1 band, of 0.25 unit intensity, and an R^+ band, of 0.4 unit intensity, were also noted at 825 and 692 nm, respectively.

The NaCl crystal was then exposed to N_1 -region light for one hour at 25°C in order to produce N_{1B} centers. As in KCl, an increase (0.05 units) was noted in the N_1 band. In the absence of excitation spectra, however, it is not known whether the increase is in part due to the N_{1B} band.

Unlike KCl, where no increase was noted in R^+ -center concentration,⁴⁹ there were in NaCl ca. 0.07 unit increases in the R_r^+ and R_v^+ bands and 0.07 unit decreases in the absorbances of the R bands.

The changes in NaCl suggest that an R_N band is excited by the light resulting in R-center ionization. The R_N band may be located in the vicinity of 860 nm, where a barely observable decrease in absorbance was noted. In KCl, unlike NaCl, the R^+ band lies in the N_1 region so that R^+ centers are excited by the N_1 light. R^+ centers may, upon

optical excitation, be converted into other centers such as N_{1B} centers. If N_{1B} -center formation does involve R^+ -center excitation, then N_{1B} centers would not be expected to be formed in NaCl upon exposure to N_1 light. A N_{1B} band study in NaCl, using excitation spectra, would therefore be helpful in the understanding of the mechanism of N_{1B} -center formation.

Other measurements in the N_1 -band region included observations of a zero phonon line with positions at 67 and 80°K of 838.1 ± 0.3 and 838.4 ± 0.3 nm, respectively. The half-widths of the band at 67 and 80°K were 2.0 and 2.4 nm respectively. Hughes³ had earlier observed a zero phonon line at 4°K with a maximum at 837.3 nm and a half-width of 0.1 nm. Considerably larger half-widths at 67 and 80°K compared to that at 4°K suggests that the half-width of the zero phonon line at the higher temperatures is due mainly to overlap with one and two phonon lines.

The intensity is by far the most temperature sensitive property of the zero phonon line. At 67°K the intensity of the zero phonon line (0.075 units) was more than double that at 80°K (0.035 units). The very large temperature sensitivity of intensity is consistent with that previously noted and explained by Fitchen.³

CHAPTER V

EXPERIMENTAL RESULTS ON M CENTERS

Purposes of Experiments

In this chapter studies of photochemically induced dichroism in the absorption spectrum of the M center in sodium chloride are discussed. Besides providing energies of various M-center electronic states, the studies provide information on the interactions of the lattice with the M center. Data of M_1 -band half-widths at various temperatures reveal the dependence of half-width on lattice vibration, while measurements of M_2' - M_2 band splittings of various salts reveal the dependence of M_2' - M_2 band splitting on specific ions.

Previous F- and M-band studies^{9,37} have demonstrated the approximate validity of the following equation:

$$H^2 = H_0^2 \coth (h\nu_g/2kT) \quad (5.1)$$

where H_0 is the half-width at 0°K and ν_g is the effective lattice frequency interacting with the ground state of the center responsible for the band. Thus, from half-width data at several temperatures, H_0 and ν_g may be determined by suitable graphing of Equation (5.1).

M-band dichroism studies on other salts have demonstrated the sensitivity of the M_2' - M_2 band splitting to the anion, i.e., $KCN > KCl > KBr > KI$. With the addition of NaCl for comparison with KCl, it is now possible to determine the cation effect on the M_2' - M_2 band splitting.

Experiments to be Discussed

As pointed out in Chapter II, an $\langle 011 \rangle$ M-band dichroism study is

sufficient for the determination of the β spectrum, e.g., the M_2 band, while both $\langle 011 \rangle$ and $\langle 010 \rangle$ dichroism studies are necessary for the determination of the γ spectrum, e.g., the M_2' band. Rather than describe every experiment performed, the best $\langle 011 \rangle$ - $\langle 010 \rangle$ pair of experiments, designated 14 and 15, will instead be discussed. In this $\langle 011 \rangle$ - $\langle 010 \rangle$ pair of experiments, the samples used were cleavage twins and the M centers of both samples were photochemically realigned at 0°C . These precautions were taken to ensure that the environments about the M center in the two experiments be nearly equal.

Another experiment to be described, designated 16, is an $\langle 011 \rangle$ photochemical realignment of M centers at 80°K . This experiment resulted in a much greater $\langle 011 \rangle$ M-band dichroism than produced at 0°C .

Lack of extensive coverage of the early experiments does not mean that they were not important. The early experiments were necessary to determine the conditions which would lead to a large M-band dichroism without accompanying higher aggregate center bands such as the R^+ bands.

$\langle 011 \rangle$ Polarized Light Experiment on M Centers Preferentially Aligned at 0°C (Experiment 14)

Procedure and Kinetics. A crystal plate of NaCl was attached to the mounting block of a stainless steel cryostat while its cleavage twin was placed in a jar dessicator where it was stored until its use in a subsequent $\langle 010 \rangle$ experiment. The crystal was x rayed (50 kV, 50 ma) at 197°K for 8 minutes and then irradiated at 80°K with 566 nm light for 20 minutes in order to remove the F' band. After bleaching the F' band with 566 nm light, the absorption spectrum contained a

V_2 band with a maximum absorbance of 0.39 units at 220 nm and an F band with a maximum absorbance of 4.8 units at 450 nm. There were no detectable F-aggregate center bands in the spectrum.

Next the sample was stored overnight in the dark at -35°C . The result of storage was a 0.3 unit decrease in the F-band absorbance, a 0.05 unit increase in the V_2 band and the appearance of a barely observable M_1 band. The crystal was then irradiated for 70 minutes at 0°C with $[0\bar{1}1]$ polarized 508 nm light, in order simultaneously to form and to align M centers preferentially in the $[0\bar{1}1]$ direction. Figure 5.1 shows the maximum absorbances of the absorptions of various color centers at various stages during the formation of a $[0\bar{1}1]$ preferentially aligned M-center distribution.

As a result of the above irradiation with 508 nm light, the F-band absorbance decreased from 4.46 to 1.68 units. An M_1 band appeared with a maximum absorbance of 1.16 units measured with $[011]$ light and a maximum absorbance of 0.53 units measured with $[0\bar{1}1]$ light. There were also appearances of small isotropic R^+ and R bands. Formation of these higher aggregate centers is probably a result of thermal reaction of M centers with α centers to form R^+ centers, some of which capture electrons to form R centers. The α centers and electrons in these reactions are decomposition products of optically excited F centers (see Chapter I). Other side reactions accompanying M-center formation, beside R^+ - and R-center formations, include F-center reactions with hole centers, as evidenced by a decrease in the V_2 band. These side reactions limit the number of M centers formed during F-band irradiation.

Figure 5.1. Maximum Absorbances of the F, M_1 , R_2 and R^+ Bands in NaCl at 80°K at Various Stages in the Formation at 0°C of a $[0\bar{1}1]$ Preferentially Aligned M-Center Distribution in Experiment 14.

After the above irradiation at 0°C with $[0\bar{1}1]$ polarized 508 nm light, the crystal was irradiated at 0°C for 40 minutes with $[011]$ polarized M_1 -band light (cf Table 3.2) in order to increase M-center anisotropy. Anisotropy of the M_1 band increased in magnitude from 0.64 to 0.86 unit while polarization increased from 38 to 52% during the dose of $[011]$ M_1 -band light. As noted in Figure 5.1, the M_1 band measured with $[0\bar{1}1]$ polarized light increased during the first twenty minutes, but thereafter remained approximately constant. This indicates that during the first half of the irradiation, M-center reorientation is chiefly responsible for an increase in M-band polarization and that during the second half, M-center annihilation is comparable with reorientation. Reorientation and annihilation of M centers are described in Chapter VI.

Along with an increase of the M_1 -band polarization during the irradiation with $[011]$ M_1 band light, the R bands decreased and the R^+ band increased indicating R-center ionization. This suggests that R centers are optically excited by the " M_1 -band" light, i.e., an R_M or R_N band lies in the spectral range of the light. An experiment on the N_{1B} band described in Chapter IV had indicated the presence of an R_N band at ca. 860 nm, which lies within the spectral region of M_1 -band light.

The R_r^+ band after irradiation with $[011]$ M_1 -band light exhibits dichroism of the same sign as the M_1 band. Such dichroism is expected (cf Table 2.3), since R_r^+ -band light is necessarily present in M_1 -band light. As shown in Figure 5.3 and mentioned in Chapter IV, dichroism

Figure 5.2. Absorption Spectra of NaCl Sample, X-Ray Colored at 197°K, Immediately after Consecutive Irradiations at 0°C with $[0\bar{1}1]$ 508 nm Light for 70 Minutes and $[011]$ M_1 -Band Light for 40 Minutes. Solid Curve Measured with $[0\bar{1}1]$ Light and Dashed Curve Measured with $[011]$ Light at 80°K in Experiment 14

Figure 5.3. The $[011]$ - $[0\bar{1}1]$ Absorption Anisotropy of the NaCl Sample of Figure 5.2. The Dashed Curve Represents the R^+ -Center Anisotropy which was Obtained by Subtracting the M-Center Anisotropy from the Composite Anisotropy (Solid Curve). Measurement at 80°K in Experiment 14

of the R^+ bands complicates not only the M_1 band, but also the M_2 and M_3 bands.

In order to remove the dichroism of the R^+ bands, the sample was stored overnight in the dark at 25°C. Examination of Figures 5.4 and 5.5 indicates that while R^+ bands are present in the absorption spectra measured at 80°K with [011] and with $[0\bar{1}1]$ light (Fig. 5.4), the bands are absent from the [011] anisotropy (Fig. 5.5). Anisotropies at four other temperatures between 66 and 274°K are shown in Figures 5.6 to 5.9.

The band position and half-width of the M_2 band were determined from each unresolved anisotropy by assuming that the band is Gaussian in shape. In each of the anisotropic spectra, the M_2 band has been drawn with a dashed line. Low M_2 -band absorbance and great overlap of the M_3 band preclude M_2 -band resolution at 274°K. The band maximum and half-width of the M_1 band, measured between 66 and 274°K, and of the M_2 and M_2' bands, measured between 66 and 197°K, are shown in Table 5.1. Assignment of the M_3 band is complicated by overlap with a Σ polarized band in the α -spectrum. Further details of the M_1 band will be discussed in the next section. This section will be followed by discussions of the M_2 band and M_3 and M_4 anisotropies.

Temperature Dependence of the M_1 Band. The M_1 -band data measured between 66 and 274°K were in excellent agreement with those from $\langle 010 \rangle$ experiments which are necessarily free of R^+ -band anisotropy (cf Table 2.1). As with color center bands in other alkali halides, the oscillator strength for the M_1 band, which is proportional to the product of the

Figure 5.4. Absorption Spectra of NaCl Sample of Figure 5.2 after Subsequent 10 Hour Storage in the Dark at 25°C. Solid Curve Measured with $[0\bar{1}1]$ Light and Dashed Curve Measured with $[011]$ Light at 80°K in Experiment 14

Figure 5.5. The $[011]-[0\bar{1}1]$ Absorption Anisotropy of the NaCl Sample of Figure 5.4. The Dashed Curve Represents the Resolved M_2 Band of Gaussian Shape. Measurement at 80°K in Experiment 14

Figure 5.6. The $[011]$ - $[0\bar{1}1]$ Absorption Anisotropy of the NaCl Sample of Figure 5.4. The Dashed Curve Represents the Resolved M_2 Band of Gaussian Shape. Measurement at 66°K in Experiment 14

Figure 5.7. The $[011]$ - $[0\bar{1}1]$ Absorption Anisotropy of the NaCl Sample of Figure 5.4. The Dashed Curve Represents the Resolved M_2 Band of Gaussian Shape. Measurement at 110°K in Experiment 14

Figure 5.8. The $[011]-[0\bar{1}1]$ Absorption Anisotropy of the NaCl Sample of Figure 5.4. The Dashed Curve Represents the Resolved M_2 Band of Gaussian Shape. Measurement at 197°K in Experiment 14

Figure 5.9. The $[011]$ - $[0\bar{1}1]$ Absorption Anisotropy of the NaCl Sample of Figure 5.2.
Measurement at 274°K in Experiment 14

Table 5.1. Optical Absorption Parameters of the M Center in NaCl Obtained from Anisotropies of Experiments 14 and 15 at Various Temperatures

Band	T, °K	66	80	110	197	274
M ₁	$\lambda_{\max}$, nm	715.5±0.5	716.0±0.5	717.0±0.5	722.0±1.0	727.0±1.0
	$\epsilon_{\max}$, eV	1.732±.001	1.731±.001	1.728±.001	1.717±.002	1.705±.001
	H _T , eV	0.080±.001	0.083±.001	0.092±.001	0.119±.002	0.144±.001
M ₂	$\lambda_{\max}$, nm	447.0±0.5	448.0±0.5	450.0±0.5	453.0±1	
	$\epsilon_{\max}$, eV	2.773±.003	2.767±.003	2.755±.003	2.736±.006	
	H _T , eV	0.273±.006	0.280±.006	0.298±.006	0.353±.010	
M ₂ '	$\lambda_{\max}$, nm	445.0±0.5	446.0±0.5	448.0±0.5	450.5±1	
	$\epsilon_{\max}$, eV	2.786±.004	2.779±.004	2.767±.004	2.752±.006	
	H _T , eV	0.270±.006	0.279±.006	0.292±.006	0.360±.010	
$\epsilon_{\max}^{(M_2')} - \epsilon_{\max}^{(M_2)}$ eV		0.013±.007	0.012±.007	0.012±.007	0.016±.012	
A(M ₂)/A(M ₁)		-0.27±.01	-0.27±.01	-0.27±.01	-0.31±.01	
A(M ₂ ')/A(M ₁)		-0.30±.02	-0.30±.02	-0.31±.02	-0.38±.02	

maximum absorbance (A_m) and the half-width (H_T) of the M_1 band, remains relatively constant with change in temperature. The value of $A_{\max} \times H_T$ was about 4.5% greater at 66°K than the corresponding value at 274°K.

Between 66 and 274°K, however, the variation in the M_1 -band half-width is considerable. The half-width, H_T , ranges from 0.080 eV at 66°K to 0.144 eV at 274°K. Uncertainty in half-width is estimated to be 0.001 eV at 66, 80 and 110°K, and 0.002 eV at 197 and 274°K, while uncertainty in temperature is estimated to be 0.5°K at all temperatures. Figure 5.10 is a graph of H_T^2 vs T in which vertical bars represent estimated uncertainty in H_T^2 . The best fit to Equation (5.1), shown by the curve in Figure 5.10 was obtained with values of ν_g and H_0 of $3.2 \pm 0.2 \times 10^{12} \text{ sec}^{-1}$ and $0.072 \pm 0.003 \text{ eV}$, respectively. Here, ν_g is the effective lattice frequency interacting with the M center in its ground state and H_0 is the half-width of the M_1 band at 0°K. All of the half-width data fit the curve in Figure 5.10 except the value of half-width at 274°K. The value of the half-width at 274°K was about 4% greater than the value predicted by the curve. The cause of the discrepancy, however, is not known.

Compton and Klick⁵⁰ had earlier measured half-widths of the M_1 band in NaCl at 77°K and at room temperature of 0.096 and 0.182 eV respectively. From these two pieces of data they calculated a value for ν_g of $1.7 \times 10^{12} \text{ sec}^{-1}$, nearly 50% lower than that obtained in the present study. Their high half-width at 77°K suggests that their M_1 -band data were complicated by the presence of the R_r^+ band, unknown at the time of their study.

Figure 5.10. Variation of the Square of the Half-width (H_T^2) of the M_1 -Band Absorption in NaCl with Temperature. Curve is Graph, H_T^2 vs T , of Equation 5.1 for $\nu_g = 3.2 \times 10^{12} \text{ sec}^{-1}$ and $H_0 = 0.072 \text{ eV}$. Straight Line Indicates H_T^2 Dependence at High Temperature Based on Coth Behavior. Vertical Bars Represent the Measured Values of H_T^2 Including Estimated Uncertainties in the Values

In addition to the variation of half-width (H_T) with temperature, there is also a variation of asymmetry. A measure of the asymmetry of a band is the skewness, ρ , defined by Siano and Metzler⁵¹ in Equation (5.2):

$$\rho = (\epsilon_v - \epsilon_m)/(\epsilon_m - \epsilon_r) \quad (5.2)$$

where ϵ_m is the energy at the band maximum and ϵ_v and ϵ_r are the high and low energies at one half the band maximum. Table 5.2 is a table of measured values of ϵ_v , ϵ_r , ϵ_m and H_T (half-width) for the M_1 band in NaCl at 66, 80, 110, 197 and 274°K.

Table 5.2. Average Values of Optical Absorption Parameters for the M_1 Band in NaCl Obtained from [011] and [010] M_1 -band Anisotropies of Experiments 14 and 15

T °K	$\lambda_{\max}$ nm	ϵ_m eV	λ_v nm	ϵ_v eV	λ_r nm	ϵ_r eV	H_T eV	ρ
66	715.5	1.732	698	1.776	731	1.696	0.080	1.222
80	716.0	1.731	698	1.776	732	1.693	0.083	1.184
110	717.0	1.729	698	1.776	736	1.684	0.092	1.091
197	722.0	1.717	698	1.776	748	1.657	0.119	0.983
274	727.0	1.705	698	1.776	760	1.631	0.144	0.946

Graphs of ϵ_m , ϵ_r and ϵ_v vs. T are shown in Figure 5.11. It may be noted that ϵ_v remains constant at 1.776 eV (698 nm), even though the temperature changes. Little or no variation of ϵ_v with tempera-

Figure 5.11. Variation with Temperature of Absorption Maximum (ϵ_m), High Energy (ϵ_v) and Low Energy (ϵ_r) Half Maximum Points and of Skewness (ρ) of M_1 Band in NaCl

ture has been noted previously for the $F^{19,41}$ and M_1^{37} bands in alkali halide crystals, but the cause is not yet known.

From the graphs of Figure 5.11, it may be noted that ρ is greater than 1 below 175°K, equal to 1 at 175°K, and less than 1 above 175°K. In order to determine the skewness, ρ , at 0°K, it was necessary to determine ϵ_v , ϵ_r and ϵ_m at 0°K. The value of ϵ_v at 0°K is 1.776 eV since ϵ_v is independent of temperature. The value of ϵ_r at 0°K is simply H_0 subtracted from 1.776 eV, or 1.704 eV (727.5 nm). In the manner suggested by Neubert *et al.*,⁵² ϵ_m at 0°K was determined (from a straight line graph of ϵ_m vs H_T^2) to be 1.734 eV (715.0 nm). The skewness is therefore determined to be 1.40 at 0°K. According to Siano and Metzler,⁵⁰ skewness is a result of the inequivalence of the vibrational frequencies associated with the ground and excited states of the species responsible for the absorption.

M_2 Band. Unfortunately, it was not possible to determine the skewness of the M_2 band because of the great mutual overlap with the M_3 band. As mentioned earlier, the M_2 band was assumed to be Gaussian in shape. The M_2 band is drawn with a dashed line in Figures 5.5 to 5.9. Table 5.1, a listing of M_1 , M_2 and M_2' band parameters, indicates that from 66 to 197°K, the M_2 band position ranges from 447 ± 0.5 to 453 ± 1 nm, while the half-width varies from $0.273 \pm .006$ to $0.353 \pm .01$ eV. Bansigir and Schneider⁴⁵ had observed at ca. 77°K an M_2 -band maximum at 457 nm in a polarized light study on stressed NaCl. This may be compared with the corresponding value of 448 nm, determined in the present study. The difference between the two values may reflect a stress perturbation on the M center.

Between 66 and 110°K, the ratio $A(M_1)/A(M_2)$ is 3.7, about the same as in NaF at 80°K, but somewhat different from the ca. 2.5 ratio found in potassium salts. The oscillator strength ratio, $f(M_1)/f(M_2)$, is ca. 1 in the sodium salts, as well as in the potassium salts studied. There thus appears to be a cation effect which regulates the $M_1:M_2$ band intensity ratio, but not the oscillator strength ratio.

M_3 and M_4 Anisotropies. Between the M_1 and M_2 bands, a small M_4 band has been observed in KBr, KCl and KI crystals of the same polarization as the M_1 band (Σ polarized). An anisotropy composed wholly or partly of the M_4 band and of about $0.01 A_{\max}(M_1)$ relative intensity is noted in Figure 5.5 by the difference between dashed and solid curves at ca. 500 nm. The relative height of the M_4 band is somewhat smaller than in the potassium salts. Very small height and overlap with the M_2 band preclude determination of M_4 -band parameters in NaCl. In NaF, the only other sodium salt in which the absorption spectrum of the M center has been studied, the M_4 band could not even be observed. It is not known at present why the M_4 band is more intense in the potassium salts than in the sodium salts.

Similarly, it is not possible to determine parameters of the M_3 band. The M_3 band, having a relative intensity of about $0.1 A_{\max}(M_1)$, is greatly overlapped on its low energy side by the M_2 band. Its position, then, depends in large part on the shape assumed for the M_2 band. According to the work of Aegerter and Lüty²⁷ in KCl, the M_3 band is also overlapped on its high energy side by a small Σ polarized band. It is not possible to resolve the weak M band from the M_3 band. Therefore, a Gaussian on the high energy side of the M_2 band is called the

M_3 anisotropy. The position of this anisotropy is 401 ± 2 nm at 80°K and equal to this value within experimental error at all other temperatures measured. Independence of the M_3 anisotropy position with temperature is consistent with previous such findings in other alkali halides. The half-width of the M_3 anisotropy is ca. 0.30 eV, which is slightly greater than that of the M_2 band. Anisotropy to the high energy side of the M_3 anisotropy is positive. This region according to Aegerter and Lütty²⁷ contains several M-band anisotropies which cannot be resolved in the present NaCl data. An attempt to resolve much of the violet and UV regions of the M-center spectrum into five symmetrical Gaussians, using a computer program developed by Struble,⁵⁴ failed. Lack of success of the computer fits is probably due to underestimation of the number of M bands and to the skewness of the actual bands.

Formation of [001] Preferentially Aligned M Centers at 0°C

(Experiment 15)

Procedure and Kinetics. Having thus determined parameters of the M bands of the α and β spectra, an $\langle 010 \rangle$ polarized light study was performed in order to determine parameters of M bands of the γ spectrum, e.g. M_2' and M_3' bands.

The cleavage twin of the crystal used in the above $\langle 011 \rangle$ experiment was attached to the aperture plate of a stainless steel cryostat at a 45° angle to the vertical edge of the aperture plate. The crystal was mounted at a 45° angle because the Cary 14 PMR measuring beam is elliptically polarized. In this way nearly equivalent $[011]$ and $[0\bar{1}1]$ polarized measuring beams were used to measure the $[010]$

and [001] spectra, respectively, of the crystal.

The crystal was colored by an eight minute x irradiation at 197°K and then irradiated at 0°C for 70 minutes with 527 nm light in order to convert F into M centers. This resulted in a drop of the F band from a maximum absorbance of 5.0 to 0.69 units, and the appearance of an M_1 band, 0.70 units at maximum, and of much weaker R and R^+ bands. The crystal was then irradiated at 0°C with [010] polarized M_1 -band light for two hours, resulting in a 0.44 unit M_1 -band dichroism and 43% M_1 -band polarization. Figure 5.12 shows the variation in maximum absorbances of the F, M_1 , R_2 and R_r^+ bands as a result of subsequent irradiations at 0°C with F band and [010] polarized M_1 -band light. As shown in Figure 5.13, [010] M_1 -band irradiation results in an increase in the R^+ band and a decrease in the R band which are indicative of R-center ionization. As expected (cf Chapter II), there was no [010] R- or R^+ -band dichroism.

A weak dichoric band did appear, however, at 900 nm as a result of the [010] M_1 -band irradiation. The band was present in the [011] and $[0\bar{1}1]$ spectra after [011] M_1 -band irradiation, but was absent from the [011] anistropy. This indicates that the 900 nm band is associated with a $\langle 100 \rangle$ type transition moment. A band with similar properties called the N_{1B} band was observed by Schneider and Kabler⁴⁹ in the N_1 region of KCl. An N_{1B} -band experiment similar to that of the above authors is described in Chapter IV.

After irradiation with [010] polarized M_1 -band light, the crystal was stored overnight (10 hours) in the dark at 25°C. This was done

Figure 5.12. Maximum Absorbance of the F, M₁, R₂ and R⁺ Bands in NaCl at 80°K at Various Stages in the Formation at 0°C of a [001] Preferentially Aligned M-Center Distribution in Experiment 15

Figure 5.13. Absorption Spectra of NaCl Sample, Irradiated with X Rays at 197°K and 527 nm Light at 0°C, after Irradiation at 0°C with [010] M_1 -Band Light for Two Hours and an Annealing at 25°C for Ten Hours. Solid Curve Measured with [001] Light and Dashed Curve Measured with [010] Light at 80°K in Experiment 15

because it was desired that the M centers in the crystals of the two experiments (14 and 15) have nearly identical histories. Storage at 25°C resulted in decreases in the absorptions of F, M, and V_2 centers, as well as in a slight decrease in M-band anisotropy. The decrease in the concentrations of F and M centers may be a result of reactions with hole centers such as V_2 centers.

<010> M-Band Dichroism. After overnight storage at 25°C, spectra were measured at slow scan (2.5 Å/sec) with [010] and with [001] light at temperatures of 66, 80, 110, 197 and 274°K. Figure 5.13 shows the [010] and [001] spectra measured at 80°K and Figure 5.14 shows the [010] anisotropy of these spectra, [010]-[011]. The [010] anisotropy includes contributions from both the primed bands (γ spectrum) and unprimed bands (α and β spectra) of the M center. Between the M_1 and M_2 , M_2' band composite, there is a broad anisotropy, ca. -0.01 units at maximum, which may be associated with the center responsible for the 900 nm band. The anisotropy results in an apparently larger M_4 to M_1 band absorbance ratio in the [010] anisotropy than in the [011] anisotropy of the previous experiment (14).

Prime Spectra. In order to determine band parameters for the M_2' and M_3' bands, the [011] anisotropy of the previous experiment (14) was combined with the [010] anisotropy of the present experiment (15) according to Equation (2.20). The spectrum so obtained is referred to as the prime ($\gamma - \alpha$) spectrum as it contains M_2' and M_3' bands free of M_2 and M_3 bands. Prime spectra at 66, 80, 110 and 197°K are shown in Figures 5.15 to 5.18. Absorption band parameters of the

Figure 5.14. The [010]-[001] Anisotropy of Absorption Spectra of Figure 5.13.
Spectra Taken at 80°K in Experiment 15

Figure 5.15. Prime M-Center Absorption Spectrum of X-Ray Colored NaCl at 66°K. This Spectrum was Determined from [011]-[0 $\bar{1}$ 1] and [010]-[001] Anisotropies of Experiments 14 and 15, Respectively, Using Equation (2.20). The Dashed Curve Represents the Resolved M_2' Band of Gaussian Shape

Figure 5.16. Prime M-Center Absorption Spectrum of X-Ray Colored NaCl at 80°K. This Spectrum was Determined from $[011]-[0\bar{1}1]$ and $[010]-[001]$ Anisotropies of Experiments 14 and 15, Respectively, Using Equation (2.20). The Dashed Curve Represents the Resolved M_2' Band of Gaussian Shape

Figure 5.17. Prime M-Center Absorption Spectrum of X-Ray Colored NaCl at 110°K. This Spectrum was Determined from [011]-[0 $\bar{1}$ 1] and [010]-[001] Anisotropies of Experiments 14 and 15, Respectively, Using Equation (2.20). The Dashed Curve Represents the Resolved M_2' Band of Gaussian Shape

Figure 5.18. Prime M-Center Absorption Spectrum of X-Ray Colored NaCl at 110°K. This Spectrum was Determined from [011]-[0 $\bar{1}$ 1] and [010]-[001] Anisotropies of Experiments 14 and 15, Respectively, Using Equation (2.20). The Dashed Curve Represents the Resolved M_2' Band of Gaussian Shape

M_2' and M_3' bands from the prime spectra are listed in Table 5.1. The M_2' -band position varies from 445.5 nm (2.786 eV) at 66°K to 450.5 nm (2.752 eV) at 197°K in agreement with a previous $\langle 011 \rangle$ - $\langle 010 \rangle$ pair of experiments. The ratio $A(M_2')/A(M_1)$ is ca. 10% higher than the ratio $A(M_2)/A(M_1)$, while the M_2 and M_2' band half-widths are nearly equal to one another. Thus the relative oscillator strength of the M_2' band is ca. 10% higher than that of the M_2 band.

M_2' - M_2 Band Splitting. The M_2' - M_2 band splitting is 0.012 ± 0.007 eV at 80°K and within experimental uncertainty, the splitting is independent of temperature. The splitting in NaCl is lower than that in NaF (0.038 eV),⁷ consistent with the anion effect observed in several alkali halides, namely $KCN > KCl > KBr > KI$. The splitting in NaCl, though, is also smaller than that of KCl (0.034 eV).²⁷ This suggests a cation effect different from the anion effect, i.e., the larger the anion, the smaller the splitting, but the larger the cation, the larger the splitting. A possible interpretation of these effects will be presented in Chapter VI.

Within experimental uncertainty (0.07 eV), there is no M_3' - M_3 anisotropy splitting and the M_3' anisotropy position appears to be independent of temperature. The $M_3':M_1$ band intensity ratio, though, appears to be slightly higher than the $M_3:M_1$ band intensity ratio of ca. 0.1.

Formation of $[011]$ Preferentially Aligned M Centers at 80°K (Experiment 16)

Purpose and Procedure. The purpose of this experiment was to

produce a large $\langle 011 \rangle$ M band anisotropy in NaCl by irradiating the crystal with $[0\bar{1}1]$ polarized M_3 -band light at 80°K , a method which had recently been employed by Aegerter and Luty²⁷ in KCl.

Prior to spectral study of M centers in NaCl, the F-band position and half-width were measured at 66, 80 and 197°K . In order to produce a F band free of the M_1 band, an NaCl crystal was x-irradiated at 80°K for 25 minutes. The F-band measurements have been discussed in Chapter IV.

After F-band measurements, the crystal was x-irradiated at 197°K for eight minutes in order to form a larger F-center concentration from which to produce M centers. This resulted in an increase in the maximum absorbance of the F band from 1.9 to an estimated 4.7 units at 80°K . The crystal was then irradiated at 80°K with 566 nm light to convert F' into F centers. Removal of the F' band was accompanied by a 0.5 unit increase in maximum absorbance of the F band. To produce M centers the crystal was irradiated at 0°C with 527 nm light for 40 minutes. Conversion of F into M centers was evidenced by a 4.0 unit decrease in the F band and the appearance of an M_1 band, 0.99 units at maximum absorbance. There were also R_2 and R_r^+ bands, each with a maximum absorbance of 0.11 units at 80°K .

The above irradiation was followed by a 30 hour irradiation at 80°K with $[0\bar{1}1]$ polarized 405 nm light (see Table 3.2) in order to preferentially realign M centers into the $[0\bar{1}1]$ direction. Figure 5.19 shows the optical densities at the maximum of the M_1 band during the 405 nm irradiation and during earlier stages of

Figure 5.19. Maximum Absorbance of the M_1 Band in NaCl at 80°K at Various Stages in the Formation of a $[011]$ Preferentially Aligned M-Center Distribution in Experiment 16. Optically Induced M-Center Formation at 0°C and Alignment at 80°K.

sample preparation. As a result of a 30 hour irradiation at 80°K with $[0\bar{1}1]$ 405 nm light, the maximum of the M_1 band measured with $[011]$ light decreased from 0.99 to 0.22 units while that measured with $[0\bar{1}1]$ light increased from 0.99 to 2.29 units. The resultant M_1 -band dichroism of 2.07 units and polarization of 82% were somewhat greater than those obtained as a result of polarized M-band irradiations at 0°C. However, the polarization of 82% is less than that obtained in KCl²⁷ (>90%) under similar conditions.

According to the analyses of Chapter II, an increase of the M_1 band measured with $[0\bar{1}1]$ light of about double the decrease of the M_1 band measured with $[011]$ light indicates that an increase in polarization is due to reorientation rather than annihilation of M centers. Annihilation of M centers is the reason for the somewhat smaller M-band anisotropies produced by polarized M-band irradiations at 0°C. A discussion of reorientation and annihilation mechanisms will be presented in Chapter VI.

In order to understand better the M-center realignment process, a graph of $\log (P - P_\infty)$ vs. time was made, which is shown in Figure 5.20. In the above expression, P is the polarization at any time while P_∞ is the polarization after an infinite dose of exciting light, which was estimated to be 83% in the present experiment. The straight line plot shows that M-center reorientation is a first order process in NaCl as was also found in NaF.⁷ A rate constant for reorientation of 0.2 hr^{-1} was determined from the slope of the $\log (P - P_\infty)$ vs. time graph. The rate constant is about one order of magnitude less than the corresponding value obtained for $[011]$ M_1 -band irradiation at 0°C.

Figure 5.20. Variations of (a) Degree of Polarization, P , and (b) $\log (P_{\infty} - P)$ with Dose of Irradiation with $[0\bar{1}1]$ 405 nm Light at 80°K. P_{∞} is Chosen to be 0.83.

There appears to have been little or no change in the R and R^+ center concentrations during the irradiation at $80^\circ K$ with $[0\bar{1}1]$ polarized 405 nm light. Such lack of change is consistent with the lack of change noted for the M-center concentration since R^+ and R center formations appear to involve M-center reaction. There was, however, slight R-center polarization (12%), indicating that an R band is in the 405 nm region.

During the irradiation at $80^\circ K$ there was also a 0.16 unit decrease in the maximum absorbance of the F band accompanied by a 0.01 unit increase in the maximum absorbance of the F' band. This suggests that some F- to F' -center conversion takes place during the irradiation at $80^\circ K$ with $[0\bar{1}1]$ 405 nm light. In order to remove the F' band, the crystal was irradiated at $80^\circ K$ with 566 nm light. This resulted in removal of the 0.02 unit F' band and a 0.33 unit increase in the F band. The ratio of the change in maximum absorbance of the F band to that of the F' band was ca. -16, the same as it was for irradiation with $[0\bar{1}1]$ 405 nm light. There was also an increase of the R^+ band and similar decreases in the R bands indicative of R-center ionization. Ionization of R centers is to be expected as 566 nm light is in the region of the R_1 and R_2 bands.

There were no observable M^+ bands either before or after F' -band irradiation. As a result of F' -band irradiation, however, the M_1 -band peak absorbance measured with $[0\bar{1}1]$ light increased from 2.29 to 2.49 units, while that measured with $[011]$ light increased from 0.22 to 0.28 units. The increases in M_1 -band peak absorbances indicate that

$[0\bar{1}1]$ preferentially aligned M^+ centers captured electrons released from F' centers during F' -band irradiation. Lack of an M^+ band in the $[0\bar{1}1]$ spectrum measured immediately before F' -band irradiation is thus probably a result of weak oscillator strength of the M^+ band.

$\langle 011 \rangle$ M-Band Anisotropy at $80^\circ K$. After the five minute irradiation at $80^\circ K$ with 566 nm light, spectra were measured at $80^\circ K$ with $[011]$ and with $[0\bar{1}1]$ light. Figure 5.21 shows these absorption spectra and Figure 5.22 shows the $[011]$ anisotropy, i.e., $A_{[011]} - A_{[0\bar{1}1]}$. As in earlier experiments, it was assumed that the M_2 band is Gaussian in shape in order to resolve the M_2 band from the complex composite of M bands. The lower dashed curve (c) in Figure 5.22 shows the difference between the composite anisotropy (a) and the M_2 -band Gaussian (b).

M-center absorption parameters determined from Figure 5.22 are shown in Table 5.3. Positions and half-widths listed in this table are in good agreement with previous data obtained from anisotropies produced by optical irradiation at $0^\circ C$. The ratios $\Delta A(M_2)/\Delta A(M_1)$, $\Delta A(M_3)/\Delta A(M_1)$ and $\Delta A(M_4)/\Delta A(M_1)$ were -0.264, -0.105 and +0.013, respectively. Because of the large M-band anisotropy, the M-band parameters obtained in this experiment are probably the most reliable ones of this work.

M^+ -Center Experiment. In order to produce M^+ -band dichroism, the above crystal with highly $[0\bar{1}1]$ oriented M centers was x rayed at $68^\circ K$ for one minute and then irradiated for three minutes at $80^\circ K$ with $[011]$ 318 nm light. A similar procedure had earlier been used

Figure 5.21. Absorption Spectra at 80°K of the NaCl Sample of Experiment 16. The Sample was Irradiated with X Rays at 197°K and 508 nm Light at 0°C. Preferential Alignment of M Centers in the $[0\bar{1}1]$ Direction was Achieved by Irradiating the Sample at 80°K with $[0\bar{1}1]$ 405 nm Light for 30 Hours. Solid Curve Measured with $[0\bar{1}1]$ Light and Dashed Curve Measured with $[011]$ Light

Figure 5.22. The $[011]-[0\bar{1}1]$ Absorption Anisotropy at 80°K of the NaCl Sample of Experiment 16. The Figure Includes: (a) A Solid Curve Representing that Anisotropy, (b) A Dashed Curve Representing the Resolved M_2 Band of Gaussian Shape and (c) A Dashed Curve in the Insert Representing Curve a Minus Curve b, i.e. the Anisotropy Without the M_2 Band. The Scale at the Lower Right is for Curve c, Only

Table 5.3. Optical Absorption Parameters of the M Center in NaCl at 80°K from the [011] Anisotropy of Experiment 16

	M_1	M_2	M_3	$\frac{A(M_2)}{A(M_1)}$	$\frac{A(M_3)}{A(M_1)}$	$\frac{A(M_4)}{A(M_1)}$
λ, nm	716.0 $\pm$ 0.5	448.0 $\pm$ 0.5	402.0 $\pm$ 1	-0.264	-0.105	+0.013
$\epsilon_{\text{max}}, \text{eV}$	1.731 $\pm$.001	2.767 $\pm$.003	3.084 $\pm$.008			
H, eV	0.083 $\pm$.001	0.286 $\pm$.003	0.298 $\pm$.006			

in KCl, except that irradiations and measurements were effected at ca. 4°K.²⁷ Spectral measurements in NaCl at 80°K indicate that during x irradiation small fractions of M and R centers were ionized and that during irradiation with [011] 318 nm light, additional M centers were ionized. A larger fraction of M centers was ionized by the latter irradiation. At the end of the irradiation with [011] 318 nm light, an M^+ band was observed in the $[0\bar{1}1]$ spectrum with an absorbance of 0.046 units at the band maximum (1020 nm) and a half-width of 0.190 $\pm$ 0.004 eV. No M^+ band was observed in the spectrum measured with [011] light. As desired then, an M^+ band with ca. 100% polarization was produced by ionization of $[0\bar{1}1]$ oriented M centers.

There was, however, no high energy M^+ band noted in either dichroic or difference spectra as had been noted in KCl at 509 nm.⁵⁶ The low energy M^+ band has about half the absorbance of that in KCl. According to Aegerter and Lüty,²⁷ x-irradiation at 4°K introduces electron traps which results in higher amounts of M^+ centers. X irradiation at 68°K

probably does not produce the desired electron traps. Success in observing the high energy M^+ band in KCl was also aided by the higher resolution obtained by taking the measurements at 4°K, i.e., electronic absorptions get narrower and taller as temperature is decreased. In order possibly to observe a high energy M^+ band in NaCl, it may therefore be necessary to perform the above irradiations and spectral measurements at 4°K.

CHAPTER VI

DISCUSSION OF RESULTS

Introduction

This chapter will explore the following topics in an effort to understand better the results of the previous two chapters. The topics discussed include:

- a) a possible explanation for the order of magnitude lower M^+ -band absorbance in NaCl with reference to this absorbance in NaF
- b) mechanisms of M-center reorientation and annihilation
- c) interpretation of cation and anion effects of $M_2'-M_2$ band splitting
- d) a possible alternative to a Mollwo-Ivey plot for the M_1 band
- e) a comparison of experimental data on the M center with the calculations of Evarestov et al.¹⁷

Inability to Form Large M^+ -Center Concentration in NaCl

As pointed out in Chapters IV and V, it was not possible to produce a large M^+ -center concentration in NaCl by either optical or thermal means. Konrad,⁷ though, was able thermally to produce a large M^+ -center concentration in NaF. A larger M^+ -center concentration in NaF than in NaCl may be a result of a larger α -center or electron trap concentration in NaF. Recent calculations²⁶ indicate that the Frenkel-pair formation energy (FPFE) for an anion in NaF is 1.2 eV lower than the corresponding value in NaCl. The FPFE for an anion is the energy necessary to move an anion from a normal lattice site into a well-removed lattice site. A low anion FPFE implies that there is a large α -center concentration available for M^+ -center production in

x-ray colored NaF. According to the calculations, one salt, KF, has an FPFE that is 0.8 eV lower than NaF.²⁶ An even larger M^+ -center concentration may be possible in KF. There have been no published papers, however, on the M^+ center in KF.

Production of M-Center Anisotropy

M-Center Reorientation. In the last chapter it was seen that a large M-center anisotropy could be produced by $[0\bar{1}1]$ M_3 -band irradiation at 80°K because it results in reorientation rather than annihilation of M centers. Schneider⁵⁵ in a study of photochemical reorientation of M centers in KCl at low temperature found that the M-center reorientation mechanism involves reorientation of excited M^+ centers. According to the Schneider⁵⁵ mechanism, M-center reorientation occurs not only because M centers are excited and ionized but because ionized M centers are also being excited by the same light and given the opportunity to reorient. This implies that a high energy M^+ band in NaCl overlaps 405 nm, the wavelength used to effect M-center reorientation in NaCl at 80°K.

In order to determine if M^+ centers are excited by 405 nm light, high energy M^+ -center transitions were calculated using the model of an H_2^+ molecular ion embedded in a continuous dielectric medium. Graphs were drawn of the log of transition energy vs. the log of internuclear separation for various H_2^+ transitions using tabulated values⁵⁷ for the H_2^+ molecular ion. The effective internuclear separation of the M^+ center (r_{ab}^e) in NaCl was adjusted to that for a free $H_2^+(R)$ by dividing r_{ab}^e by K_0 as in Equation (1.4). Transition energies were obtained by scaling the logarithmic curves using the

adjusted separation (R) and the first transition energy (1.215 eV) which was determined experimentally. Transition energies for the $1s\sigma_g \rightarrow 2p\pi_u$, $3p\sigma_u$ and $4p\sigma_u$ transitions of 2.61 (475 nm), 3.30 (376 nm) and 3.86 eV (321 nm) were obtained. For these calculations, it was assumed that r_{ab}^e is 14% lower than the anion-anion nearest neighbor separation³ (r_{ab}) and that the effective high frequency dielectric constant (K_o^e) is six percent higher than the bulk value³ (K_o), as for KCl.⁵⁶ Similar calculations using r_{ab} and K_o resulted in somewhat higher transition energies. It thus appears from the calculated transition energies that M^+ centers were excited into higher states by 405 nm light as required by the Schneider⁵⁵ mechanism for reorientation.

Calculated transition energies of M^+ centers also make it possible to understand better the appearance of an M^+ band in the $[0\bar{1}1]$ spectrum of Experiment 16 resulting from irradiation at 80°K with $[011]$ polarized 318 nm light. Before irradiation nearly all of the M centers were aligned in the $[0\bar{1}1]$ direction as a result of exposure at 80°K to $[0\bar{1}1]$ 405 nm light. Irradiation with $[011]$ 318 nm light ionizes M centers along the $[0\bar{1}1]$ direction. Any M^+ centers that are in the $[011]$ direction are excited by the Σ polarized M^+ -band light ($1s\sigma_g \rightarrow 4p\sigma_u$) causing them to reorient into the safe $[0\bar{1}1]$ direction.

M-Center Annihilation. As was indicated in the last chapter, M-center annihilation plays an important role in polarized M_1 -band bleaching at 0°C resulting in less dichroism than would be obtained by M-center reorientation alone. Annihilation of M centers may be

a result of decomposition into F centers. Increase in the F band was, in fact, observed during [011] M_1 -band irradiation at 0°C, but was not observed during [011] M_3 -band irradiation at 80°K. It thus appears that M-center stability and ease of photochemical reorientation make M-center realignment the favored process at low temperatures, while lack of M-center stability at higher temperature (0°C) results in some M-center annihilation.

Cation and Anion Effects of M_2' - M_2 Band Splitting

The present study on M centers in sodium chloride has shown that the M_2' - M_2 band splitting in NaCl is smaller than that of both NaF and KCl. Figure 6.1 depicts the (010) and (011) planes of NaF, NaCl and KCl as well as the π_y and π_x electron clouds associated with the M_2 - and M_2' -transition dipole moments respectively. The circles representing the various ions were drawn in proportion to one another according to the crystal radii data of Tosi and Fumi.⁵⁸ As Figure 6.1 shows, the environments about the π_y and π_x clouds differ. The greatest interaction of the π clouds appears to be with the nearest neighbor cations. If the cations were very far from the π electron clouds, there would be no difference between the two π electron cloud environments, i.e., $E(M_2') = E(M_2)$. The larger the anion, the greater the cation- π electron cloud separation, and hence, smaller M_2' - M_2 band splitting would be expected. For the same anion, a larger cation overlaps the π orbitals to a greater extent than a smaller cation. A larger overlap should magnify differences between π_y - and π_x -cation interactions. Larger M_2' - M_2 band splittings are, therefore, to be expected for salts of larger cations. Further

Figure 6.1. The (110) and (100) Planes of NaF, NaCl and KCl and the π_y and π_x Orbitals of the M Center.

M-center studies on other alkali halides such as NaBr and RbCl are desirable to further verify the existence of a cation effect.

Possible Alternative to Mollwo-Ivey Plot for M_1 Band

The best straight line for a Mollwo-Ivey plot for the M_1 band, i.e., $\log (M_1\text{-band energy})$ vs. $\log (\text{lattice constant})$, has a slope of 1.5. There is, however, a considerable scatter of points about this line. A better fit is obtained by a series of cation salt lines of slope two and a series of anion salt lines of slope one as shown in Figure 6.2. The x-intercepts of the lines decrease with increasing size of the cation. The cation and anion effects of the x-intercept are the same as those for the M_2' - M_2 band splitting.

Comparison of M_1 -, M_2 - and M_2' - Band Data with Calculated Values

Evarestov et al.¹⁷ have made calculations of the transitions associated with the M_1 , M_2 and M_2' bands for KBr, KCl, NaF, LiCl, LiF and RbBr using a rigid point ion lattice (RPIL) model. This model takes into account only the charges and positions of the ions of the crystal. Most of the calculated M_1 -band energies appear to be higher and most M_2 - and M_2' -band energies appear to be lower than their experimental counterparts.

The calculated M_2' - M_2 band splittings¹⁷ are all positive, as are experimentally determined splittings. However, calculated values of splitting are from two to ten times larger than experimental values. The calculated anion effect, $\text{Br}^- > \text{Cl}^- > \text{F}^-$, for both sodium and potassium families of salts is contrary to that observed. On the other hand, the calculated cation effect in the chlorides, $\text{K}^+ > \text{Na}^+$, is consistent with that observed. Refinements of the RPIL model are

Figure 6.2. Graph of $\log E_{\max}$ vs. $\log a_0$ for the M_1 Band in Several Alkali Halide Crystals. Solid Lines are of Common Cation and Dashed Lines are of Common Anion

necessary in order to get better agreement with measured $M_2'-M_2$ band splittings. Such refinements may include taking into account the size of the nearest neighbor cations.

CHAPTER VII

CONCLUSIONS

Optical absorption energies for the M, M^+ and R^+ centers in x-ray colored NaCl crystals were determined using a Cary 14 PMR Spectrophotometer.

Additively colored NaCl samples were unsuitable for the study of M-center absorptions. Not only was the concentration of F centers inadequate for necessary M-center formation, but a colloid band persisted in the M_1 -band region. U-band irradiation of such an additively colored sample results in a large increase in the F band, but also results in the appearance of absorptions of M, R and other F aggregate centers. For M- and R^+ -center studies crystals of NaCl were x-ray colored at 196°K, while for M^+ -center studies, they were x-ray colored at 80°K in order to form larger α -center concentrations.

Position and half-width were measured at 80°K for the M^+ band obtained in an experiment in which the sample was annealed. This experiment is described in Chapter IV. An M^+ band was observed at 1020 nm (1.215 eV) with a maximum absorbance of 0.07 units and a half-width of 0.184 ± 0.003 eV. Earlier an M^+ band was observed in NaCl at 4°K with a position of 1033 nm and half-width of 0.145 eV.⁴⁷ The shift of the peak position to longer wavelength for a decrease in temperature appears to be a general property for absorptions of ionized aggregate centers in alkali halides, inasmuch as it had been noted in LiF, NaF, KCl, KBr and KI.

Higher energy M^+ bands could not be observed in NaCl at 80°K as had been observed in KCl at 4°K.²⁷ It was found,⁵⁶ using the tabulated

data of Bates et al.,⁵⁷ that absorption energies of the M^+ center in KCl are in excellent agreement with the model of an H_2^+ molecular ion embedded in a continuous dielectric medium. Application of the model to NaCl in the manner described in Chapter VI yields band positions of 475, 376 and 321 nm for M^+ bands associated with the $1s\sigma_g \rightarrow 2p\pi_u$, $3p\sigma_u$ and $4p\sigma_u$ transitions, respectively.

For the R^+ center, on the other hand, it was possible to observe both low and high energy absorptions as in NaF.⁷ Low and high energy R^+ -center absorptions are related to the $^1A_1 \rightarrow ^1E$ and $^1A_1 \rightarrow ^1A_1$ transitions corresponding to (x, y) and (z) transition dipoles, respectively. The H_3^+ molecular ion is analogous to the R^+ center except that it has D_{3h} rather than C_{3v} symmetry. Transitions $^1A_1' \rightarrow ^1E'(x,y)$ and $^1A_1' \rightarrow ^1A_2''(z)$ of H_3^+ molecular ion, which correspond to the above R^+ -center transitions, have not been experimentally observed. Calculations⁴⁸ indicate that the $^1E'$ state is unstable but the excited $^1A_2''$ state is stable with respect to dissociation.

The absorption spectrum of R^+ centers in NaCl was obtained by subtracting the [011] anisotropy containing only M-center absorptions from the [011] anisotropy containing M- and R^+ -center absorptions. R_R^+ and R_V^+ bands were noted at 692 ± 2 and 401 ± 2 nm measured at 80°K. Earlier an R^+ band in NaCl at 4°K was noted at 700 nm, but the R_V^+ band was not reported.⁴⁷ The R_R^+ and R_V^+ bands in NaCl have similar properties to those in NaF.⁷ The R_V^+ band has about the same maximum absorbance as the R_R^+ band and the ratio of R_V^+ - to R_R^+ -band energies is 1.72 in both salts. In both NaF and NaCl, R_R^+ - and R_V^+ -absorption

energies could be fit to the model of an H_3^+ molecular ion embedded in a dielectric medium using published⁴⁸ potential energy curves and Equations (1.4) and (1.5).

Absorption energies of the M center in NaCl, however, could not be fit to the model of an H_2 molecule in a dielectric medium. This lack of fit is consistent with that observed for M-center absorption energies in other alkali halides, but is not as yet understood. The absorption spectrum of M centers was determined from the [011] and [010] anisotropies produced by excitation of M centers at 0°C with appropriately polarized light (See Chapter V). Somewhat larger [011] anisotropy was produced by exciting M centers at 80°K with [011] M_3 -band light because alignment is achieved exclusively by M-center reorientation rather than by a mixture of reorientation and annihilation at 0°C. The [011] anisotropy produced by M-center excitation at 80°K is in excellent agreement with that produced at 0°C.

Between 66 and 274°K the position of the M_1 band ranged from 715.5 to 727 nm, while the half-width ranged from 0.080 to 0.144 eV. The temperature dependence of the M_1 band was found to obey Equation (5.1) with values for ν_g and H_0 of $3.2 \pm 0.2 \times 10^{12} \text{ sec}^{-1}$ and 0.072 ± 0.002 eV, respectively. Here, ν_g is the effective lattice frequency interacting with the M center in its ground state and H_0 is the half-width of the M_1 band at 0°K. As in KI,³⁷ the skewness, ρ , of the M_1 band increases with decreasing temperature. The skewness, ρ , is equal to $(\epsilon_v - \epsilon_m)/(\epsilon_m - \epsilon_r)$ where ϵ_m is the energy at the band maximum and ϵ_v and ϵ_r are the high and low energies, respectively, at half the band

maximum.

Between 66 and 197°K, the M_2 -band position ranges from 447 to 453 nm, while the half-width ranges from 0.273 to 0.353 eV. Because the M_2 band is not well resolved from higher energy M-center absorptions, it was assumed that the M_2 band is Gaussian in energy. With this approximation, the position of the M_3 anisotropy was found to be at 401 ± 2 nm and invariant, within experimental uncertainty, with temperature change.

Parameters of the M_2' band were obtained from a spectrum made up of [011] and [010] anisotropies according to Equation (2.20). These parameters as well as M_1 - and M_2 -band parameters are shown in Table 5.1. An M_2' - M_2 band splitting of 0.012 ± 0.007 eV was determined which is less than that of both NaF⁷ and KCl.²⁷ A lower splitting in NaCl than in KCl points to a possible cation effect different from the anion effect, i.e., the larger the anion, the smaller the splitting, but the larger the cation, the larger the splitting. A possible explanation of these effects has been presented in Chapter VI. Investigations of M_2' - M_2 band splittings in other chloride salts are necessary for verification of the cation effect.

APPENDIX

This section contains derivations of many of the anisotropy relations of Chapter II. For the reader's convenience, the labeling of equations is the same as in Chapter II. Equations not appearing in Chapter II, however, are labeled (A.1), (A.2), etc.

M-Center Anisotropy

<011> Polarized Light Measurements. Interaction between an electric vector of light and an optical transition dipole is proportional to $\cos^2\theta$, where θ is the angle between the two vectors. For any M-center distribution, therefore, the absorption coefficients for measurement with $[011]$ and with $[0\bar{1}1]$ light (cf Fig. 2.1) are:

$$\begin{aligned}
 K_{[011]} = & (\alpha m_1 + \beta m_2) \cos^2 0 \\
 & + (\alpha m_2 + \beta m_1 + \gamma m_1 + \gamma m_2) \cos^2 90 \\
 & + (\alpha + \beta)(m_3 + m_4 + m_5 + m_6) \cos^2 60 \\
 & + \gamma(m_3 + m_4 + m_5 + m_6) \cos^2 45 \\
 K_{[011]} = & \alpha m_1 + \beta m_2 + (1/4)[(\alpha + \beta + 2\gamma)(m_3 + m_4 + m_5 + m_6)] \quad (A.1)
 \end{aligned}$$

$$\begin{aligned}
 K_{[0\bar{1}1]} = & (\alpha m_2 + \beta m_1) \cos^2 0 \\
 & + (\alpha m_1 + \beta m_2 + \gamma m_1 + \gamma m_2) \cos^2 90 \\
 & + (\alpha + \beta)(m_3 + m_4 + m_5 + m_6) \cos^2 60
 \end{aligned}$$

$$+ \gamma(m_4 + m_4 + m_5 + m_6)\cos^2 45$$

$$K_{[0\bar{1}1]} = \alpha m_2 + \beta m_1 + (1/4)[(\alpha + \beta + 2\gamma)(m_3 + m_4 + m_5 + m_6)] \quad (A.2)$$

The dichroism, $\Delta K_{[011]}$, is therefore:

$$\Delta K_{[011]} = (\beta - \alpha)(m_2 - M_1) \quad (A.3)$$

The M centers formed either thermally or photochemically with ordinary light are randomly oriented. Each of the $\langle 011 \rangle$ directions numbered 1 to 6 in Figure 2.1, is populated equally with M centers. If concentration m_0 is substituted for each m_i in Equations (A.1), (A.2), and (A.3), the following is obtained:

$$K_{[011]}^{[ran]} = K_{[0\bar{1}1]}^{[ran]} = (2\alpha + 2\beta + 2\gamma)m_0 \quad (2.5)$$

$$\Delta K_{[011]}^{[ran]} = 0$$

Next consider that the sample is irradiated with M_1 -band light moving in the negative x direction (cf Fig. 2.1) and polarized in the $[011]$ direction. M_1 -band light interacts with only the transition dipole along the molecular axis of an M center. The above polarized M_1 -band light, therefore, excites the centers in direction 1 by $\cos^2 0^\circ$, in direction 2 by $\cos^2 90^\circ$ and in directions 3, 4, 5 and 6 by $\cos^2 60^\circ$. M centers along direction 2 are consequently not excited. If after

excitation the M centers reorient into any $\langle 011 \rangle$ direction with equal probability, those that fall back into directions 1, 3, 4, 5 and 6 will be excited repeatedly until they reorient into direction 2, the safe direction. An $[011]$ M_1 -band irradiation is thus expected to produce the following M-center distribution:

$$m_2 > m_3 + m_4 = m_5 = m_6 > m_1 \quad (2.6)$$

Concentrations m_4 , m_5 and m_6 may, therefore, be replaced by m_3 , resulting in the following absorption coefficients and anisotropy:

$$K_{[011]}^{[011]M_1} = \alpha(m_1 + m_3) + \beta(m_2 + m_3) + 2\gamma m_3 \quad (2.7)$$

$$K_{[0\bar{1}1]}^{[011]M_1} = \alpha(m_2 + m_3) + \beta(m_1 + m_3) + 2\gamma m_3 \quad (2.8)$$

$$\Delta K_{[011]}^{[011]M_1} = (\beta - \alpha)(m_2 - m_1) \quad (2.9)$$

$\langle 010 \rangle$ Polarized Light Measurements. For any M-center distribution, the absorption coefficients for measurement with $[010]$ and with $[001]$ light (cf Fig. 2.1) are:

$$\begin{aligned} K_{[010]} &= (\alpha + \beta)(m_1 + m_2 + m_5 + m_6)\cos^2 45^\circ \\ &+ (\alpha + \beta)(m_3 + m_4)\cos^2 90^\circ \\ &+ \gamma(m_1 + m_2 + m_5 + m_6)\cos^2 90^\circ \end{aligned}$$

$$+ \gamma(m_3 + m_4) \cos^2 0$$

$$K_{[010]} = (1/2)(\alpha + \beta)(m_1 + m_2 + m_5 + m_6) + \gamma(m_3 + m_4) \quad (A.4)$$

$$K_{[001]} = (\alpha + \beta)(m_1 + m_2 + m_3 + m_4) \cos^2 45$$

$$+ (\alpha + \beta)(m_5 + m_6) \cos^2 90$$

$$+ \gamma(m_1 + m_2 + m_3 + m_4) \cos^2 90$$

$$+ \gamma(m_5 + m_6) \cos^2 0$$

$$K_{[001]} = (1/2)(\alpha + \beta)(m_1 + m_2 + m_3 + m_4) + \gamma(m_5 + m_6) \quad (A.5)$$

The dichroism, $\Delta K_{[010]}$, is therefore:

$$\Delta K_{[010]} = (1/2)(2\gamma - \alpha - \beta)(m_5 + m_6 - m_3 - m_4) \quad (A.6)$$

A sample containing randomly oriented M centers has an equal population in each of its six $\langle 011 \rangle$ directions. If concentration m_0 is substituted for each m_i in Equations (A.3), (A.4), and (A.5), the following is obtained:

$$K_{[010]}^{[ran]} = K_{[001]}^{[ran]} = (2\alpha + 2\beta + 2\gamma)m_0 \quad (A.7)$$

$$\Delta K_{[010]}^{[ran]} = 0 \quad (A.8)$$

Next consider that the sample is irradiated with M_1 -band light moving in the negative x direction (cf Fig. 2.1) and polarized in the $[011]$ direction. Such light excites M centers in directions 1, 2, 5 and 6 by $\cos^2 45^\circ$ and in directions 3 and 4 by $\cos^2 90^\circ$. M centers in directions 3 and 4 are thus not excited by the light. Centers upon optical excitation may reorient into directions 3 and 4 but would not reorient out of the two directions. Consequently, the following M-center distribution is expected after $[010]$ M_1 -band irradiation:

$$m_3 = m_4 > m_1 = m_2 = m_5 = m_6 \quad (2.16)$$

Concentration m_4 may be replaced by m_3 and concentrations m_2 , m_5 and m_6 may be replaced by m_1 . Such substitutions into Equations (A.3), (A.6), and (A.5) result in the following absorption coefficients and anisotropy:

$$K_{[010]}^{[010]M_1} = (2\alpha + 2\beta)m_1 + 2\gamma m_3 \quad (2.17)$$

$$K_{[001]}^{[010]M_1} = (\alpha + \beta + 2\gamma)m_1 + (\alpha + \beta)m_3 \quad (2.18)$$

$$\Delta K_{[010]}^{[010]M_1} = (2\gamma - \alpha - \beta)(m_3 - m_1) \quad (2.19)$$

The $[010]$ anisotropy thus contains absorptions of the α , β , and γ spectra. Absorptions of the γ spectrum occur in the same region as

those of the spectrum, i.e., in the F-band region. In order to "see" the γ absorption spectrum, the β absorption spectrum must be eliminated from $\Delta K_{[010]}^{[010]M_1}$. This may be done by adding to (2.19) the quantity $(\beta - \alpha)(m_3 - m_1)$. The quantity $(\beta - \alpha)(m_2 - m_1)$, however, is already known from Equation (2.9). If Equation (2.9) were multiplied by the ratio $(m_3 - m_1) \frac{[010]M_1}{[011]M_1} / (m_2 - m_1)$ and added to Equation (2.19), a combination spectrum free from the β spectrum would be obtained. The above ratio, though, is simply:

$$\Delta K_{[010]}^{[010]M_1}(M_1) / \Delta K_{[011]}^{[011]M_1}(M_1)$$

since the M_1 band is part of only the α spectrum. Hence the absorptions of the γ spectrum may be obtained free from the overlapping β spectrum in the following way:

$$\Delta K_{[010]}^{[010]M_1} + G \Delta K_{[011]}^{[011]M_1} = 2 (\gamma - \alpha)(m_3 - m_1) \quad (2.20)$$

where $G = \Delta K_{[010]}^{[010]M_1}(M_1) / \Delta K_{[011]}^{[011]M_1}(M_1)$.

R^+ -Center Anisotropy

For any R^+ -center distribution, absorption coefficients for measurement with $[011]$ and with $[0\bar{1}1]$ polarized light are found, with the aid of Table 2.1, to be:

$$\begin{aligned}
K_{[011]} = & \delta(r_a + r_b + r_{a'} + r_{b'}) \cdot 2/3 + \delta(r_c + r_d + r_{c'} + r_{d'}) \cdot 0 \\
& + \epsilon(r_a + r_b + r_{a'} + r_{b'}) \cdot 0 + \epsilon(r_c + r_d + r_{c'} + r_{d'}) \cdot 1 \\
& + 2\epsilon(r_a + r_b + r_c + r_d + r_{a'} + r_{b'} + r_{c'} + r_{d'}) \cdot 1/4 \\
& + 2\zeta(r_a + r_b + r_{a'} + r_{b'}) \cdot 1/12 + \zeta(r_c + r_d + r_{c'} + r_{d'}) \cdot 1/3 \\
& + 2\zeta(r_c + r_d + r_{c'} + r_{d'}) \cdot 3/4 + \zeta(r_c + r_d + r_{c'} + r_{d'}) \cdot 0
\end{aligned}$$

$$\begin{aligned}
K_{[011]} = & [(2/3)\delta + (1/2)\epsilon + (1/2)\zeta](r_a + r_b + r_{a'} + r_{b'}) \quad (A.9) \\
& + [(3/2)\epsilon + (3/2)\zeta](r_c + r_d + r_{c'} + r_{d'})
\end{aligned}$$

$$\begin{aligned}
K_{[0\bar{1}1]} = & \delta(r_a + r_b + r_{a'} + r_{b'}) \cdot 0 + \delta(r_c + r_d + r_{c'} + r_{d'}) \cdot 2/3 \\
& + \epsilon(r_a + r_b + r_{a'} + r_{b'}) \cdot 1 + \epsilon(r_c + r_d + r_{c'} + r_{d'}) \cdot 0 \\
& + 2\epsilon(r_a + r_b + r_c + r_d + r_{a'} + r_{b'} + r_{c'} + r_{d'}) \cdot 1/4 \\
& + 2\zeta(r_a + r_b + r_{a'} + r_{b'}) \cdot 3/4 + \zeta(r_a + r_b + r_{a'} + r_{b'}) \cdot 0 \\
& + 2\zeta(r_c + r_d + r_{c'} + r_{d'}) \cdot 1/12 + \zeta(r_c + r_d + r_{c'} + r_{d'}) \cdot 1/3
\end{aligned}$$

$$\begin{aligned}
K_{[0\bar{1}1]} = & [(3/2)\epsilon + (3/2)\delta](r_a + r_b + r_{a'} + r_{b'}) \quad (A.10) \\
& + [(2/3)\zeta + (1/2)\epsilon + (1/2)\zeta](r_c + r_d + r_{c'} + r_{d'})
\end{aligned}$$

The dichroism, $\Delta K_{[011]}$, is therefore:

$$\Delta K_{[011]} = [(2/3)\delta - \epsilon - \zeta](r_a + r_b + r_{a'} + r_{b'} - r_c - r_d - r_{c'} - r_{d'}) \quad (A.11)$$

The R^+ centers formed either thermally or photochemically are randomly oriented. Each of the eight orientations is populated equally. If r_o is substituted for each r_i ($r_{i'}$) in Equations (A.8), (A.9) and (A.10), the following is obtained:

$$K_{[011]}^{[ran]} = K_{[0\bar{1}1]}^{[ran]} = [(8/3)\delta + 8\epsilon + 8\zeta]r_o \quad (2.21)$$

$$\Delta K_{[011]}^{[ran]} = 0 \quad (2.22)$$

Next consider that the sample is irradiated with R_V^+ -band light moving in the negative x direction and polarized in the $[0\bar{1}1]$ direction. R_V^+ -band light interacts with only the $\langle 111 \rangle$ transition dipoles of R^+ centers. It is seen in Table 2.1 that the interaction ($\cos^2\theta$) of $[0\bar{1}1]$ R_V^+ -band light is 0 with $\langle 111 \rangle$ transition dipoles of a, b, a' and b' and is 2/3 with $\langle 111 \rangle$ transition dipoles of c, d, c' and d'. The above irradiation thus results in the following R^+ -center distribution:

$$r_a = r_b > r_c = r_d \quad (2.23)$$

Since orientation i is optically indistinguishable from i', the concentrations of orientations i and i' will be equal to one another regardless of the type of light used. Concentration r_a may therefore be

substituted for r_a , r_b and r_b , and concentration r_c may be substituted for r_c , r_d and r_d . These substitutions in Equations (A.9), (A.10) and (A.11) result in the following:

$$K_{[011]}^{[0\bar{1}1]R_v^+} = r_a[(8/3)\delta + 2\epsilon + 2\zeta] + r_c[6\epsilon + 6\zeta] \quad (2.24)$$

$$K_{[011]}^{[0\bar{1}1]R_v^+} = r_a[6\epsilon + 6\zeta] + r_c[(8/3)\delta + 2\epsilon + 2\zeta] \quad (2.25)$$

$$\Delta K_{[011]}^{[0\bar{1}1]R_v^+} = (r_a - r_c)[(8/3)\delta - 4\epsilon - 4\zeta] \quad (2.26)$$

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