

RETURNING MATERIALS: Place in book drop to remove this checkout from your record. <u>FINES</u> will be charged if book is returned after the date stamped below. VAPOR DEPOSITED THIN FILM STUDIES OF ALKALIDES AND ELECTRIDES AND THE SYNTHESIS AND CHARACTERIZATION OF TWO CRYSTALLINE ELECTRIDES

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Ву

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ABSTRACT

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VAPOR DEPOSITED THIN FILM STUDIES OF ALKALIDES AND ELECTRIDES AND THE SYNTHESIS AND CHARACTERIZATION OF TWO CRYSTALLINE ELECTRIDES

By

Margaret K. Faber

A high vacuum evaporator was modified to grow thin solid films of alkalides and electrides by the physical vapor deposition of alkali metals and macrocyclic complexants. The thickness and stoichiometry of films were monitored. An optical spectrometer was designed to measure the <u>in situ</u> transmittance of these films. A method was also devised to measure d.c. conductivities both parallel and perpendicular to the surface of films.

Films of Na⁺C222·Na⁻, K⁺C222·K⁻, Na⁺C222·e⁻, and $K^{+}C222\cdote^{-}$ were studied. These materials were grown in two ways. First, films were produced by the simultaneous deposition of the metal and organic vapors. Second, films were produced by alternate deposition of layers of metals and complexants.

Qualitative results were obtained for all four materials that agreed well with the spectra of films produced from solution. Na⁺C222·Na⁻ films were studied more extensively. The oscillator strength of this compound was measured but while the values were consistent with the value of 2 obtained for Na⁻ in solution some films deviated significantly from this value. Four spectra with reproducible lineshapes were scaled to an oscillator strength of 2, and were used to estimate the average molar decadic absorption coefficients. The peak position was at 650 nm and the maximum absorption coefficient was $7.0\pm.5 \times 10^4$ $M^{-1}cm^{-1}$, corresponding well with the value in solution of $8.2\pm.3 \times 10^4 M^{-1}cm^{-1}$.

Crystalline samples of the electrides $K^+C222 \cdot e^-$, Rb⁺C222 $\cdot e^-$ and Li⁺C2ll $\cdot e^-$ were grown from solution. Previous studies of these materials had been done only on powders or films. The optical spectra of $K^+C222 \cdot e^$ and Rb⁺C222 $\cdot e^-$ had a plasma-edge type of absorption. Both compounds had high microwave conductivities. Both electrides had nearly temperature independent magnetic susceptibilities above 20K, with 1% and 4% of the spins in the samples exhibiting Curie-Weiss paramagnetism. The expression for the Pauli paramagnetism of conduction electrons was used to estimate the conduction electron densities and effective masses of $K^+C222 \cdot e^-$ and Rb⁺C222 $\cdot e^-$, with values of 1.1 x 10^{21} cm⁻³, 9.6 x 10^{20} cm⁻³, 2m, and 4 m, respectively.

Preliminary measurements of the magnetic susceptibility of crystalline Li⁺C2ll·e⁻ as a function of temperature gave a broad maximum, indicative of electron-electron coupling, as previously detected in powder samples.

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ii

TABLE OF CONTENTS

Chapter		Page
LIST OF	TABLES	vi
LIST OF	FIGURES	viii
CHAPTER	ONE: INTRODUCTION AND BACKGROUND	1
Α.	Introduction	1
В.	Theoretical Models for Solvated Electrons	3
С.	Systems Related to Alkalides and Electrides	6
	l. Expanded Metal Compounds	6
	2. F-Centers in Alkali Halides	11
	3. Trapped Electrons in Frozen Glasses	15
D.	Alkalides and Electrides	19
E.	Magnetic Properties of Electrides	24
CHAPTER	TWO: GENERAL EXPERIMENTAL	30
Α.	Reagents	30
	1. Complexing Agents	30
	2. Metals	31
	3. Solvents	31
в.	Glassware Cleaning	33
С.	Sample Preparation and Instrumental Techniques	33
	1. General Procedure for Synthesis	33
	2. Bulk Magnetic Susceptibility Measurements.	37
	3. Electron Spin Resonance	ı ر
	Measurements	39

Chapter

Page

	4. Optical Absorption Spectra	40
	5. Pressed Powder Conductivity	42
D.	Stoichiometric Analysis of Crystalline Electrides	44
CHAPTER	THREE: THE HIGH VACUUM EVAPORATOR	47
Α.	Introduction	47
В.	The Experimental Design	48
с.	Materials	52
D.	Design for Alkalide and Electride Synthesis	57
Ε.	Measurement of Films	64
F.	Data Treatment	72
CHAPTER	FOUR: OPTICAL AND ELECTRICAL MEASUREMENTS OF VAPOR DEPOSITED FILMS	73
Δ	Introduction	70
n •		15
В.	Feasibility Study	83
С.	Physics of Thin Films	84
	1. Deposition Technology	84
	2. Adsorption of Atoms and the Growth of Films	86
	3. Optical Properties of Thin Films	89
	4. Electrical Properties of Thin Films	101
D.	Optical Spectra of Vapor Deposited Films	109
	1. Na ⁺ C222·Na ⁻	109
	(a) Co-Deposition	109 124

	2. $Na^{+}C222 \cdot e^{-}$	4
	3. к ⁺ с222·к ⁻	C
	4. к ⁺ C222·e ⁻ 142	2
	5. Discussion. 149	5
E.	Electrical Measurements of Vapor	
	Deposited Films 14	7
CHAPTER	FIVE: CRYPTATE ELECTRIDES 159	9
Α.	Introduction 159	9
В.	Synthesis and Properties of Crystalline	
	$K^+C222 \cdot e^-$ and $Rb^+C222 \cdot e^-$	2
		\mathbf{r}
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	- 2
	2. Optical Spectra) 5
	Magnotia Suggentibilities	2
	4. Magnetic Susceptibilities 100	ر
С.	Conclusions	5
D.	LiC2ll Electride	С
CHAPTER	SIX: SUMMARY AND SUGGESTIONS	
	FOR FUTURE WORK 201	1
Α.	Summary	1
	1. Crystalline Electrides 20	1
	2. Thin Film Deposition 201	3
В.	Suggestions for Future Work 20	5
	1. Crystalline Electrides 20	5
	2. Thin Film Studies	7
LIST OF	REFERENCES	1

LIST OF TABLES

Table		Page
l	Stoichiometric Analysis of Cryptate	
	Electrides	46
2	Values for the Mean Free Paths of	
	Common Gases at Various Pressures	53
3	Temperaures in °C Required to	
	Achieve the Vapor Pressures Listed	
	for Materials Used in the Thin Film	
	Preparation of Alkalides and Elec-	
	trides	58
4	Thickness Ratios for Alkalide and	
	Electride Films	63
5	Peak Positions for the Alkali Metals	
	Na and K in Various Solvents	75
6	Variations of the Optical Absorp-	
	tion Peak Positions for Several	
	Alkalides Showing Cation, Complex-	
	ing Agent, and Solvent Dependence	80
7	Estimated Oscillator Strengths for	
	Films of Na ⁺ C222·Na ⁻ Produced Both	
	by Co-Deposition and Layering	120

vi

Table

8	Average Values of the Molar Decadic
	Absorption Coefficient $\alpha(\lambda)$, and the
	Optical Constant $k(\lambda)$, Obtained from
	Four Composite Films of Na ⁺ C222·Na ⁻ 125
9	Deposition Parameters of Layered
	Films of Na ⁺ C222·Na ⁻ 128
10	Conductivity Parameters for Thin
	Films of Na ⁺ C222·Na ⁻ . Results
	from KINFIT IV 154
11	Parameters from a Fit to Curie-Weiss
	Paramagnetism
12	Experimental and Calculated Values
	for the Pauli Susceptibilities of K
	and Rb Metals
13	Conduction Electron Densities 182
14	Values of Fitted Parameters for
	Wojciechowski's Equation

Page

_

-

LIST OF FIGURES

Figure		Page
1	Apparatus for the synthesis	
	of crystalline electrides	34
2	Schematic diagram of the Ultek	
	MX-14 vacuum system	49
3	(a) Source boats for resistive	
	heating; (b) source boat in	
	position in evaporation oven	54
4	Schematic diagram of the	
	evaporation ovens inside the	
	vacuum space	60
5	Block diagram of the optical	
	spectrometer	67
6	(a) Electrodes for longi-	
	tudinal conductivity; (b)	
	electrodes for transverse	
	conductivity	70
7	Absorbance peaks for films	
	from methylamine	78
8	Generalized densities of	
	levels <u>vs</u> . energy for a semi-	
	conductor and a metal	103

9	Resistivity <u>vs</u> . l/T for antimony
	doped germanium 106
10	Band diagrams for intrinsic
	and extrinsic semiconductors 107
11	Unnormalized absorbance <u>vs</u> .
	wavenumber for Film I of Na ⁺ C222•
	Na produced by co-deposition 110
12	Unnormalized absorbance <u>vs</u> .
	wavenumber for Film II of Na ⁺ C222•
	Na produced by co-deposition 113
13	Unnormalized absorbance <u>vs</u> .
	wavenumber for Film III of Na ⁺ -
	C222·Na produced by co-
	deposition
14	Unnormalized absorbance <u>vs</u> .
	wavenumber for Film IV of
	Na ⁺ C222·Na ⁻ produced by co-
	deposition
15	The molar decadic absorption
	coefficient <u>vs</u> . energy in
	electron volts for a composite
	curve of $Na^+C222 \cdot Na^-$

16	The optical constant, k, <u>vs</u> the
	energy in electron volts calculated
	from the average values of the absorp-
	tion coefficient
17	Unnormalized absorbance <u>vs</u> wavenumber
	for layered Films I, II, III of Na ⁺ C222.
	Na ⁻
18	Layered Na ⁺ C222'Na ⁻ Film IV. Un-
	normalized absorbance <u>vs</u> wavenumber 132
19	Layered Na ⁺ C222·Na ⁻ Unnormalized
	absorbance <u>vs</u> wavenumber for Film
	V 135
20	Layered Film of Na ⁺ C222·e ⁻ . Un-
	normalized absorbance <u>vs</u> wavenumber
	for Film I
21	Layered Film of Na ⁺ C222·e ⁻ . Un-
	normalized absorbance <u>vs</u> wavenumber
	for Film II
22	Co-deposition film of K ⁺ C222·K ⁻ .
	Unnormalized absorbance <u>vs</u> wave-
	number
23	Unnormalized absorbance <u>vs</u> wavenumber
	for (a) Film I of Layered $K^+C222 \cdot e^-$
	and (b) Film II of co-deposited
	к ⁺ C222·e ⁻

24	Normalized absorbance <u>vs</u> wave-	
	number from a solution of $K^+C222 \cdot e^-$	
	crystals in dimethylether	164
25	Normalized absorbance <u>vs</u> wave-	
	number from a solution of $Rb^+C222 \cdot e^-$	
	crystals in dimethylether	166
26	Static molar susceptibility <u>vs</u>	
	temperature of K ⁺ C222·e ⁻ crystals	
	ina Delrin bucket. Sample mass =	
	0.02717 g	170
27	Static molar susceptibility <u>vs</u>	
	temperature of K ⁺ C222·e ⁻ crystals	
	ina Delrin bucket. Sample mass =	
	0.05953 g	171
28	Static molar susceptibility <u>vs</u>	
	temperature of Rb ⁺ C222·e ⁻ crystals	
	ina Delrin bucket. Sample mass =	
	0.0355 g	172
29	Reciprocal molar susceptibility <u>vs</u>	
	temperature of Rb ⁺ C222·e ⁻ crystals in a	
	Delrin bucket. Sample mass = 0.0355 g .	173
30	Static gram susceptibility <u>vs</u> tem-	
	perature of Li:C2ll electride	
	crystals in a Kel-F bucket. Nom-	
	inal mole ratio = 0.978	195

xi

Page

•

Figure

Page

CHAPTER I

INTRODUCTION AND BACKGROUND

I.A. Introduction

The work that will be presented in this thesis involves the synthesis and characterization of two new classes of solid state compounds which have been named alkalides and electrides. Alkalides are semiconducting ionic salts in which the cations are large macrocyclic complexed alkali metal cations, M^+ , where M = Na, K, Rb, Cs, and the anions are the alkali metal anions, M⁻. The general formula for alkalides can be written as $M^+C\cdot M^-$ or $M^+C\cdot N^-$. The former is the formula for an alkalide that contains only one alkali metal and the latter is the formula for an alkalide which has a mixture of two different alkali metals. The complexing agents used to complex the alkali metal cations fall into two different classes. The first is that of cryptands, which are three dimensional cage-like polyethers. An example is 2.2.2 cryptand (commonly referred to as C222) which has the following structure:

-1-



The second class is that of crown ethers, which are planar polyethers. An example is 18 Crown 6 (18C6) which has the following structure:



Electrides have the same cations as alkalides but have stoichiometric numbers of trapped or localized electrons as the anions. Thus, they have often been referred to as stoichiometric F-centers. The general formula is written as $M^+C^-e^-$.

The work presented here falls into two parts. First, studies of three different electride salts, each of which has a cryptand complexing agent, will be presented. These three salts are $K^+C222 \cdot e^-$, $Rb^+C222 \cdot e^-$, and $Li^+C211 \cdot e^-$. The bulk studies on these highly temperature and air sensitive materials include the measurement of their bulk magnetic susceptibilities, d.c. conductivities, electron spin resonance spectra, and their optical properties. Secondly, a major effort has been made to design and build a high vacuum evaporator to grow thin solid films of alkalides and electrides by physical vapor deposition, and to begin quantitative measurements of the electrical and optical properties of these films.

This chapter has the purpose of describing the behavior and properties of electrons in condensed media, such as alkali metal ammonia solutions, metal ammonia compounds, F-centers in alkali halides and trapped electrons in organic glasses. This discussion will not only serve to present the historical development of the study of alkalides and electrides, but will also help to indicate the position that alkalides and electrides occupy in the framework of solid state chemistry and physics.

I.B. Theoretical Models for Solvated Electrons

Before initiating a discussion of specific systems containing trapped or solvated electrons, it is advisable to briefly consider the theoretical model for the solvated electron as found in systems such as metal ammonia solutions or electrons in frozen glasses. This is an essential concept since electrides are thought of as ionic solids in which the anions are completely replaced by trapped electrons. Although many different models have been used to describe the solvated electron, including some ab initio calculations using molecular orbital theory, a relatively simple and yet fairly successful model is the so-called semi-continuum model. A brief description of this model will help to highlight many of the concepts used in any model for the solvated electron.

Earlier models had accounted only for short-range interactions or only for long-range interactions, but the semi-continuum model incorporates both interactions in the expression for the energy of the system, and as a result has been found to agree better with experimental observa-The model pictures the solvated electron as a tions. particle-in-a-box, in which the potential well is created by the symmetrically arranged solvent molecules which surround the electron. The semi-continuum model considers the electron to be a charge distribution at the center of this spherically symmetric cavity. The solvent molecules which surround the cavity are assumed to be point dipoles which are polarized by the presence of the electron. In fact, the charge distribution is assumed to extend beyond the first solvation shell so that the next shell solvent molecules are also polarized and thus help to localize the electron. This is the concept of "selftrapping" of the electron. The semi-continuum model can be used by making one of two different approximations. These approximations are necessary in order to reduce this n electron problem to a one electron problem. The first approximation has been termed the adiabatic approximation, in which the average velocity of the solvated

-4-

electron is assumed to be much less than the velocity of the electrons of the solvent molecules. This enables the trapping potential to be written only as a function of the distance between the solvated electron and the solvent molecules, and not as a function of the charge distribution of the electron. The other approximation is the self-consistent field theory in which the solvated electrons and the electrons of the solvent are assumed to be equivalent, but the solvated electrons are assumed to be in an average potential field created by the solvent electrons. This potential is in turn affected by the presence of the excess electrons. Finally, the energy terms in the expression for the solvated electron include the kinetic energy of the electron, short and long-range medium rearrangement energies, a repulsive energy between the solvated electrons and the electrons of the solvent, and a screening Coulombic potential which accounts for the interaction of the electron with the solvent molecules beyond the first shell. This model has been found to be successful for treating the problem of the solvated electron in a wide variety of solvents at different temperatures and pressures. It has been especially successful in simulating the band shapes of optical absorption spectra (1).

-5-

I.C. Systems Related to Alkalides and Electrides

1. Expanded Metal Compounds

A class of compounds known as expanded metals, and consisting of the metal-ammonia compounds, has attracted considerable interest for many years as a result of the unusual properties that these materials exhibit. Because of their close relationship to the materials studied in this thesis, a consideration of their properties can shed some light on the nature of alkalides and electrides. These compounds consist of the alkaline earth hexammines, $M(NH_3)_6$, where M = Ca, Sr, Ba, the lanthanide hexammines where M = Eu, Yb, and also the single alkali metal tetraammine, $Li(NH_3)_4$. The $Li(NH_3)_4$ compound forms near the eutectic composition of 20 mole percent metal (MPM) of Li in ammonia solutions, when the solution is frozen. The hexammines are also prepared by cooling the metal solutions which have concentrations above 8 MPM. In all cases, the compounds form with only approximate stoichiometry and solidify as polycrystalline solids with no evidence for good single crystal formation.

Structural studies have been done on these compounds both by powder x-ray diffraction and powder neutron diffraction techniques. The hexammines are known to crystallize in body centered cubic (b.c.c.) structures above 50 K, in which the molecular complexes $M(NH_3)_6$ are located at each lattice site (2). The ammonia molecules are arranged

-6-

octahedrally about the metal. The situation in the case of the $Li(NH_3)_4$ compound is slightly more complex, and the structural data were initially interpreted in a different way than the current method. It is now thought (3) that the $Li(NH_3)_4$ compound solidifies in one type of body centered cubic structure but with three different space groups. The first b.c.c. phase, solid phase I, forms between 89 and 82 K with a = 14.98 Å, and has a different space group than solid phase II. Phase II is also b.c.c. with a = 14.93 Å, and forms between 82 and 25 There is some evidence for a third solid phase below Κ. 25 K. In all cases the ammonia molecules are tetrahedrally arranged about the Li⁺ ions. The energy levels of this expanded metal are conceived of as follows. The 2s electron of the Li is probably promoted to a 3s orbital, leaving the 2s2p orbitals free to hybridize into sp³ orbitals. These sp^3 orbitals are then occupied by the lone pair electrons from the ammonia molecules. The 3s orbital, containing the promoted 2s electron, which lies outside the NH_3 molecules, forms the basis for the conduction band (4). As a final note on the structure of these compounds, it has been postulated that the ammonia molecules in the hexammines may have very unusual geometries (5). That is, powder neutron diffraction studies of the deuterated compounds have indicated that the ammonia molecules have nearly planar geometry, with two long N-D distances of 1.4 Å, and one short N-D distance of 0.9 Å.

-7-

The metal ammonia compounds have been termed expanded metals because of the large distances between the metal centers, due to the fact that each metal is surrounded by several ammonia molecules which have the effect of greatly increasing the volume of the metal. An estimate was made of the largest possible conduction electron density of these low-electron density metals, assuming that each of the hexammine molecular complexes is doubly ionized. The results gave conduction electron densities of $0.52 \times 10^{22} \text{ cm}^{-3}$ for $Ca(NH_3)_6$, $0.46 \times 10^{22} \text{ cm}^{-3}$ for $Sr(NH_3)_6$, and 0.40 x 10^{22} cm⁻³ for $Ba(NH_3)_6$ (6). Some of the physical properties of these compounds that have been measured include their electrical resistivities, optical properties, conduction electron spin resonances, and static magnetic susceptibilities. Measurements of the electrical resistivities of $Ca(NH_3)_6$, $Sr(NH_3)_6$, and $Ba(NH_3)_6$, were done by an electrodeless method described in Reference 6. In all three cases the resistivities increased with increasing temperature as expected for metals due to the increase in conduction electron-phonon scattering with temperature, as is discussed in more detail in Chapter IV. However, there were some additional features of interest which included the presence of sharp inflections at various temperatures, indicating that phase transition may occur. For example, in the case of $Sr(NH_3)_6$, the resistivity data as well as the static magnetic succeptibility and structural data, all show a transition

-8-

near 60 K, which is probably due to a transition from a high temperature b.c.c. phase to a rhombohedral phase.

Optical properties of Li-NH₃ solutions and the solid phases of the Li(NH₃)₄ compound have been measured by reflectance spectroscopy (7). The general features are all similar, and show the onset of a high absorbance at a photon energy of 2 eV, which is indicative of the metallic plasma edge absorption. However, the spectral shapes do differ slightly from that predicted by the perfect nearly free electron model. The nature of the plasma edge absorption is also discussed in further detail in Chapter IV, in the context of the discussion of alkalides and electrides.

The Faraday balance method had been used to measure the static magnetic susceptibilities both of the hexammines $Ca(NH_3)_6$, $Sr(NH_3)_6$, $Ba(NH_3)_6$, (2), and of the lithium compound $Li(NH_3)_4$ as well as the lithium compound that forms with methylamine, $Li(CH_3NH_2)_4$ (8). The susceptibilities of the hexammines did not show the temperature independent Pauli paramagnetism that is usually observed in metals. Instead all three compounds showed strong temperature dependence, in which the susceptibility decreased with decreasing temperature, and all three had diamagnetic molar susceptibilities. An exception to this general trend occurred in $Ca(NH_3)_6$ which had a peak in the susceptibility occurring near 10 K, which may be indicative of an antiferromagnetic ordering of localized

-9-

electron spins. The tendency for localization and even antiferromagnetic ordering to occur at lower temperatures, as well as the overall diamagnetism of these materials, reinforce the picture of low conduction-electron density existing in these metals. In fact, more conventional metals such as Sb and Bi are also diamagnetic and show the same positive temperature dependence of the susceptibility that is observed in $Sr(NH_3)_6$ and $Ba(NH_3)_6$. Antimony and bismuth are extremely low conduction electron density metals, of as low as 3 x 10^{17} cm⁻³ for Bi and 5 x 10^{19} cm⁻³ for Sb, and in fact have been called semimetals (9). They can therefore be roughly compared to the low electron density metal ammonia compounds. In the case of these pentavalent semimetals the Fermi surface consists of ellipsoidal pockets of carriers, which means that they have a low Fermi surface area and therefore a low density of levels at the Fermi energy which accounts for the low carrier density. A similar situation is thought to exist in the hexammine compounds (2). The anomalous behavior of $Ca(NH_3)_6$ is not clearly paralleled in other metals.

The magnetic behavior of the lithium compounds is slightly different. In the case of $\text{Li}(\text{NH}_3)_4$ the behavior has to be divided into three regions corresponding to the three different phases of this compound. For the liquid phase above the melting point of phase I at 89 K, a metallic, temperature independent paramagnetism is seen.

-10-

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Solid phase I from 89-82 K also has a slightly smaller temperature independent paramagnetism. Solid phase II shows Curie-Weiss paramagnetism from 82-25 K, and finally phase III below 25 K shows the onset of antiferromagnetic ordering. Finally, the compound $Li(CH_3NH_2)_{\downarrow}$, not previously discussed, has a quite different behavior. This compound crystallizes from lithium-methylamine solutions at 155 K and has a diamagnetic susceptibility which becomes more diamagnetic as the temperature is lowered while in the liquid phase, and reaches a constant diamagnetism in the crystalline phase, with a slight increase at the lowest temperatures. It has been suggested (8) that the liquid phase is a highly correlated metal, and the crystalline phase is a spin-paired semiconductor. The behavior near 0 K suggests that the electrons begin to localize at individual sites so that the antiferromagnetic coupling decreases. The behavior of this compound is particularly reminiscent of the behavior of some electrides.

2. F-Centers in Alkali Halides

An example of trapped electrons in solid media, which is especially pertinent to this subject because of its similarity to the model proposed for electrides, is that of F-centers, or color centers, in alkalide halides. Fcenters are a special example of point defects in perfect crystals. Crystalline defects are regions in a crystal

-11-

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lattice where the arrangement of the ions is not the same as that in the perfect crystal. Point defects are either the presence of extra ions at lattice sites or the absence of ions at the sites, or finally interstitials, which are ions that are present in locations that are not occupied in the perfect crystal. The condition of charge neutrality must still be met, and this can be accomplished in one of three ways. There may be equal numbers of positive and negative ion vacancies, or there may be equal numbers of vacancies and interstitials of the same ion. Finally, missing negative ions may be replaced by one electron which is localized in the vacancy point defect (9). This defect is known as an F-center, and can be most simply considered as an electron in a spherical potential well. The energy of this three-dimensional particle-ina-box is proportional to the inverse of the box dimensions, which are in this case directly related to the lattice dimensions (10).

F-centers can be created in pure alkali halide crystals either by irradiation with x-rays or γ rays, or by exposing the crystals to an alkali metal vapor. In this case, the alkali metal vapor atoms are ionized and take up lattice sites in a positively charged perfect sublattice, thus donating the excess electrons to form the F-center imperfections. It is known that this occurs, rather than the interstitial incorporation of metal atoms, because the

-12-

density of the colored crystal decreases in proportion to the concentration of the additional alkali metal atoms (9).

The optical properties of F-centers have been extensively studied. In general, a single large band in the visible or near ultraviolet is observed which is due to the F-centers. An empirical equation has been developed for these bands, which relates the energy of maximum absorption, E_{max} , to the interionic distance, a. This is known as the Mollwo-Ivey Law, and is given in Equation [1].

$$E_{max}(eV) = (17.6)a^{-1.84}$$
 [1]

Thus, the simple model of a particle in a spherical energy well gives fairly good agreement with the experimentally observed behavior. The energies of the absorption maximum depend most strongly upon the ionic spacing and at room temperature vary from 4.96 eV for LiF to 1.58 eV for CsI (11). Good optical measurements were typically made for crystals with F-center concentrations of 10^{16} cm⁻³. In addition to the main band due to the F center, other small optical bands associated with the F band have been observed. For example, four weak absorptions have often been observed at higher energies than the F band. One of these, known as the K band, is always formed when the F center is formed and it is thought that it is due to a transition to the next higher state of the F-center (11).

Another major band, known as the F' band, was observed when F-center crystals were exposed to light. This band is found at lower energies than the F band. If the crystal is then re-exposed to light the F' band disappears. The quantum yields of these processes are defined as follows:

Y(F') = # F centers destroyed/# quanta absorbed by F centers; Y(F) = # F centers created/# quanta absorbed by F' centers. The measured values for these quantum yields were equal to 2 which led to the following description of the F' centers that were responsible for the F' bands. The absorption of the light quantum can cause the release of one electron from an F center which is then trapped by a second F center to form the F' center, or doubly occupied potential well. Thus, two F centers are destroyed to form one F' center. Similarly, when an electron is given up by the F' center as it is trapped at another imperfection (11). This model of an F' center also has an analogy in the electride systems as will be discussed in Chapter V.

Finally, it should be noted that electron spin resonance has been used to study F centers in alkali halides. In this case, it was usually found necessary to increase the concentration of imperfections to $10^{18} - 10^{19}$ cm⁻³. The unpaired electrons of the F centers are paramagnetic

-14-

and have rather broad absorptions. The ESR absorption lines are broadened by the hyperfine interactions with the surrounding nuclei of the positive and negative ions of the pure alkali halide crystals. In fact, ENDOR (electron nuclear double resonance) techniques have been used to resolve the hyperfine splittings, and interactions with as many as seven concentric shells of nuclei have been accounted for (12).

3. Trapped Electrons in Frozen Glasses

Another system which can contain isolated trapped electrons is that of various frozen liquids. It has been known since 1962 that trapped electrons can be formed in liquid water upon irradiation. Since then a large number of other solvents have been found to contain trapped or solvated electrons at low temperatures. These liquids include aqueous solutions of NaOH or sugars, alcohols, ethers, amines, and various hydrocarbons. The liquids are formed into glassy or amorphous states by rapidly quenching them in liquid nitrogen. These glasses have been found to stabilize much larger yields of trapped electrons than the same solvents in crystalline states. When the cold glasses are irradiated with γ rays or xrays, trapped electrons are produced within the glass. A typical concentration range for electrons produced in this way is $10^{17}-10^{19}$ cm⁻³ in 3-methylpentane or ethanol(13).

-15-

The two most useful techniques for probing the nature of electrons in glasses are electron spin resonance and optical spectroscopy. The optical bands are broad absorptions found in the visible or near infrared regions of the spectrum. They also have tails on both the high and low energy sides of the position of maximum absorption, although the high energy tail is longer. The spectra in the various glasses are comparable to the spectra in the respective liquids but are both narrower and shifted to slightly higher energies, suggesting that the nature of the electron trapping is similar in the liquids and glasses, but that the electrons are in deeper and more stable traps in the glasses. In fact, the optical spectra can in general be used to obtain information about the nature of the electron traps. Workers in the field have obtained a smooth curve from a plot of the photon energy at the maximum absorption versus the static dielectric constants of a series of glasses, indicating that the electrons are trapped in deeper potential wells as the polarity of the glass increases (13).

Three major experimental observations have indicated that the electrons become trapped in glasses in a two step process. They are first weakly localized in the medium and then induce a rearrangement of the solvent molecules around them. This has the effect of deepening the trap as the molecules of the glass take up an equilibrium configuration (13,14). This also implies that the

-16-

spectral bands are actually envelopes of the absorptions due to many electrons which occupy a variety of trap depths. These conclusions are reached from the following results. It is known that the optical spectra of electrons trapped in a glass held at 77 K undergo a shift to higher energies with time. The change can continue for as long as 380 seconds in glassy hydrocarbons or for 10^{-7} to 2 seconds in glassy alcohols. This indicates that the electrons are found in deeper traps after a sufficiently long period of time. Moreover, if the spectra are first observed in glasses which are cooled to 10 K at which temperature the rearrangement process of the molecules of the glass is hindered, and the glass is then warmed to 77-97 K, the spectra again show a strong shift to higher energies. This can be explained by the increased ability of the molecules to achieve equilibrium positions around the electron, thus forming a deeper trap. Finally, the ability to use monochromatic light to preferentially decrease (or bleach) the absorption in the high energy tail, suggests that the spectra are indeed envelopes of a continuum of trap depths (13).

The ESR spectra of trapped electrons in organic glasses are broad Gaussian lines with g values near the free electron value. They are broadened by the hyperfine interactions of the electron with the surrounding nuclei. In general, the line widths increase as the polarity of the glass increases, suggesting that the hyperfine

interactions increase as the traps deepen. The widths also irreversibly broaden with an increase in temperature. Traditionally ENDOR techniques can be used to resolve hyperfine splittings and to probe the structural information on the solvation shell of the localized electron. In this case ENDOR spectroscopy also gives a single line in which the weak hyperfine coupling is still hidden. However, the solvation structure of the electron has been elucidated in a variety of solvents, primarily by the application of electron spin echo modulation (15). This technique is a pulsed experiment in which the pulses produce an echo, or short burst of microwave power. The echo decays with an envelope function that is a product of a relaxation function and a modulation function that contains the desired structural information. The modulation pattern is analyzed by comparing it to a theoretical pattern calculated for an assumed geometry of n nuclei at a distance r from the electron and with an isotropic hyperfine coupling constant, a. A typical result is a 10 M solution of NaOH in H_2O , in which it was found that the Na molecules were not in the first solvation shell. Tnstead, the solvation structure consists of 6 octahedrally arranged water molecules that are oriented with the OH bonds pointing towards the trapped electron. It is also interesting to note that the resulting isotropic constant for the nearest proton of the first solvation shell water molecule is 2.1 G and the constant for the oxygens of the

-18-

first shell is 4 G. These constants correspond to a total unpaired electron spin density on the molecules surrounding the electron of 4%. Thus, the electron density is primarily found near the geometrical center of the trap indicating that localized electrons in glasses are very similar to more conventional solvated anions (15).

I.D. Alkalides and Electrides

The ability of liquid ammonia to dissolve the alkali metals has been well known for over 120 years. In fact, it is known that Sir Humphry Davy first observed the deep blue solution of K metal in ammonia in 1808 (16). This preceeded the more extensive, and first published, work of W. Weyl that began in 1864, and the work of C. A. Kraus that spanned a thirty year period beginning at the start of the twentieth century (4). All of the alkali metals dissolve readily in liquid ammonia. The solubilities vary considerably, and for Li, Cs, Na and K are respectively 20, 65, 16, and 15 mole percent metal (MPM) at 239.8 K, the normal boiling point of liquid ammonia (4). At concentrations below 3 MPM, alkali metal solutions are electrolytic in nature with a characteristic blue color. The species present in dilute solutions are the solvated metal cations, M⁺, and the solvated electron, e⁻, formed by the reaction

$$NH_3 + M \to M^+ + e^- + NH_3.$$
 (Ref 17)

As the concentration is increased the cations and solvated electrons begin to form solvent-separated ion pairs, as is common in ordinary salt solutions in low dielectric media (4). The optical absorption spectra of metal ammonia solutions help to explain the striking blue color. The main absorption is that of the solvated electron, e, which is completely independent of the metal used and which peaks at 0.9 eV (1389 nm). The absorption line is asymmetric and the long tail which extends beyond 1.8 eV (700 nm) is responsible for the color (4). In contrast to the behavior at lower concentrations, metal ammonia solutions at concentrations greater than 8 MPM behave as liquid metals. They are bronze colored liquids which, for those metals that show a liquid-liquid phase separation, float on the denser more dilute blue solutions. There is a very large body of data on these solutions but for this discussion it suffices to point out that concentrated metal ammonia solutions are good liquid metals with metallic conductivities ranging from 3 x $10^{3}\Omega^{-1}$ cm⁻¹ to 6 x $10^{3}\Omega^{-1}$ cm⁻¹ for 15 MPM solutions of Cs in NH₂ or Li in NH₂. In fact, saturated solutions of Li in NH₂ have conductivities of 15 x $10^{3}\Omega^{-1}$ cm⁻¹, which are higher than the conductivity of liquid mercury at room temperature (4).

Solutions of the alkali metals in solvents other than liquid ammonia had not been extensively investigated until the 1960's and 1970's, and J. L. Dye was one of the main

-20-

workers in this field. Metal solutions in various liquid amines and ethers, such as methylamine, ethylamine, and dimethylglyoxime, were studied by using a variety of techniques including ESR and optical spectroscopy (see for example, Reference 18). It soon became apparent that the amine and ether solutions contained quite different species than ammonia solutions. These less polar solvents favored the formation not only of solvent-shared ion pairs between the M^+ and e^- , but also of contact ion pairs. In addition, the optical spectra for the various metals showed strongly metal dependent bands occurring at higher energies than the band for the solvated electron. These bands were ultimately identified as arising from the alkali metal anions, M, formed by the equilibrium $2e^{-} + M^{+} \neq M^{-}$ (17). The irrefutable evidence for the existence of M^- in solution came from the solution NMR work of Reference 19, in which the extremely narrow line for Na, at a chemical shift value nearly identical to that of Na in the gas phase, with no solvent induced paramagnetic shift, indicated the presence of a centrosymmetric anion with filled 3s orbitals.

The major difficulty in working with the solutions of amines and ethers was that the alkali metals were much less soluble in these solvents than in liquid ammonia. The use in the early 1970's of macrocyclic complexing agents, which selectively complex the alkali metal cations, was found to greatly enhance the solubilities
of the metals in these solvents, and also to increase the range of solvents that could be used. The new-found ability to create concentrated solutions containing solvated electrons, e, alkali metal anions, M, and complexed alkali metal cations, M⁺C, led Dye to attempt to prepare solids that contained these ions. In 1974 (20) the preparation and crystal structure of the first alkalide, Na⁺C222·Na⁻, was reported. These golden colored crystals, possessing a metallic luster, were found to crystallize in a hexagonal ABC repeat pattern with the Na occupying the octahedral holes. The compound was stable for short periods of time at room temperature under vacuum or in an inert atmosphere, and for extended periods when held below -50°C. It was found to be a semiconductor with a large band gap of 2.5 eV. Since the isolation of this compound many other crystalline alkalides have been synthesized and characterized (21). These salts include a wide variety of alkalides with crown ethers as the complexants. The crown ethers 18C6 and 1505 have been found to be very versatile and even form alkalide salts in which the cation is "sandwiched" or complexed between two crown ether molecules. The alkalide salts are all semiconductors, many exhibiting various degrees of extrinsic behavior due to doping from excess electrons. All these salts react readily with water or oxygen, and only a few are stable for more than one to two minutes at room temperatures. However, the alkalides

-22-

are relatively stable at lower temperatures in well controlled atmospheres. The difficulty in preparing good single crystals of these materials, and also the difficulty in handling the materials to prevent decomposition had impeded the measurement of the crystal structures of these materials. However, within the past year two new structures have been obtained as a result of better crystal growing and handling techniques (22). These structures are for $Cs^{+}(18C6)_{2} \cdot Na^{-}$ (22) and $Rb^{+}(15C5)_{2} \cdot Na^{-}$ (23).

Electrides were not isolated as single crystals until 1983 when the existence of the first crystalline electride $Cs^+(18C6)_2 \cdot e^-$ was published (24). Since then, at least five other crystalline electrides have been isolated. These deep black materials are in general far more reactive than the alkalides. Their properties are also far more diverse, with the stoichiometric trapped electrons giving rise to varying degrees of electron-electron interactions. The electride $Cs^+(18C6)_2 \cdot e^-$ is perhaps the simplest example of an electride. Its static magnetic susceptibility has a strong Curie-Weiss paramagnetism, in common with several other electrides. The d.c. conductivity results gave a band gap of 0.9 eV, and the optical spectrum showed a single peak for the trapped electron at 6700 cm^{-1} (0.83 eV). The properties of several other electrides will be discussed in more detail in Chapter V.

-23-

I.E. Magnetic Properties of Electrides

It has been mentioned that electrides exhibit a variety of magnetic properties. This diversity is striking in view of the very slight changes in chemical composition, such as a different metal or complexing agent, which can give rise to these physical differences. It is also remarkable that these systems, containing extremely diffuse s-type electrons, can exhibit electronelectron interactions that lead to properties such as a metallic-like temperature independent paramagnetism, or a spin-paired diamagnetism, Curie-Weiss paramagnetism, or antiferromagnetism. This section will present a brief summary of the physical principles and equations associated with these magnetic properties. This will help to facilitate the discussion of specific electride systems in Chapter V.

The most fundamental terms which must be defined are the magnetization density or magnetic moment, M(H), and the susceptibility, χ . M(H) for a system with volume, V, at temperature, T, and in a magnetic field, H, is given by the derivative of the ground state energy, $E_0(H)$, of the system.

$$M(H) = -\frac{1}{V} \frac{\partial E_0(H)}{\partial H}$$
[2]

-24-

At temperature, T, the magnetization density can be written in the thermodynamic form $M = -1/V \partial F/\partial H$, where F is the magnetic Helmholtz free energy. The susceptibility can then be defined as

$$\chi = \frac{\partial M}{\partial H} = -\frac{1}{V} \frac{\partial^2 F}{\partial_H^2}$$
[3]

In practice, since M is frequently linear with field, χ is often calculated by $\chi = M/H$ (9). The starting point for calculations of the magnetic susceptibilities of atoms, ions, or molecules, or ionic and molecular solids, is the equation for the energy perturbation of a quantum mechanical system in a magnetic field. The effect on the Hamiltonian of the system can be written, and then the second order perturbation correction to the energy, $E_n + \Delta E_n$, can be expressed as follows:

$$\Delta E_{n} = \begin{cases} \mu_{B} \hat{H} \cdot \langle n | \hat{L} + g_{0} \hat{S} | n \rangle + \sum_{n' \neq n} \frac{|\langle n | \mu_{B} \hat{H} \cdot (\hat{L} + g_{0} \hat{S}) | n' \rangle|^{2}}{E_{n} - E_{n'}} \\ + \frac{e^{2}}{8mc^{2}} H^{2} \langle n | \frac{\Sigma}{i} (\chi_{i}^{2} + y_{i}^{2}) | n \rangle \end{cases}$$
[4]

In this expression, \hat{H} is the magnetic field, \hat{L} is the total electronic orbital angular momentum, \hat{S} is the total electron spin, μ_{B} is the Bohr magneton, g_{0} is the electronic g factor. (which is equal to 2.0023). To sufficient accuracy in solids g_{0} can be approximated by 2 (9). The

first term is the largest term and the other two terms can often be neglected.

The first term can be equal to zero, however. For example, in the case of all spins being paired as in a solid containing ions with filled shells, the operators \hat{S} , \hat{L} and $\hat{J} = (\hat{L} + \hat{S})$ operating on the ground state give 0. The third term is the only term that contributes to the perturbation energy, and the susceptibility that is calculated from this expression is found to be a small diamagnetic susceptibility on the order of 10^{-5} . This socalled Larmor diamagnetism is a negative susceptibility in which the induced moment is opposite to the applied field.

An expression for a paramagnetic susceptibility which is more applicable to electrides can be derived from a consideration of a solid that contains ions with incompletely filled shells, so that the total angular momentum J is not equal to zero. In this case, the first term in the energy expression is dominant and the other two terms can be ignored. The matrix element must be evaluated by noting that the ground state is (2J + 1) - fold degenerate. It is then found that if the energy difference between the ground state multiplet and the first excited state multiplet is large compared with k_BT then only the (2J + 1)states in the ground state will contribute to the free energy. Then the first term in the perturbation energy can be viewed as the interaction between the field and

-26-

the magnetic moment, $\hat{\boldsymbol{\mu}},$ of the ion where

$$\hat{\mu} = -g\mu_B \hat{J}$$

and

$$g = 3/2 + 1/2 \left[\frac{S(S+1) - L(L+1)}{J(J+1)}\right]$$
[5](9)

To calculate the susceptibility from Equation [2] it is necessary to evaluate the free energy, F. When this is done, the resulting expression for the magnetization density for N ions in a volume V is given in terms of a Brillouin function, where in general the Brillouin function of x is

$$B_{J}(x) = \frac{2J+1}{J} \operatorname{coth} \frac{2J+1}{2J} x - \frac{1}{2J} \operatorname{coth} \frac{1}{2J} x$$
[6]

The result for M is given in Equation [7].

$$M = \frac{N}{V} \mu_{B} g J B_{J} \left(\frac{J H \mu_{B} g}{\kappa_{B} T} \right)$$
[7]

The susceptibility can be evaluated for the most commonly encountered case where $g\mu_B << k_B T$ so that the Brillouin function can be expanded for small x. The result for the molar susceptibility is Curie Law paramagnetism given by Equation [8].

$$\chi_{\text{molar}} = N_{\text{AV}} \frac{\left(g\mu_{\text{B}}\right)^2}{3} \frac{J(J+1)}{k_{\text{B}}T}$$
[8]

where $N_{\Delta V}$ = Avogadro's Number

or
$$\chi = \frac{C}{T}$$
 (Ref.9)

This paramagnetic susceptibility is usually on the order of 10^{-2} to 10^{-3} mol⁻¹, and occurs only for materials with a permanent magnetic moment. A modification for this law exists when there are interactions between the spins. This is known as the Curie-Weiss law

$$\chi = \frac{C}{T - \theta}$$
 [9]

where θ , the Weiss constant accounts for the exchange interactions (25). The Weiss constant is positive when the exchange interactions are ferromagnetic or parallel to each other, and is usually negative when the moments tend to interact in an antiparallel fashion.

The susceptibility for a degenerate free electron gas (that is, for conduction electrons in a metal), is quite different from Curie paramagnetism. As in the calculation for Curie magnetism the expression for the Pauli paramagnetism is calculated by assuming that the electrons are independent of each other. The resulting susceptibility is found to be independent of temperature and has the same order of magnitude as diamagnetic susceptibilities, that is, on the order of 10^{-6} cm⁻³.

CHAPTER II

GENERAL EXPERIMENTAL

II.A. Reagents

1. Complexing Agents

The crown ether, 18-crown-6, IJPAC name 1,4,7,10,13,16hexaoxacyclooctadecane, (18C6), was purchased from Parish Chemical Company. It was purified in two steps. It was first recrystallized from warm acetonitrile followed by vacuum pumping of the acetonitrile complex. It was then sublimed at high vacuum and stored under vacuum or in a Vacuum Atmospheres Company helium glove box. The 2,2,2 cryptand, IUPAC name 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, (C222), was purchased from Fluka Chemical Company. It was sublimed onto a cold finger vacuum sublimation apparatus purchased from Ace Glass, and stored in an inert atmosphere glove box. The 2,1,1, cryptand, IUPAC name 4,7,13,18-tetra-oxa-1,10diazabicyclo-[8.5.5]eicosane, (C211), was a gift from Professor Jean-Marie Lehn. It was sublimed under vacuum in semi darkness in a liquid sublimation apparatus. The purified C211 was stored in the glove box.

-30-

2. Metals

Lithium metal was cut from a block of lithium kept in the helium glove box. The block of lithium metal was purchased from Atomergic Chemetals Company and was of 99.99% purity. Weighed pieces of metal were placed in the apparatus used for synthesis. The apparatus was removed from the glove box and pumped to about 10^{-5} torr. The potassium and rubidium metals were purchased from Alfa Ventron in Breakseal glass ampoules under argon. They were distributed under vacuum into a glass apparatus that contained several tubes of varying diameters, by attaching the ampoules to the apparatus which was then evacuated. The metals were transferred into the glass tubes by gently heating and shaking them, and appropriate lengths of tubes were removed by vacuum seals for use in synthesis. The inner diameters of the glass tubes were measured in advance to allow the accurate determination of the volume of the metals, and hence the number of moles of metal used.

3. Solvents

The general procedure for solvent purifications was the same for all the solvents used. They were first distilled under vacuum over about five grams of calcium hydride, and were stirred for 24 hours. They were

-31-

occasionally degassed by evacuating the solvent bottles which were frozen with liquid nitrogen. This step was omitted in some cases depending on the purity of the starting material. The solvents were then distilled under vacuum over Na or K metal or over a Na-K alloy (1:3 ratio). They were then degassed and stored overnight. If the blue color of the solution persisted for at least 24 hours at room temperature they were distilled into a storage vessel. Otherwise, they were distilled over a fresh metal surface until a lasting blue color was obtained. The solvents were occasionally degassed before use. Many of the solvents were stored in heavy walled glass bottles under vacuum. The storage vessels for the ethers contained some Na metal in order to prevent the formation of peroxides. The highest vapor pressure solvents were stored in high pressure metal gas tanks purchased from the Whitey Company. The solvents used were methylamine, dimethylether, anhydrous trimethylamine, ammonia, dimethylamine, 1,2-dimethoxyethane (all purchased from Matheson Gas Products), and 2-aminopropane (purchased from Eastman Kodak), and diethylether (from Fisher). In all cases, except for methylamine and ammonia, it was necessary to add benzophenone ketyl to the bottles containing the metals. The radical formed from this reaction served as a drying agent, with the characteristic blue color serving as an indicator of dryness.

II.B. Glassware Cleaning

The glassware used for syntheses, metal purification and solvent purification, was rigorously cleaned by the following procedure. It was first rinsed in an HF cleaner containing 33% HNO₃, 5% HF, 60% H₂O, and 2%detergent which was used only with Pyrex. Quartz glassware was cleaned without the detergent. The HF cleaner was rinsed out with distilled water, and the glassware was filled with aqua regia, and was left soaking over night. The aqua regia was rinsed at least six times with distilled water and six times with conductance water, and was dried in an oven at about 150°C overnight.

II.C. Sample Preparation and Instrumental Techniques

1. General Procedure for Synthesis

All the crystalline samples were prepared in an apparatus such as that shown in Figure 1, which had been previously cleaned. The metals were removed from the main storage tubes by vacuum seals. The length of metal was measured in order to determine the number of moles contained in the tube. These tubes were then scored with a glass knife, and were put in the sidearm, A, of the apparatus by attaching an end cap, B, to it with heat shrinkable tubing, C. Weighed amounts of the solid complexants were placed in the apparatus through the



Figure 1. Apparatus for the synthesis of crystalline electrides.

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Fischer-Porter stopcock, D. The amount of complexant was chosen to give the desired mole ratio of metal to complexing agent. The apparatus was then connected to a high vacuum manifold through a liquid nitrogen tee trap, and was evacuated to about 10^{-5} torr. The tube containing the metal was then broken in the heat shrinkable tubing, and the tubing and the end cap were removed by a vacuum seal-off at E. The metal was heated with a flame until it distilled into the metal chamber, F. The remainder of the side arm was then removed by a second seal-off at G. At this point, the solvent was added to the apparatus through the tee. The main chamber, H, of the apparatus containing the complexant, was cooled with a dry iceisopropanol bath and the solvent was distilled into this chamber. In most cases this solvent was dimethylether. The apparatus was then removed from the vacuum line and placed in a cold isopropanol bath, and the starting materials were dissolved. The apparatus was then reattached to the vacuum line and some of the solvent was removed by distilling it through the tee into an evacuated bottle. The solvent of crystallization was then added to the solution. In most cases this solvent was either diethylether or trimethylamine. In some earlier sample preparations the solvents used were first, methylamine, followed by the addition of diethylether and 2-aminopropane. In either case, the solution was then cooled

-35-

to dry ice temperatures and was left overnight. Once the crystals had formed a small amount of the dimethylether was distilled away from the mother liquor. This differential distillation was possible because the vapor pressure of dimethylether is much higher than that of diethylether or trimethylamine. The solvent remaining over the crystals was usually pale blue or colorless. The crystals were transferred into the sample isolation chamber, I, and were washed by repeatedly distilling the solvent onto the crystals and decanting it off. The crystals were dried by freezing the solvent in the main chamber and pumping on the crystals, held at about -50°C, for one hour. The sample chamber was separated from the main chamber by a vacuum seal at J. The dry crystals were shaken into the sample tubes, K, which were individually removed by vacuum seals.

The preparation of the LiC2ll electrides differed very slightly from this general procedure. The Li metal and the liquid cryptand C2ll were stored in a helium glove box. The apparatus was brought into the box via an evacuable oven port where it was heated and pumped for several hours. The Li metal was cut with an Exacto knife and weighed on a Mettler AC 100 electronic balance. The C2ll was stored in quartz funnels with closed end tubes, into which the liquid was drained. The inner diameter of the tubes had been previously measured. The

-36-

tubes were scored and broken off and were placed in the apparatus after measuring the length of the liquid. This was done in order to calculate the number of moles of cryptand. The correct amount of Li was also placed in the apparatus and the side arm was capped by connecting a closed end glass tube to it with a Cajon Ultra-Torr Union. The apparatus was removed from the glove box, was evacuated, and the sidearm was removed by a vacuum seal. The apparatus was then ready for the introduction of the solvents in the usual fashion.

2. Bulk Magnetic Susceptibility Measurements

The bulk magnetic susceptibilities of the crystalline samples were measured in an S.H.E. 800 Series SQUID (Superconducting Quantum Interference Device) Susceptometer. The susceptibility samples were prepared by opening evacuated sample tubes in a nitrogen flushed glove bag. The samples were kept on a liquid nitrogen cooled plate. The materials were placed in small buckets made either out of Delrin or Kel-F. The buckets had tightly fitting caps, and were suspended by undyed sewing thread, which was threaded through small holes drilled in the rims of the bottom of the bucket and in the top of the cap. The buckets were carried to the SQUID from the glove box while immersed in liquid nitrogen contained in a small dewar. They were placed in the SQUID airlock,

-37-

or sample entrance, which was surrounded by a helium flushed glove bag. For the most temperature sensitive samples one further step was necessary. A copper block, which had a hole drilled through it, was cooled in liquid nitrogen. The block was then placed in the SQUID airlock and the bucket was inserted in the hole in the block. This ensured that the sample was surrounded by the cold copper during the short time required to evacuate and flush the airlock. Once the airlock was sufficiently flushed, the ball valve separating the airlock from the sample chamber was opened and the sample was lowered into the sample measuring chamber. The susceptibility data were taken from about 1.4 K to 250 K. The fields used were between 0 kG and 9 kG. The data were collected with a Smoke Signals Broadcasting microcomputer, which was also used to control and run the experiment itself. In a typical experiment, the sample was run at the various temperatures and fields desired. The sample was then removed from the sample cavity and was allowed to thermally decompose in the air. The decomposed sample was then run under the same conditions as the good sample. The electronic susceptibility was calculated by first plotting the susceptibility, χ , versus temperature, T, curve of the decomposed sample. The susceptibility values of the decomposed sample were then read from the curve and were subtracted from the susceptibilities of the

good sample at the various temperatures. This was done according to the equation

Xelectronic = Xsample + bucket - Xdecomposed sample +
bucket

This method removes the diamagnetic susceptibility from the total susceptibility, leaving only the paramagnetic electronic susceptibility. Finally, it was necessary to correct the susceptibilities for the actual mass of the sample. This mass was calculated by weighing the decomposed sample and bucket, and then carefully washing and drying the bucket in order to obtain the weight of the bucket. The data were usually treated in this manner prior to a more careful data treatment using the nonlinear curvefitting program KINFIT IV. The actual equations that were used for fitting the data for the various samples will be discussed in Chapter V.

3. Electron Spin Resonance Measurements

The Electron Spin Resonance (E.S.R.) spectra were recorded for powdered or microcrystalline samples on an X-band Bruker Model 200 spectrometer. The samples were prepared in a nitrogen flushed glove bag and were loaded into fused silica ("Spectrosil") tubes with outer diameters

between 3 mm and 4 mm. These tubes were attached to high vacuum Fischer-Porter/Kontes valves. The sample tubes were evacuated immediately after removal from the glove bag, and the tubes were removed from the valve by a vacuum seal. The tubes were chilled in liquid nitrogen during the entire procedure. The temperature dependence of the ESR spectra was measured from about 4 K to 230 K. For temperatures below 100 K an Oxford Instruments Model ESR 9 flowing liquid helium system was used. The temperature immediately below the sample was monitored with an Au + 0.03% Fe/chromel thermocouple. For temperatures above 100 K a Varian Model 4341 variable temperature controller was used to control and monitor the flow of $N_{\rm O}$ gas through a liquid nitrogen cooled coil. The temperature was measured with a copper/constantan thermocouple inserted just above the sample, and was digitally displayed on an Omega Model 199 thermocouple indicator. The magnetic field was measured with a Model ER 035M NMR Gauss Meter (ImG resolution), and the microwave frequency was measured with a Hewlett-Packard Model 5245L frequency counter to ±0.01 MHz.

4. Optical Absorption Spectra

The samples for optical spectra were prepared by redissolving a small amount of crystals in a fused silica apparatus under vacuum. The solvent used to dissolve

the crystals was either methylamine or dimethylether. The fused silica apparatus contained an optical cuvette at the bottom of the main chamber, as well as a second chamber at the side. The optical sample was prepared in the form of a thin film on the walls of the cuvette, by pouring most of the solution into the second chamber and then freezing it with liquid nitrogen. The cuvette was kept at about -40°C and solid dry films formed on the walls as the solvent was flash evaporated away. These films. however, were of unknown thickness, and were usually not of uniform thickness. The spectra were measured with a Beckman DK2 double beam spectrophotometer, with a blank reference cell. The sample cell was cooled by flowing cold nitrogen gas through insulated tubes connected to the cell. The temperature could be varied from about -100°C to room temperature, although in practice the temperature was kept lower than about -30°C in order to avoid decomposition. The temperature was monitored with a copper/ constantan thermocouple inserted just below the sample cell. The temperature was digitally displayed on an Omega Digicator thermocouple indicator. The accessible spectral range was from 400 nm (25,000 cm^{-1}) to 2500 nm (4000 cm^{-1}) . The baseline was measured each time by placing a clean cuvette in the sample beam. The spectra were baseline corrected and normalized.

-41-

5. Pressed Powder Conductivity

The d.c. pressed powder conductivities of the samples were measured in a two probe apparatus designed and built by J. L. Dye and M. R. Yemen (26). The samples were prepared in a nitrogen flushed glove bag and were loaded into small quartz cylinders which had a 2 mm hole bored through them. The two stainless steel electrodes were inserted into either end of the sample cylinder, and the electrodes were pressed against the sample by using a calibrated spring. The pressure was adjusted until there was no change in the measured resistance with pressure. A Heathkit L.V. Regulated Power Supply (Model 1P-27), was used to apply a voltage across the pressed sample. The currents were measured with a Keithley Instruments Model 417 high speed picoammeter. A copper/constantan thermocouple was attached to the casing near the sample cylinder and the temperature was monitored with an Omega Digicator thermocouple indicator. The temperature was controlled by the nitrogen gas boil-off produced by heating a large reservoir of liquid nitrogen with a resistive wire coil. The samples were all tested for Ohm's law behavior by measuring the resistance versus voltage dependence at a fixed temperature. The temperature dependence of the resistance (and hence of the conductivity) was then measured, at a fixed voltage. These data were used to determine the band gap of the bulk semi-conducting material using the relationship

$$\sigma \propto e^{-E_g/2k_BT}$$
 [10]

where σ = the conductivity, T = the temperature (K), k_{B} = Boltzmann's constant, E_{g} = the energy gap between the valence and conduction bands. The data were also extrapolated to infinite temperature in order to estimate the value of σ_{∞} or ρ_{∞} , where ρ is the resistivity of the material. The order of magnitude of ρ_{∞} can be used to determine whether a semiconductor is intrinsic or extrinsic. This is discussed in greater detail in Chapter IV, but essentially the log ρ vs. l/T curves for intrinsic semiconductors extrapolate to typical values for ρ_{∞} of 10^{-3} to $10^{-4}\Omega$ -cm (see Figure 9), whereas for extrinsic semiconductors the extrapolated values may be much higher. This is because the curves for extrinsic semiconductors have a discontinuous change in the slopes, so that the curves eventually coincide with the intrinsic curve at higher temperatures. This results in lower values of ρ_{ϖ} than the values that are found by extrapolation. The experimental circuit was tested by measuring the bandgaps of well known semiconductors such as TiO and HgS (26).

II.D. Stoichiometric Analysis of Crystalline Electrides

An analysis for the stoichiometry of the crystalline electrides was done in the following way. The crystalline samples were weighed, if this was possible. For these especially temperature sensitive samples this could not be done without risking extensive thermal decomposition, so that this step was sometimes omitted. The crystals were placed in an evacuable vessel and were attached to a vacuum line. This vacuum line was also attached to a modified Toepler pump. Conductance water, which previously had been degassed, was distilled onto the crystals and was allowed to react with the materials at the lowest possible temperature in order to avoid thermal decomposition. This reaction proceeded according to

 $M^+C \cdot e^- + H_2O + M^+C + 1/2 H_2 + OH^-$.

The hydrogen gas evolved was collected in a calibrated volume and the pressure was measured by using the Toepler pump. This step gave the reducing equivalent of the crystalline electride. However, the extreme thermal instability in particular of $K^+C222 \cdot e^-$ usually resulted in an order of magnitude error in this step. Thus, the H_2 evolution step was omitted for $K^+C222 \cdot e^-$ and the crystals were decomposed with gentle and gradual thermal decomposition, and were then weighed. In the second step,

the dried residue from the H_2 evolution procedure was dissolved in a standardized HCl solution. An aliquot of the acidic sample solution was back-titrated with standardized NaOH under nitrogen gas. This gave the number of moles of OH due to the electride, and the number of moles of base due to the cryptand. In the third step, an aliquot of the sample was analyzed by flame emission spectroscopy using a set of standards to form a calibration curve. This gave the number of moles of alkali metal present in the original crystalline sample. In the fourth and final step, an aliquot of the sample solution was vacuum dried. The residue was dissolved in a solution of Na acetate in D_2O and the ¹H NMR spectrum of the sample was measured to give the number of moles of complexing agent present. The results were compared and used to determine the stoichiometric ratio of the alkali metal to the complexing agent. The results for the compounds studied in this work are shown in Table 1.

к+с222.е-	к ⁺ с222•е ⁻	Rb ⁺ C222·e ⁻		
# Moles from Mass	4.95 x 10 ⁻⁴			
# Moles M ⁺ from H ₂ Evolution		7.2 x 10 ⁻⁴		
Flame Emission Moles M ⁺	5.9 x 10 ⁻⁴	6.84 x 10 ⁻⁴		
pH Titration				
Moles M ⁺ Moles C222		7.4 x 10 ⁻⁴ 7.2 x 10 ⁻⁴		
^l h NMR Moles C222	4.93 x 10 ⁻⁴			

Table 1. Stoichiometric Analysis of Cryptate Electrides.

CHAPTER III

THE HIGH VACUUM EVAPORATOR

III.A. Introduction

This chapter will give a detailed description of the design and construction of a high vacuum evaporator for use in the physical vapor deposition of thin films of alkalides and electrides. These films were grown from the starting materials which were alkali metals and organic macrocyclic complexing agents. The motivation for, and interest in studying alkalides and electrides formed in this manner will be fully discussed in Chapter IV. It should be noted here that the essential nature of this project was that of a pioneering investigation of the feasibility and usefulness of this technique for extending our understanding of these compounds. As a result, the experiments were designed to be as simple and inexpensive as possible, so that they would simply demonstrate our ability to carry out the ideas that had been conceived for the thin film studies. Thus, for example, optical spectra were taken on a point by point basis, with no computer interfacing for either data collection or treatment. However, it should also be

-47-

noted that as a result of the preliminary results of these investigations, we now have plans for greatly extending the experimental capabilities. These plans are presented in Chapter VI.

III.B. The Experimental Design

The device used for the physical vapor deposition of thin solid films of the alkalides and electrides was a Perkin-Elmer (Ultek Model MX-14), high vacuum system, shown in Figure 2. The top portion of the Ultek evaporator consisted of a 14 by 24 inch belljar protected by a screen. This rested on top of the stainless steel collar which contained the copper gasketed 2 3/4 inch feedthroughs used to provide access to the vacuum system. The feedthrough collar in turn rested on the pumping mechanism of the evaporator. The vacuum seals between the various sections were made with booted Viton gaskets. The pumping system was divided into three parts. The rough pumps consisted of two molecular sieve sorption pumps, which were attached to the side of the vacuum system, as shown in Figure 2. The cans containing the molecular sieves were cooled with liquid nitrogen, and were used to pump to a vacuum between 10^{-2} and 10^{-3} It was necessary to achieve this pressure or torr. lower before the high vacuum pumps could be started. The advantage of these rough pumps was that they contained



Figure 2. Schematic diagram of the Ultek MX-14 vacuum system.

no mechanical parts and therefore could not contaminate the vacuum system with oil or grease. The necessary rough vacuums could also be obtained very quickly under ideal conditions. The disadvantage, in this particular case, was that the liquid nitrogen chilled molecular sieves were not able to pump He gas which was present at high levels in the laboratory in which the evaporator was situated. It was sometimes found necessary to remove the He with a mechanical pump before the sorption pumps were able to operate to specifications. The second part of the pumping mechanism consisted of six ion pumps that were sandwiched between permanent magnets. The ion pumps and magnets were encased in compartments in the bottom half of the evaporator. The ion pumps were controlled by an Ultek Combination Boostivak Control Unit. The operating voltage for the ion pumps was about 4.5 kV. The pressure was determined by measuring the current (in microamperes), produced by the ion pumps. The current was related to the pressure by a calibration curve which was provided for the particular ion pumps in the system. Finally, the high vacuum pumping was also assisted by a Ti sublimation pump. This consisted of four spiral filaments that were made of a titanium-molybdenum alloy. The filaments were used one at a time. They were resistively heated by a 50 ampere current, which was produced by the Boostivak control unit. This current

-50-

was sufficient to evaporate Ti metal films, which condensed on the water cooled cryoshroud shown in Figure 2. The Ti metal films evacuated the system in two ways. They reacted with some gases, such as nitrogen, and thus removed the gas in this so-called "gettering" fashion. In addition, as successive layers of Ti film were deposited, they physically covered ions or atoms of less reactive gases such as Ar or He, which were adsorbed on the surfaces of the ion pumps, so that these gases were also removed from the atmosphere. In this way, the sublimation pump was used in conjunction with the ion pumps to produce pressures between 1×10^{-5} and 1×10^{-7} torr in the entire system.

The lower half of the evaporator could be separated from the belljar portion by a poppet valve. Thus, a high vacuum could be maintained by the ion pumps while the top half of the evaporator was at atmospheric pressure. This enabled new experiments to be prepared while the ion pumps were operating. Once the experiment was ready to be done the entire vacuum system could be evacuated by a so-called "hot-start". The top half was first evacuated with the sorption pumps. The poppet valve was then very slowly opened while the Ti was subliming. This step had to be done with care in order to prevent the ion pump voltage from dropping below 2.5 kV, since the ion pumps essentially stopped operating at lower voltages.

-51-

The high vacuums which were obtained with the ion pumps and the Ti sublimation pump, were necessary for vapor deposition in order to ensure that the vapor molecules travelled with long mean free paths, so that the deposition of atoms occurred with essentially straight line geometry. Table 2 gives some calculated values for mean free paths for the most common gases that were expected to be present in the vacuum system. The expression used for λ , the mean free path, is

$$\lambda = 2^{-1/2} \sigma^{-1} \frac{k_{\rm B}T}{p}$$
[11]

where σ = the collision cross section in nm. The values for σ were taken from Table 24.3, page 802 of Physical Chemistry, P. W. Atkins, W. H. Freeman and Company, San Francisco, 1978. The ambient temperature was assumed to be 22°C.

III.C. Materials

The materials that were evaporated were contained in microelectronic source boats purchased from the R. D. Mathis Company. The source boats were made of tantalum and were of two types. The cryptand C222 was evaporated from a baffled box evaporator, originally designed to evaporate SiO. The sodium and potassium metals were evaporated from simple covered boats (see Figure 3).

Gas	Pressure (torr)	λ(cm)
Air	10 ⁻⁵ 10 ⁻⁷ 10 ⁻⁹	720 7.2 x 10 ⁴ 7.2 x 10 ⁶
н ₂ о	10 ⁻⁵ 10 ⁻⁷ 10 ⁻⁹	940 9.4 x 10 ⁴ 9.4 x 10 ⁶
02	10 ⁻⁵ 10 ⁻⁷ 10 ⁻⁹	800 8.0 x 10 ⁴ 8.0 x 10 ⁶
Не	10 ⁻⁵ 10 ⁻⁷ 10 ⁻⁹	1.7 x 10 ³ 1.7 x 10 ⁵ 1.7 x 10 ⁷

Table 2.	Values	for	the	Mean	Free	Paths	of	Common
	Gases a	at Va	iriou	is Pre	essure	es.		



(a) Source boats for resistive heating; (b) source boat in position in evaporation oven. Figure 3.

Li metal was evaporated from a similar container that was machined at M.S.U. out of stainless steel shim stock. It was necessary to use stainless steel since hot Li metal reacts with many ordinary source materials. The C222, which was stored in the helium glove box, was placed in the evaporation source boat and was removed and loaded in the belljar under atmospheric conditions. The crown ether, 18C6, was also contained in a similar source boat, but because its vapor pressure was higher than that of the cryptand, it was necessary to cool it when it was under vacuum. At ambient temperatures and at 10^{-6} torr, it was found that the 1806 spontaneously vaporized, thus poisoning the vacuum system to such an extent that the ion pumps could not be operated. Thermoelectric coolers (Models 930-35 and 930-71), were purchased from Borg-Warner Thermoelectrics. The power supplies to operate these modules were designed and built by M. Rabb of the Chemistry Department Electronics Design Shop. A copper heat sink was used to cool the hot side of the thermoelectric coolers. The copper block was cooled by a water flow which was directed through stainless steel pipes and flexible hosing with vacuum tight Cajon VCR connections. The water was taken directly from the cold water supply into a liquid feedthrough in the vacuum system.

The alkali metals used in this study were Na, K, and Li. In the earliest experiments the Na and K were

-55-

contained in glass ampoules which were scored and broken before the vacuum was obtained. This was found to be unsatisfactory because of the difficulty of heating the glass tubing uniformly. This made it difficult to obtain either steady or well controlled rates of evaporation of the metals. Therefore, in subsequent experiments a new method was used for all three metals. The bulk metals were stored in the Vacuum Atmospheres helium glove box. The metals were cut and loaded into the source boats in the inert atmosphere. They were removed in an evacuable jar, which was placed in a glove bag that was attached in an accordian-like fashion to the belljar apparatus This was done by hanging the bell jar from a itself. pulley above the evaporator. The top of the glove bag was attached to the bell jar, and the bottom of the bag was attached to the body of the evaporator. The bag was then flushed with dry N_2 gas until the relative humidity was reduced to at least 10%, the evacuated jar was opened, and the metal source boats were placed in the resistive The belljar dome was lowered and the entire heaters. system was immediately evacuated using a previously chilled sorption pump. This method was found to be quite satisfactory for handling Na, K and Li, especially since the metals were exposed to the glove bag atmosphere for a relatively short time. It is possible that more stringent measures might be required to handle the more reactive alkali metals, such as Rb and Cs.

III.D. Design for Alkalide and Electride Synthesis

The technique of physical vapor deposition relies on the resistive heating of materials to the temperature required to vaporize them. The vapor atoms then recondense on a surface, called the substrate, which is held above the vapor source. The condensed atoms form thin solid films of the heated materials. The ovens used in this study to resistively heat materials are shown in Figure 3. There were four ovens in the evaporation area. The currents were forced to pass through the source boats by using an insulating machinable ceramic on the entry side of the resistive heating ovens. The currents were supplied and controlled by a high current regulated power supply designed and built by M. Rabb. The currents that were sufficient to vaporize K, Na, Li, and C222 varied from 20 to 35 amps. If currents greater than 40 amps were required to vaporize a material, as in the case of Ag(s), or SiO(s), the current was supplied by a variac connected to a 200 amp voltage to current transformer. Table 3 shows some typical temperatures required to vaporize the materials that were most commonly used in this study.

The substrate on which the thin films were deposited, was supported on the bottom of a copper block containing a hole through which light could pass. The copper block could be rotated through approximately 260° by means of a mechanically rotatable feedthrough, which was connected

-57-
	T (°C)	т (°Ç)
Material	[V.P.=10 ⁻⁴ torr]	[V.P.=10 ⁻⁶ torr]
Na	192	124
К	125	60
Li	407	307
Ag	1105	958
SiO	850	Sublimes
C222		70-80*
Al	1010	820

Table 3. Temperatures in °C Required to Achieve Vapor Pressures Listed for Materials Used in the Thin Film Preparation of Alkalides and Electrides.

*Source - found by experimental observation -

All other references taken from:

Material Evaporation Guide Inficon, Leybold-Heraeus 7500 Fly Road East Syracuse, NY 13057 to the block by a series of gears. This enabled the substrates to be moved from a position above one source boat to a position above another during the deposition of films. In addition, the substrate could be moved into the light path for optical transmission measurements. The copper block was cooled by stainless steel pipes which were sandwiched between the top and bottom halves of the block. These pipes were connected to stainless steel flexible tubing by VCR high vacuum Cajon connectors. Liquid nitrogen, or cooled nitrogen gas, was used as the coolant and was directed through the cooling system via a liquid nitrogen feedthrough. It was necessary to cool the substrate in order to prevent decomposition of the reactive alkalide and electride films. The materials used for the substrate were either Pyrex or fused silica microscope slides. The fused silica slides were purchased from Heraeus-Amersil, Inc., and were used exclusively in the later studies. The substrate slides were cleaned with ethanol in an ultrasonic cleaner. The shapes of films deposited on the substrate were controlled by placing suitable masks over the vapor streams. The ability to control the shapes of films was especially useful when the electrodes and films were grown for d.c. conductivity studies, as is discussed later. A schematic diagram of the copper substrate block is shown in Figure 4.

A dual copper-constantan thermocouple was used to

-59-



Figure 4. Schematic diagram of the evaporation ovens inside the vacuum space.

monitor the temperature in two places. One thermocouple was placed at the source boat containing the C222, since it was possible to control the evaporation rate of the cryptand roughly, by monitoring the source temperature. The second thermocouple was soldered to the substrate itself, using indium metal as the soldering material, in order to measure the temperature of films. The rate of deposition of films, and thus their stoichiometry and thickness, was monitored by a piezo-electric quartz crystal oscillator. This operated on the principle that the change in the natural period of oscillation of the crystal is directly proportional to the change in mass of a material deposited on it. The crystal was controlled by a Veeco Thickness Monitor, Series QM-300, Model 301. Since this monitor gave thickness readings only, the rates of deposition were calculated manually by directly measuring the number of angstroms deposited per minute. The readings were also manually corrected for the actual densities of materials since the Veeco Thickness Monitor was scaled to a density of 1.00 $g-cm^{-3}$. The correct stoichiometry of films was calculated from the relative thickness of the materials by the following relation. The areas of the metals, M, and the complexants, C, were assumed to be the same, since they were both deposited on the substrate through the same mask, that is $A_{M} = A_{C}$.

-61-

$$\frac{\text{Mole } M}{\text{Mole } C} = \frac{(A_{M})T_{M}(\rho_{M})(MW)_{M}^{-1}}{(A_{C})T_{C}(\rho_{C})(MW)_{C}^{-1}}$$
[12]

$$\frac{T_{C}}{T_{M}} = \frac{Moles C}{Moles M} \cdot \frac{\rho_{M}(MW)_{C}}{\rho_{C}(MW)_{M}}$$

where T = film thickness, ρ = density, MW = g/mole. The results for the materials Na⁺C222·Na⁻, Na⁺C222·e⁻, K⁺C222·K⁺, and K⁺C222·e⁻, are given in Table 4.

Alkalide and electride films were grown by two methods. The first method was a co-deposition synthesis. Figure 4 gives a cross-sectional diagram of the experimental design for this technique. The co-deposition method relied on the simultaneous deposition of the metal and the complexant, which were heated in adjacent ovens. The wall between the ovens was partially cut away to allow the two vapor streams to mix in the central position. The films were grown by suspending the cooled substrate over this position, after the individual rates of deposition of the metal and complexant had been set to the desired values. The second method used to grow films was by layering. It was essential to develop this technique since in order to make alkalide films containing two different alkali metals, it was necessary to heat three oven sources simultaneously. This made it impossible to use the co-deposition configuration to grow

or

Film Material	Mole Ratio M/C	Thickness Ratio C/M
Na ⁺ C222 Na ⁻	2	7.4
Na ⁺ C222 e ⁻	l	14.8
к ⁺ с222 к ⁻	2	3.9
K ⁺ C222 e ⁻	l	7.7

Table 4	4.	Thickness	Ratios	for	Alkalide	and	Electride
		Films.					

films. Layered films were grown by alternately depositing a layer of the metal, followed by a layer of the complexant, and then a second layer of the original metal or a second metal. This was continued until the film contained as many layers of as many components as desired. This was done by moving the substrate back and forth between the various sources. Thus, the layering technique relied on the complexation reaction taking place between the layers in the solid state, on the surface of the cooled substrate. This is in contrast to the codeposition synthesis in which the solid state reaction took place between the more intimately mixed components.

III.E. Measurement of Films

Some of the early studies of alkalide and electride films were directed towards the removal of films from the vacuum in order to do <u>ex situ</u> measurements. At first, films were coated with materials that would protect them from exposure to H_2O or O_2 , but that would still allow optical or electrical measurements to be made. The first material used was SiO, which is a commonly used coating material. The numerous attempts to remove films coated with this material were unsuccessful, due partially to the fact that the temperature required to evaporate SiO (850°C), was high enough to decompose films held above the heated source, and

-64-

partially to non-uniform coatings which allowed air to penetrate to the surface of the film. The second material used was undyed paraffin wax. This was equally unsuccessful, again because the material tended to coat the films unevenly. A more successful attempt to remove films for ex situ studies used a mechanical trapping device designed and built by S. Dawes. In this case, films were protected by a cover plate that pressed firmly against the substrate material, making a vacuum seal with a Viton o-ring. In a few cases, films remained intact for about one to two minutes after removal from the vacuum, and then decomposed. More often, the films decomposed immediately. In either case, the reason for the failure was due to various mechanical difficulties. Nevertheless, the method of mechanical protection of films seems to be promising, and should be pursued, especially since the ex situ study of films is of primary importance as is discussed in Chapter VI. However, since the in situ measurements of films is also of intrinsic interest, and since the primary purpose of this work was to demonstrate the feasibility of thin film growth and characterization by producing good quantitative data, the attempts to remove films from the vacuum space were temporarily abandoned, and the in situ studies became the primary focus of this work.

The major piece of equipment that was designed for

-65-

the in situ measurements was a spectrometer that was used to measure the optical transmission spectroscopy of the thin films. A schematic diagram of the spectrometer can be seen in Figure 5. The light beam was brought into the vacuum system via a sapphire window feedthrough. The light source was an Aries Quartz Tungsten Halogen lamp (100 W), in an Universal lamp housing, Model 40-130, which was controlled by a DC regulated power supply. The light beam was chopped by an Optical Engineering attenuator, which was monitored by a photodiode detector that provided a signal for the frequency lock-in amplifier. The light was monochromated by a Jarrell-Ash Model 82-000 series Ebert Scanning Monochromator, with an f number equal to 8.6. The entrance and exit slits were both on the front face of the monochromator. The limitations of space made it necessary to use a right angle mirror to direct the light onto the entrance slit. The slits were straight-edged slits, and were variable between $0-2000 \mu$. In order to monitor wavelengths ranging from 500 nm (2.48 eV), to about 2000 nm (0.62 eV), two Jarrell-Ash diffraction gratings were used. The first, Model 980-28-20-22, was blazed for 500 nm with 1180 grooves/nm and was used with a 470 nm cutoff filter. The second, Model 980-28-40-30, was blazed for 1.0 μ with 295 grooves/nm, and was used with an 875 nm cutoff filter. The light was directed in the vacuum apparatus through an aluminum light pipe. A right angle



Figure 5. Block diagram of the optical spectrometer.

mirror brought the light beam vertically through a focussing lens. The beam passed through the film and the hole cut in the substrate support block, and was then directed onto the detector which was permanently mounted on a bracket.

The first detector used was a Barnes Thermopile detector that was mounted on a small copper block. This block was cooled in a similar fashion to the substrate support block, by flowing water through stainless steel flexible pipes. However, this thermal detector was found to be unsatisfactory for two reasons. First, it was not sensitive enough to the monochromated light, thus giving poor signal to noise ratios. Secondly, the detector was extremely sensitive to the thermal radiation from the substrate support block. Two other detectors were found to be much more useful. The first was a United Detector Technology photovoltaic photodiode detector, Model PIN-5DP, which required no cooling. This was controlled by a pre-amplifier circuit designed by S. Jaenicke, and built by M. Rabb, which was housed with the detector in an evacuable Al can mounted on a support bracket (see Figure 5). This detector was most useful for the visible region of the spectrum. The second detector was a Kodak Ektron PbS detector that could be operated at ambient temperatures. It was also housed in the vacuum space along with a self-zeroing pre-amplifier circuit, designed and

built by M. Rabb. This detector was found to be sufficiently sensitive in both the visible and near infrared regions of the spectrum to allow the entire spectral region to be examined by simply exchanging the two gratings in the monochromator. In both cases the signal from the pre-amplifier was transmitted via an instrumentation feedthrough to a lock-in amplifier. The signals were recorded as a function of voltage versus wavelength on a X-Y Linear recorder (Model 8036), with the X channel in the time base mode.

The second major experiment that was designed and constructed was for the measurement of D.C. conductivities of thin films. This experimental arrangement was also intended to be a fore-runner for measurements of photoconductivities of films. Two different configurations for the electrodes were designed. The first was intended to allow the measurement of the resistance of films across the width of the film deposited on the substrate. The mask, in this case, allowed an initial deposition of electrode strips. These strips were then covered by an alkalide or electride film as shown in Figure 6(a). The actual dimensions and spacing of the electrodes could be varied by using different masks. In contrast to this longitudinal conductivity measurement, Figure 6(b) shows the design for a transverse measurement of the resistance through the thickness of the thin film of the alkalide

-69-



Figure 6. (a) Electrodes for longitudinal conductivity; (b) electrodes for transverse conductivity.

or electride. In this second configuration, it was necessary to devise a method to deposit electrodes that would sandwich the alkalide film without requiring the vacuum to be broken. This was achieved by stacking two masks on top of each other above the electrode source boat. The bottom electrode was deposited first as shown in Figure 6(b). The film was then grown over this electrode, and finally the copper block was used to push the first electrode mask to the side, thus exposing the mask for the second, or top electrode. This electrode was then deposited and the film resistance was measured. In both the longitudinal and transverse conductivity cases, the vapor deposited electrode strips were connected to the measuring circuit by the following means. Teflon insulated copper thermocouple wires (.003 inches, Omega Engineering, Inc.), were attached to the quartz substrate with indium metal. This was done prior to evacuating the system, so the wires had to be carefully positioned so that the electrodes would cover the indium, thus making good electrical contact. The resistance of films was measured by transmitting the signals through an instrumentation feedthrough. The experimental arrangement for the electrical circuit, and the methods of measuring Ohm's Law behavior and the temperature dependence of the resistance, were identical to those described in Chapter II for the measurement of pressed powder conductivities.

-71-

III.F. Data Treatment

The optical spectra were measured on a point by point basis and the data were manipulated by hand. Since this very rudimentary system was designed without any means to move the light beam, reference and sample spectra could not be obtained simultaneously. It was therefore necessary to measure the reference spectra through the quartz substrate prior to the formation of a film on the slide. These voltage versus \overline{v} values were termed V_0 , and the values for the substrate with film were termed V_1 . The absorbance, A, of a particular film was calculated for each wavelength by A = $-\log (V_1/V_0)$. The wavelengths were calibrated with a He-Ne laser, and also by measuring the known spectrum of a didymium oxide glass filter. Absorbances were calibrated with neutral density filters.

CHAPTER IV.

OPTICAL AND ELECTRICAL MEASUREMENTS OF VAPOR DEPOSITED FILMS

IV.A. Introduction

In order to understand the purpose behind the attempt to measure the properties of vapor deposited films of alkalides and electrides, it was necessary to address two questions. The first concerns the reason for growing films by physical vapor deposition. The second question concerns the reason for the study of the optical transmission spectra of films formed in this way. A brief consideration of the history of the study of alkalides and electrides will answer these questions most easily.

Optical transmission spectroscopy had been a useful tool for the identification of the alkali metal anions long before the existence of the solid materials, alkalides and electrides. That is, it had been used extensively for the study of alkali metals in liquid ammonia, and also in other liquid amines and ethers. For example, the spectra of the anions Na⁻, K⁻, Rb⁻, and Cs⁻ in ethylenediamine were reported in the 1964 paper by R. R. Dewald and J. L. Dye (18). The positions of the

-73-

absorption maxima were found to be at 660 nm (Na⁻), 845 nm (K⁻), 899 nm (Rb⁻), and 1030 nm (Cs⁻). In all cases there were also peaks due to the presence of trapped electrons at 1280 nm. The nature of these peaks was not well established at the time that the paper was written, and in fact, the assignment of the peaks to the respective alkali metal anions was not made then. However, in a later paper (27), Lok, Tehan and Dye reported the absorptions of K⁻, Na⁻, and the solvated electron in several amine and ether solvents, and were also able to describe the spectra theoretically by reference to a well known model of charge-transfer-to-solvent (ctts) spectra. The absorption peak maxima for a few of the solvents that they studied are reported in Table 5; the reported values are taken from Reference 27.

In many of these solvents, the solubilities of the metals were enhanced by the addition of either cryptand or crown ether complexing agents. As was mentioned previously, the behavior of these broad, featureless bands can be fairly well described by ctts theory. Without overemphasizing this point, it is of interest to briefly examine the results that led to this conclusion. In the 1972 paper, Dye, Lok and Tehan found that the peak positions for Na⁻, K⁻ and e⁻ were strongly temperature dependent and shifted to higher energies with decreasing temperature. In addition, the variation of the

Table 5. Peak Positions for the Alkali Metals Na and K in Various Solvents. The complexing agents indicated in the parentheses were added to enhance solubilities.

Na λ(nm)	$K \lambda(nm)$	e λ(nm)
660	850	1316
735	900	2050
770	935	1930
725	877	1920
	Na λ(nm) 660 735 770 725	Na λ (nm)660850735900770935725877

temperature coefficient was found to be a linear function of the position of the maximum. That is, the slope of a plot of \overline{v}_{max} vs. $d\overline{v}_{max}/dT$ was found to be equal to T, as predicted by ctts theory (28). All the peaks were also solvent dependent, although the solvated electron absorption was found to be the most highly solvent and temperature dependent. Finally, a linear correlation was found between the positions of the absorption maxima of Na and K measured in the same sets of solvents. This correlation is also predicted by ctts theory. However, no such correlation was found between the peak positions of Na and I. It should be noted here that the absorption band of I^- is perhaps the quintessential example of a ctts band. Several possible explanations for the lack of correlation were proposed, including the fact that the iodide ctts transition is very dependent on the cation, especially in solvents of low dielectric constants such as were used in this study. The lack of correlation in this case, then, was thought to be due to the effect of ion-pairing (27).

The theory of ctts spectra was most successfully developed by G. Stein and A. Treinin in a 1959 paper (28). They developed the theory to describe the spectra of halide anions. The physical picture used to calculate the energy of the optical absorption was as follows. The ion was considered to be in a spherical cavity of radius

-76-

 r_0 in the solvent. The energy was calculated by referring to a cycle in which the ion is first removed from the cavity leaving the cavity undisturbed. The second step of the cycle involves the ionization of the ion in the gaseous state, and in the final step the electron is promoted to its excited state and the radical is reintroduced into the organized solvent medium. The energy calculated in this manner depends explicitly not only on the optical and static dielectric constants of the medium itself, but also on the reciprocal of the cavity radius. This expression (Equation 9 of Reference 28) leads directly to the experimentally observed dependence of the absorption maximum on the temperature. The theory relied on the assumption that the solvent medium could be assumed to be a continuous dielectric from infinity to a distance r' from the center of the ion. This theory was first applied to solutions of alkali metals by Matalon, Golden and Ottolenghi (29), in which they identified the peaks as the absorptions of the metal anions, M⁻.

It is therefore not surprising that Dye and coworkers began using optical transmission spectroscopy as a means of characterizing the new solid compounds they had isolated. The experimental method used to form films of alkalides and electrides by redissolving the materials in appropriate solvents, and then flash evaporating the solutions, has been described in Chapter II. Figure 7 shows some typical absorption peaks of M⁻ obtained from

-77-



Figure 7. Absorbance peaks for films from methylamine. Peaks from left to right: Cs+C222.Cs-, Rb+C222.Rb-, K+C222.K-, Na+C222.Na-. From Reference 30.

films of the following alkalides: Na⁺C222·Na⁻, Rb⁺-C222·Rb⁻, $K^+C222\cdot K^-$, and $Cs^+C222\cdot Cs^-$ (30). It can be seen that these peaks were very similar to the peaks of the alkali metal anions in solution. The peak positions occurred at approximately the same positions as those of the respective anions from the earlier work. However, the exact positions of the absorption maxima were slightly dependent on the solvents from which the dry films were formed, and very dependent on the complexing agents used, that is in essence, on the counter ion present. Table 6 shows some of these deviations for several alkalides. This table not only shows the deviations of the value of the absorption from one system to another, as for example, the peak of K⁻ shifts from 11.9 x 10^3 cm⁻¹ in K⁺C222·K⁻ from methylamine, to 12.2 x 10^3 cm⁻¹ for K⁺18C6·K⁻ from methylamine, to 11.2 x 10^3 cm⁻¹ for K⁺C222·K⁻ from NH₃, but also illustrates an intrinsic difficulty of this method of anion identification. That is, in alkalide systems containing two different metals, as for example the K, Na, 18C6 system shown in Table 6, it is not always possible to unequivocally identify the anion. Thus, the major peak position occurs at 13.3 x 10^3 cm⁻¹ (1.65 eV), which could be either an Na⁻ absorption shifted to lower energies from its "usual" value of about 15 x 10^3 cm⁻¹, (1.86 eV), or a K⁻ absorption shifted to higher energies from its usual value of about $12 \times 10^3 \text{ cm}^{-1}$ (1.49 eV). Although the details of the solution to this problem are

	Solvent Used To Prepare Dry Film	Peak Positions of M			
System		$\overline{v}(cm^{-1}) \cdot 10^{-3}$	E(eV)	λ(nm)	
Na ⁺ C222 Na ^{-*}	CH3NH2	15.4	1.9	650	
к ⁺ с222 к ^{-*}	"	11.9	1.48	840	
Rb ⁺ C222 Rb ^{-*}	"	11.6	1.44	860	
Cs ⁺ C222 Rb ^{-*}	"	10.5	1.3	950	
Na ⁺ 18C6 Na ^{-**}	11	16.7	2.07	600	
к ⁺ 18с6 к ^{-**}	NH ₃	11.2	1.39	890	
Rb ⁺ 18C6 Rb ^{-**}	CH3NH2	12.0	1.49	830	
Na,K, 18C6 ^{**}	11	13.3	1.65	750	

Table 6. Variations of the Optical Absorption Peak Positions for Several Alkalides Showing Cation, Complexing Agent, and Solvent Dependence.

*Reference 30

** Reference 31 beyond the scope of this discussion, it is worthwhile to point out that the unambiguous identification of the anions and cations present in alkalides and electrides can be made most elegantly by the use of solid state MASS NMR spectroscopy. However, this drawback of the method of optical spectroscopy is one that is intrinsic to the nature of the absorptions in these media, and good optical measurements should provide other equally interesting information on these systems. That is, optical measurements of thin films of alkalides and electrides can be used to calculate their optical constants. A more thorough discussion of the details of the parameters that can be measured and the methods of measuring them, is found in the following sections of this chapter.

What is important to note here is that all the early work done on the optical spectra of thin films of alkalides and electrides was entirely qualitative in nature. It must be recalled that all films were made by flash evaporation of solvent, that left dry films on the wall of the optical cell. These films were therefore of unknown thickness, which immediately rade any attempts to quantify the data dependent on an estimation of the film thickness. Moreover, the films were not only of unknown thickness but also of non-uniform thickness, that in the worst possible case, could have meant that the film did not completely cover the path of the light beam. The

-81-

effect that these two factors had on the resulting line shapes of absorption bands was calculated and is presented in the Appendix of Reference 32. The results showed that the most strongly absorbing films were most affected by the varying thickness, so that the absorption maxima were decreased in amplitude. The calculations for films that only partially covered the light beam cross section indicated that the peaks were broadened and the peak heights were reduced. Thus, the lack of any quantitative optical data that could provide fundamental understanding of alkalides and electrides, was the major motivation behind this preliminary investigation into the possibility of growing uniform films of known thickness by the technique of physical vapor deposition. However, there were two other considerations that originally drew our attention to this experimental technique. First, the method was an entirely new way of synthesizing alkalides and electrides, in which these compounds could be made without the use of solvents, thus entirely avoiding the problem of solution decomposition which had always been one of the major problems in harvesting these materials. Secondly, the technique was thought to promise more than just the ability to provide quantitative optical data, or to avoid the difficulties involved with the unstable The hope was that the ability it would provide solutions. to control the thickness and stoichiometry of films would

-82-

facilitate the creation of new classes of these materials. That is, by selectively varying the mole ratios of metals and complexants, or by doping films with electron donors, it was hoped that the technique would allow the study of materials with low electron concentrations as well as those with high electron concentrations. This is more fully described in Chapter VI, in the discussion on suggestions for future work.

When this project was first undertaken, these ideas were all entirely unrealized. Therefore, the project was intended to address, perhaps cursorily, as many problems as possible, in order to determine whether all the experiments that we wanted to do would actually work. This chapter, then, after discussing the background of the experiments that were done, presents the results of these preliminary measurements together with indications of the larger scope that these experiments will have in the very near future.

IV.B. <u>A Feasibility Study for the Formation of Solvent-</u> Free Films

One experiment was performed before the full scale belljar operation was begun, in order to demonstrate the feasibility of reacting alkali metals and complexing agents in the solid state without the use of solvents (33). In fact, indications that this would be possible

-83-

had been obtained from many observations of films, possessing the typical blue color of alkalides or electrides, which formed above dry complexing agents as the metals were distilled in evacuated preparation vessels. The experiment used a simple evacuable quartz apparatus in which the metals and complexants could be vaporized by heating them with Nichrome wire wrapped around the sidearms. The materials condensed on a cooled optical cell in the center of the apparatus, and the optical spectra of the resulting films were measured. In this way several different alkalides and electrides were made, and good agreement was found with the early results obtained from films grown from the solvent. Of course, this experiment did not allow any control of the film thickness nor accurate control of the stoichiometry of the materials, but it did provide a concrete demonstration that the experiment was feasible.

IV.C. Physics of Thin Films

1. Deposition Technology

There are essentially three major ways to grow thin solid films (34). The first major method is that of thermal evaporation. The second is cathodic sputtering, which depends on the bombardment of the surface of a material with energetic particles that can eject atoms

-84-

that condense to form the film of the material. The third consists of various chemical methods that include electroplating and chemical vapor deposition. There are many different kinds of thermal evaporation techniques, but in all cases the principle depends on the fact that materials vaporize upon heating. When the vapor atoms condense on a cooled surface, or substrate, they form thin solid films of the material being heated. One of the most widely used methods of thermal evaporation is that of resistive heating, also used in this study, which vaporizes materials by passing currents through a resistive boat or wire filament usually made out of a tantalum or molybdenum alloy. This method is particularly straightforward and works for many materials, which may account for its extensive use. Thermal evaporation, in common with most methods of forming films, requires a high vacuum both to lengthen the mean free path of the vapor atoms to ensure that they travel in straight paths from the source to the substrate, and to reduce the amount of residual air present in the vacuum system. The residual air can absorb on the film and can change the properties of the material being measured, or can even seriously damage the film by chemical reaction. In fact the number of monolayers of air which deposit on a substrate, assuming a sticking coefficient of 1, is tabulated in Reference 34. The results show that at ambient temperatures and a

-85-

pressure of 1×10^{-5} torr as many as 4.4 monolayers of air deposit per second, whereas at 1×10^{-7} torr, the typical operating pressure for the work presented here, one can expect only 4.4 x 10^{-2} monolayers per second, which corresponds to about 158 layers per hour. Even at this relatively low pressure, then, significant amounts of air can deposit on films over several hours.

Finally, it is worthwhile to note that in many cases the material used for the substrate, the temperature at which the substrate is maintained, the rate of evaporation, and the angle of incidence of the vapor atoms, among other experimental parameters, can have a significant effect on the way in which the polycrystalline films grow and thus on the physical properties of the films.

2. Adsorption of Atoms and the Growth of Films

It is of some interest to briefly consider the fundamental processes that occur during the growth of thin solid films, especially since some of these processes may have a profound effect on the results obtained in this study. The review article by Venables, Spiller, and Hanbucken (35) has a clear exposition of the thermodynamics and kinetics of the nucleation and growth of films. In general, most workers acknowledge the existence of three different forms in which crystals can grow on a substrate. The first is that of layer growth, in

which the atoms of the condensate are more strongly attracted to the material of the substrate than to each other, so that layers are formed in which the first monolayer is very tightly bound to the substrate and subsequent layers are less tightly bound. The second mode is that of island growth in which the atoms (or molecules) of the condensate are more tightly bound to each other than to the substrate material, so that they tend to nucleate in the form of small clusters on the surface. As the clusters increase in size they can then be termed islands. The final form is an intermediate mode which consists of layers and islands. The first monolayer (or, in some cases the first few monolayers), forms on the substrate but after that the growth of the film in layers is unfavorable and islands begin to form instead. There are several factors that can cause this growth mode to occur, which include, for example, the lattice parameter or the molecular orientation of the monolayers which form at first. These parameters may lead to a high free energy of the interface between the new deposit and the previously formed layers and this leads to island formation (35). All three growth modes have mainly been studied by electron microscopy and Auger electron spectroscopy.

In addition to this macroscopic point of view of the nucleation and growth of films, one can consider these effects from a molecular or atomic vantage point. The

-87-

individual atomic processes are the direct causes for the growth of films (35). As the vapor atoms arrive at the substrate, single atoms (or molecules) are created at the surface. The single atoms or molecules then diffuse over the surface until one of several possibilities The atoms or molecules may re-evaporate and thus occurs. be lost from the surface. They may begin to nucleate to form clusters, or they may be captured by clusters which already exist. They may also be captured at defect sites on the surface, since real surfaces in general, are not perfectly flat, but contain many ledges or steps, kinks, point defects, etc. They may also interdiffuse with the atoms of the substrate material itself. All of these processes are influenced by two experimental variables, one being the rate, R, at which the vapor atoms or molecules arrive at the surface, and the other being the temperature of the substrate, and also by the energies of the adsorption, diffusion and nucleation processes. Finally, the large clusters or islands that initially form on the surface may not be in their equilibrium or most stable state, and thus can undergo certain rearrangement processes. This means that, for example, defects may anneal, shape changes may occur due to surface diffusion, or alloys may form as the species mix (35).

-88-

3. Optical Properties of Thin Films

Before initiating a general discussion of the measurement and significance of the optical properties of thin solid films, it is important to consider the nature of the optical absorptions of films of alkalides and electrides. The absorption spectra of alkalides are very similar to those of the M⁻ species in solution. The broad metal dependent bands occur in the visible to near infrared region of the spectrum and have been attributed to an ns to np transition of the metal anion. It should be understood that since this transition occurs in a solid, the nature of the transition cannot be directly compared to the ctts spectra of the solutions. Nevertheless, since the shapes and positions of these solid state transitions are so strikingly similar to the solution peaks, the ctts analogy cannot be ignored. The ground and excited states of the transition must be affected by the surrounding cations, as evidenced by the large differences in the positions of the peak maxima depending on the metals and/or complexing agents used. Thus, perhaps these transitions are similar to the ctts transitions in that there is some transfer of electron density to the wave functions of the positive lattice surrounding the anions. In this sense, the positive lattice has taken the place of the solvent. A similar comparison between the solution spectra of I and the

spectra of NaI, KI, RbI, and CsI in the solid state has been made (36). In this case also, the optical bands for the solid were in very good agreement with the ctts bands in solution.

The absorption spectra of the electrides can be divided into two distinct cases. The first class of electrides contain localized electrons which have a spectrum characterized by no absorption at high energies, followed by an intense peak occurring near 1.0 eV, which is due either to a bound-bound transition or a boundconduction band transition. The absorption then falls to zero again at lower energies. The second class of electrides have spectra which have no absorption at high energies followed by a sharp rise in absorption going to lower energies which may peak very slightly at about 0.70 eV, but continues to show absorption at even lower energies. This is characteristic of the plasma absorption of conduction electrons, thus indicating that some electrides may be metallic or nearly metallic in nature.

The object of the optical measurements carried out in this work was to measure the quantitative transmission spectra of both alkalides and electrides for the first time. It was desired to use the quantitative data to find the absorption coefficient, the band shapes or integrated absorption coefficients, and the oscillator strengths of these materials. Finally, it soon became

-90-

apparent that if the transmission coefficient, T, could be measured accurately, measurements of the reflectance, R, would be necessary as well, in order to obtain the complex dielectric functions and the complex refractive indices of these materials. The motivation for obtaining these fundamental parameters can be best understood by a consideration of the theory of the optical properties. Essentially, the reflectance and transmittance of light in semiconducting or metallic media, can be understood by a knowledge of the behavior of electromagnetic ratiation in conducting media. This theory is based on the use of Maxwell's field equations. Much of the following discussion is taken from (37), Chapter 1. Wave equations for both the electric field, E, and the magnetic field, H, can be derived and are of the form

$$\nabla^{2} \vec{E} - \sigma \mu \mu_{0} \frac{\partial \vec{E}}{\partial t} - \mu \mu_{0} \varepsilon \varepsilon_{0} \frac{\partial^{2} \vec{E}}{\partial t^{2}} = 0 \qquad [13]$$

where σ is the conductivity of the medium, μ and μ_0 are the specific permeabilities of the medium and of vacuum respectively, ε and ε_0 , are the dielectric constants of the medium and of vacuum. The specific permeability of vacuum is the proportionality constant between the magnetic field, \vec{H} , set up by a current, i, travelling a distance, r, through a wire, where $H = \mu_0 i/2\pi r$. The dielectric constant is defined by the force, F, between two charges, q_1 and q_2 , separated by a distance, r. In a vacuum this force is given by $F = q_1 q_2 / (4\pi\epsilon_0)r^2$, whereas in a medium of dielectric constant, ϵ , the force is $F = q_1 q_2 / \epsilon (4\pi\epsilon_0)r^2$. The solution for one of the components, say x, of either E or H in Equation [13] has the form of a wave equation as follows:

$$U_{x} = U_{0}e^{i\omega(t-x/v)} \qquad [14]$$

provided that the velocity, v, obeys the expression

$$\frac{1}{v^2} = \mu \varepsilon \mu_0 \varepsilon_0 - \frac{i \sigma \mu_0 \mu}{\omega}$$
 [15]

However, by the definition of the refractive index, N', of the medium, which is the proportionality of the speed of light, c, in a vacuum to the speed of light in the medium, Equation [15] can give

$$N'^{2} = \mu \varepsilon - \frac{i\sigma\mu}{\omega\varepsilon_{0}} \qquad [16]$$

Thus, for $\sigma \neq 0$ an absorbing medium has a complex refractive index which can be written as N' = n-ik. Insertion of this expression into Equation [14] gives

$$U_{x} = U_{0}e^{i\omega t} e^{-i\omega nx/c} e^{-\omega kx/c}$$
[17]

which represents a wave travelling with frequency $\omega/2\pi$ and velocity c/n, and undergoing absorption given by the exp ($-\omega k_X/c$) term. A similar equation can be derived for the magnetic vector.

The two expressions for N' can be equated to give

$$n^2 - k^2 = \varepsilon$$
 and $2nk = \frac{\sigma}{\omega \varepsilon_0}$ [18]

where $\mu = 1$, and $\sigma =$ the conductivity at the optical frequency, ω , (which may not be equal to the d.c. conductivity). In general, this equation also defines the real and imaginary parts of the complex dielectric constant, $\varepsilon' = \varepsilon_1 - i\varepsilon_2$, where

$$\epsilon_1 = \epsilon = (n^2 - k^2)$$
 and $\epsilon_2 = 2nk = \frac{\sigma}{\omega \epsilon_0}$ [19]

A quantity of interest is the absorption coefficient, K, of the medium. K can be related to k by the definition that the energy of an electromagnetic wave in an absorbing medium must decrease by 1/e in a distance K. The rate of energy flow per unit area in an electromagnetic wave is given by the Poynting vector, \vec{s} , where $\vec{s} = 1/\mu_0 \text{ExB}$. Thus, K is proportional to the product of the electric and magnetic vector amplitudes. Equation [17] shows that each expression contains the term $e^{-\omega kx/c}$ so finally we have that
$$K = \frac{2\omega k}{c} = \frac{4\pi k}{\lambda}$$
 [20]

where λ is the wavelength in vacuum. Thus, as in the experiments to be described in this work, measurements of the transmission through films of different thickness should give the values of K and k quite easily. This comes from the fact that, if the incident intensity of radiation on an absorbing medium of thickness x, is given by I_0 , and the transmitted intensity of radiation is given by I_t , then to a first approximation we have $I_t = I_0 e^{-Kx}$. The full expression is as follows:

$$I_t = I_0(1-R)^2 e^{-Kx} + I_0(1-R)^2 R^2 e^{-Kx} e^{-2Kx} + ...$$

which sums to

$$I_{t} = I_{0} \left[\frac{(1-R)^{2} e^{-Kx}}{1-R^{2} e^{-2Kx}} \right]$$

The transmission coefficient, T, is defined as I_t/I_0 . In fact, it is in general true that accurate measurements of the value of k, can only be made in this way when the thickness of the samples is not much larger than 1/K, and in many cases in order to obtain k, and also the value of n or the real part of the complex refractive index, it is necessary to simultaneously measure both T and R, for the same specimen, since the value of n can be found from R once k is known.

The general expressions for T and R involving the optical constants n and k, may be derived by using Maxwell's equations, and the general approach to the derivation will be outlined here. One considers a plane wave travelling through a medium of refractive index N' which is incident on the interface of an absorbing, conducting medium of complex refractive index N". The permeabilities, μ_1 and $\mu_2,$ of the two media are taken to be equal to one. Wave equations can be written for the incident, reflected and refracted waves, and by use of a boundary condition that the electric and magnetic intensities do not change upon passing through the boundary plane of the two media, the four equations can be solved resulting in the Fresnel equations for the reflected and refracted wave amplitudes. This procedure can be carried out for both the electric and magnetic vectors. By use of Fresnel's equations and by the definition of T and R, the following expressions are found for normal incidence between two media of refractive indices n_1 and n_2 .

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$

[21]

$$T = \frac{4n_2n_1}{(n_2+n_1)^2}$$

The expressions for R may be rewritten for the case when the first medium is vacuum with N' = 1 and the second absorbing medium has N'' = (n-ik). Then

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$
[22]

One of the many methods of finding both n and k from measurements of R is the technique of ellipsometry. It involves the use of plane polarized light which becomes elliptically polarized upon reflection from an absorbing surface. The optical constants are found by solving two simultaneous equations which are in terms of the principal angles of incidence, and the angle between the final plane of polarization and the plane of incidence, all angles being measured at the minimum value of the reflected light (34). Without methods such as these, measurement of R alone requires the use of the Kramers-Kronig relations for the frequency dependent n and k. Experimentally, this analysis can be complicated by the need to measure R over a wide range of frequencies in order to properly evaluate the integrals which occur in the Kramers-Kronig equations.

It is of interest to consider the application of dispersion theory to derive the fundamental relationship of the optical constants to the frequency, ω . For our purposes, it is sufficient to use the classical approach in which the electromagnetic radiation is viewed as setting the group of oscillators in the solid into forced vibration (37). For semiconductors the results for both bound electrons and conduction electrons are important since at longer wavelengths the conduction electron absorption can become noticeable. The general approach can be outlined as follows. The equation of motion of a bound electron experiencing the applied electric field E of the electromagnetic radiation is written, by considering that the electrons are displaced a distance, x, from their equilibrium positions. The equation then contains a restoring force which is proportional to x, and a damping force which is proportional to the velocity dx/dt. Thus

$$\frac{\mathrm{md}^2 x}{\mathrm{dt}^2} + \mathrm{mg} \frac{\mathrm{d}x}{\mathrm{dt}} + \mathrm{m\omega}_0^2 x = \mathrm{eEexp}(\mathrm{i}\omega t) \qquad [23]$$

where m is the mass of the electron, and the proportionality constant, g, is related to the breadth of the spectral line. ω_0 is the resonance frequency. The solution of the equation gives an amplitude for x of

$$\mathbf{x} = \frac{\mathrm{eE/m}}{(\omega_0^2 - \omega^2 + \mathrm{i}\omega_\mathrm{g})}$$
[24]

The polarizability, P, of a medium containing N electrons per unit volume is given by the ratio of the dipole moment to the electric field, that is P = Nex/E. Taking the complex dielectric constant to be equal to $1 + P/\epsilon_0$, and remembering that the complex dielectric constant is given by the square of the complex refractive index, n-ik, we have (using Equation [24])

$$(n-ik)^{2} = 1 + \frac{Ne^{2}/m\varepsilon_{0}}{(\omega_{0}^{2}-\omega^{2}+i\omega_{g})}$$
[25]

It is fairly easy to solve for the real and imaginary parts of this equation to obtain

$$n^{2}-k^{2}-1 = \omega_{p}^{2} \left[\frac{\omega_{0}^{2}-\omega^{2}}{(\omega_{0}^{2}-\omega^{2})^{2}+\omega^{2}g^{2}} \right]$$
[26]

and

$$2nk = \omega_p^2 \left[\frac{\omega g}{(\omega_0^2 - \omega^2)^2 + \omega^2 g^2}\right]$$

In these expressions $\omega_p^2 = Ne^2/m\epsilon_0$, where ω_p is the plasma frequency. In the case of conduction electrons these equations can be simplified since the restoring force is equal to zero for free electrons which means that $m\omega_0^2 x = 0$, or $\omega_0 = 0$. This gives

$$n^{2}-k^{2}-1 = -\frac{\omega_{p}^{2}}{(\omega^{2}+g^{2})}$$
[27]

and

$$\omega^{2}nk = \omega_{p}^{2} \frac{g}{(\omega^{2}+g^{2})}$$

It can be seen that the square of the plasma frequency occurs in these expressions. The plasma frequency is the frequency of the collective plasma oscillation, or plasmon. In the free electron picture this plasmon is simply a charge density wave in which the entire electron gas can be pictured as being displaced a distance, d, with respect to the stationary positive lattice. This leads to an oscillating equation of motion with frequency ω_p (9).

Finally, the oscillator strength of a transition is another quantity of interest in optical studies, and should be considered here. The nature of the oscillator strength, f, is related to the probability of a radiation induced transition to occur. The expressions for the probabilities are given in terms of the Einstein coefficients A and B. If the energy density of external radiation of frequency v is given by ρ_v , where the energy per unit volume in the frequency range v to v+dv is equal to $\rho_v dv$ then for emission, or the transition from a higher energy state to a lower energy state, we have that the Probability of Radiation = A + B ρ_v , and for absorption, or the transition from a lower state to a higher state, we have that the Probability of Absorption = B ρ_v , where A is the probability of spontaneous emission with no external radiation, and $B\rho_v$ is the probability of induced emission (38). The quantum mechanical theory of the interaction of radiation with matter is needed in order to find expressions for the Einstein probabilities. The full treatment is beyond the scope of this discussion, but it is found that the Einstein coefficient, B, is directly proportional to the dimensionless quantity f, the oscillator strength.

Thus, knowledge of the oscillator strength is of value because of its relation to the probability of radiation induced transition, but it is also significant because of the Kuhn-Thomas sum rule, $\sum_{n mn} = N$, where N is the total number of electrons in the system (38). In fact, it has been found that for the case of the optical transitions of alkali metal anions in solution, f = 2, indicating that the transitions are indeed due to the two 3s electrons (39). The oscillator strength can be experimentally measured by the following relationship. Optical absorptions are in practice spread over a range of frequencies so it is often necessary to calculate the integrated absorption coefficient K where $K = \int K(v) dv$. This measures the total strength of an absorption band and is related to the oscillator strength by

$$f = \left(\frac{4mc\varepsilon_0}{Le^2}\right) K$$
 [28]

where c = speed of light, and L = Avagadro's number. The other constants are defined as before (40).

4. Electrical Properties of Thin Films

Some results for the measurements of the d.c. conductivities of thin films of alkalides and electrides are presented in the experimental section of this chapter. To understand the goals behind these experiments, it is necessary to consider the properties of semiconductors in general, since alkalides and electrides are semiconductors. The basis for the discussion that follows can be primarily found in Chapter 28 of Reference 9.

In general, metals and insulators are distinguished by the energy gap, that exists in insulators, between the bottom of the lowest unoccupied energy bands (or conduction band) and the top of the highest occupied bands (or valence band). At absolute zero a solid with such an energy gap, E_g , will not conduct electricity. However, at temperatures above T = 0 some electrons can be thermally excited across the energy gap into the conduction band, leaving holes behind in the valence band. This causes conduction to occur. For solids in which the energy gap is not too large compared with the thermal energy, k_BT , the conductivity is large enough to be significant, and these solids are referred to as semiconductors. The number of electrons, or the number of carriers, that can be promoted to the conduction band is on the order of $\exp(-E_g/2k_BT)$ so we have the following proportionalities for the conductivity, σ , or the resistivity, ρ .

$$\sigma \propto e^{-E_g/2k_BT}; \quad \rho \propto e^{+E_g/2k_BT} \qquad [29]$$

In practice the actual value for the band gap, E_g , of semiconductors can vary considerably from a few tenths of an electron volt to approximately 2 electron volts, and the resistivity values also vary from $10^{-3} - 10^{+9}\Omega$ -cm, compared with typical values for metals of $10^{-6}\Omega$ -cm or for insulators of as much as $10^{22}\Omega$ -cm. The simplest band picture of an insulator or semiconductor versus a metal can be shown by the plot of energy versus the density of states in Figure 8, where g(E) is the density of states. The figure shows that in a metal, in contrast to a semiconductor, the boundary between the occupied and unoccupied states occurs in a region of allowed energy levels.

The energy gap can be measured in several ways. Obviously, one method involves the measurement of the temperature dependence of the resistivity of the semiconductor, in order to use expression [29]. A plot of ln R vs. $1/2k_{\rm B}T$ gives a slope that is proportional to the energy gap, $E_{\rm g}$. This method has been used in the present work. It should also be noted that the band gap



Figure 8. Generalized densities of levels \underline{vs} . energy for a semiconductor and a metal.

undergoes a slight temperature dependence due to the effect that lattice vibrations and thermal expansion have on the band structure. Thus, since E_g often has a linear dependence on temperature, $E_g = E_0 - AT$, the slope of lnp $\underline{vs} \cdot 1/2k_BT$ is nearly equal to E_g but is actually given by E_0 .

Thus, the conductivity of semiconductors increases with increasing temperature, in contrast to metals where the conductivity decreases with temperature, since the relaxation time, τ , decreases with the increase in T and hence gives an increase in electron-phonon scattering. In fact, semiconductors also have a power law dependence of the relaxation time with increasing temperature, but the effect is hidden by the exponential increase in the number of carriers. Thus, the conductivity is not a good measure of the collision rate in semiconductors, and it has been found useful to define a quantity, known as the mobility $\mu_{i}\,,$ that accounts for the collision rate, where μ_1 is the ratio of the drift velocity of a carrier in a field to the field strength: $\mu_i = v_d/E$. The current density, j, is given by j = nqv_d where n is the density of carriers and q is their charge, so that the conductivity is given by $\sigma = nq\mu_1$.

The final point to consider is that the properties of semiconductors are highly influenced by the purity of the material; that is, the presence of impurities which either

donate extra electrons, or accept electrons (donate holes) has a significant effect on the properties measured. Pure semiconductors in which the properties are due to electrons that are thermally excited from the valence to the conduction band, are referred to as intrinsic semiconductors, whereas those which have properties due to electrons donated from impurities are called extrinsic semiconductors. The effect that this can have on the resistivity, for example, can be seen in Figure 9, which is taken from Reference 9. It can be seen that even for the most highly doped samples the curve at high temperatures falls onto the common curve, or intrinsic resistivity curve. The simple band diagram for an intrinsic semiconductor is shown in Figure 10(a) where the energies of the bottom of the conduction band and top of the valence band are E_{c} and E_{v} respectively, and the chemical potential, μ , of the semiconductor falls within the band gap and is far from either E_c or E_y . In extrinsic semiconductors impurity levels exist that are either donor levels, if they supply extra electrons, or acceptor levels if they capture electrons from the valence band. The level density is seen in Figure 10(b) where the donor levels ${\rm E}_{\rm d}$ are close to the conduction band, and the acceptor levels E_a are close to the valence band. This arises from the model used to describe a donor impurity, for example. The model considers donor impurities to be



Figure 9. Resistivity <u>vs.</u> 1/T for antimony doped germanium (used with permission from Reference 9).



(a) intrinsic semiconductor (b) Extrinsic semiconductor

Band diagrams for intrinsic and extrinsic semi-conductors. Figure 10.

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irregularly spaced attractive centers with charge, +e, that donate and weakly bind the same number of extra electrons with charge -e. Since these attractive centers are located in the semiconductor medium with its large dielectric constant, the binding energy of the +e center for the -e electron is considerably reduced from the value expected for the impurity atom in free space, that is, from the first ionization energy. The additional electrons are in a superposition of the conduction band levels of the intrinsic semiconductor which are changed by the presence of the attractive charges +e. The impurity electrons are then represented, to a first approximation, as free electrons with an effective mass m*, rather than the free electron mass, m, that are moving in the presence of an attractive charge $+e/\epsilon$. This is the same problem as the hydrogen atom so the ground state binding energy can be readily obtained and is (9).

$$E = (\frac{m^*}{m\epsilon^2})(13.6 \text{ eV})$$
 [30]

The value for E can be much smaller than 13.6 eV and in fact, the binding energy of an electron to a donor impurity is very small compared with the energy gap. It is this that accounts for both the fact that the donor levels are close to the conduction band minimum compared to E_g , and also for the fact that impurity levels are an important source of carriers, since it is much easier

to thermally excite an electron from these levels into the conduction band than to excite an electron across the entire energy gap.

IV.D. Optical Spectra of Vapor Deposited Films

l.a. Co-Deposited Films of Na⁺C222·Na⁻

The major emphasis of this work has been the codeposition synthesis of $Na^+C222 \cdot Na^-$ films. This sodide was chosen for several reasons, including its thermal stability, and the large variety of data from studies of the material in the crystalline form, and in solvent evaporated films. This section will first describe several qualitative results obtained in this study, and will then present some calculations of the absorption coefficient, K, and the oscillator strength, f, of the transition.

The spectra of one of the earliest films made is shown in Figure 11. The film was deposited at -20°C for about 3 minutes. The mole ratio of metal to cryptand was 1.45, which was slightly lower than usual. The total film thickness was 740 Å. Spectrum 1, shown in Figure 11, was taken immediately after the film was made. It is a good representative spectrum of Na⁺C222·Na⁻. The peak maximum occurs at 15.5 x 10^3 cm⁻¹, or 645 nm. The peak width at half height is about 2 x 10^3 cm⁻¹. These values



Figure 11. Unnormalized absorbance <u>vs</u>. wavenumber for Film I of Na⁺C222·Na⁻ produced by co-deposition.

were typical for films of Na⁺C222.Na⁻, for which the peak maximum was usually between 15.35 x 10^3 cm⁻¹ (650 nm) and 15.5 x 10^3 cm⁻¹, and the width was between 2000- 3000 cm^{-1} . The spectra also show the typical asymmetry of the Na⁻ absorption, for which the high energy side of the peak has more absorption in the wings than the low energy side. However, Figure 11 also demonstrates another important problem. Spectrum 2 of this figure shows a large decrease in the peak amplitude. This spectrum was taken at -27° C two hours after the film had been made. Finally, Spectrum 3 is entirely featureless. It was taken 3 hours after the film was deposited and at a temperature of +20°C. It was later found to be generally true that if films made at low temperatures were allowed to warm up even to 0°C, the absorption of Na⁻ disappeared. The disappearance of absorption peaks with time was found to be less significant if the temperature was held below -30°C. The simplest explanation for the loss of the absorption peak is that the film decomposed by reaction with the residual water vapor in the vacuum system. The system was usually at an ambient pressure of 1 x 10^{-5} torr, and a substantial fraction of this pressure was due to water. For example, a recently acquired Residual Gas Analyzer was installed in the vacuum system and indicated that for a fairly good operating total pressure of 5 x 10^{-6} torr, the partial pressure of H₂O was

 1×10^{-6} torr. This may have been enough water to react with the films. It has been suggested that films grown at low temperatures may contain substantial amounts of unreacted sodium and cryptand. The sodium metal atoms are highly reactive with water and may account for the substantial loss of absorption.

Figure 12 shows the results from an experiment in which several layers of material were added, and spectra were measured each time. The first three depositions were done for 7 seconds, 10 seconds, and 30 seconds, and it was surprising to discover that no material deposited. The first absorption appeared after 1 minute of deposition and is shown in Spectrum 1 in the figure. The Na absorption is very slight. The layer was deposited at -60°C with a mole ratio of 2.24, and a thickness of 195 Å. Spectrum 2 shows a slightly more pronounced peak and is the result of an additional minute of deposition at -53° C, with a mole ratio of 2.15. The thickness was 420 Å. Spectra 3, 4, and 5 are far better resolved and all have the expected peak maximum at 15.4 x 10^3 cm⁻¹ and widths at half height of 2.2 x 10^3 cm⁻¹. These layers were deposited at temperatures between -46 and $-40^{\circ}C$ with mole ratios of 2.1 to 2.24. The three thicknesses were 760 Å, 1420 Å, and 2050 Å. It was thought that the lack of deposition during very short deposition times was due to a low sticking coefficient of the Na and C222 to the



Figure 12. Unnormalized absorbance <u>vs</u>. wavenumber for Film II of Na⁺C222·Na⁻ produced by co-deposition.

quartz substrate. These materials may have a stronger attraction to each other than to the substrate.

Figure 13 shows the spectra for an anomalous experiment. These films were grown at temperatures of -124°C and -100°C which were lower than any other deposition temperatures. Spectrum 1 is for a layer that was 660 Å thick with a mole ratio of 2.3, and Spectrum 2 is for a layer that was 1180 Å with a mole ratio of 2.2. The spectral shapes are remarkably different from any other Na⁺C222·Na⁻ films. The absorption peaks are very broad and appear to have a maximum at 14.8 x 10^3 cm⁻¹ (676 nm). The widths at half height are 6 x 10^3 cm⁻¹ and 5.5 x 10^3 cm^{-1} which are nearly three times larger than the usual values. In addition, the absorptions did not drop to zero at low energies but show a nearly constant, very high value of absorbance between 0.25 and 0.30. It is possible that the high absorption at low energies was due to the presence of trapped electrons. The other possibility is that the film scattered light more strongly than usual. However, this film may have contained large amounts of unreacted metal and cryptand because of the very low temperature of deposition. The inhomogeneous nature of the film would then be directly responsible for the breadth of these spectral lines.

The fourth co-deposition synthesis of Na⁺C222·Na⁻ is shown in Figure 14. This experiment is especially



Figure 13. Unnormalized absorbance <u>vs</u>. wavenumber for Film III of Na⁺C222·Na⁻ produced by co-deposition.



Figure 14. Unnormalized absorbance <u>vs</u>. wavenumber for Film IV of Na⁺C222·Na⁻ produced by co-deposition.

significant because each layer of the film was deposited at +26°C. The room temperature deposition of thin films was done in spite of earlier observations of the loss of absorption of films made at low temperatures, because of repeated observations of sodide films that grew on the room temperature walls of the belljar. Spectra 1-3 in Figure 14 show that the films produced in this way were essentially the same as those grown at low temperatures. The peak maxima occurred at 15.34×10^3 wavenumbers, and the widths at half height were 2.3 x 10^3 cm⁻¹. The mole ratios of metal to cryptand were slightly high (2.5). The three thicknesses were 850 Å, 1730 Å, and 2530 Å, respectively. However, this film also has a high absorption at low energies that could be due to scattering of light, or electride absorption. Further investigations would be required to determine whether the low energy absorption is generally present in room temperature films, or whether it was an artifact of the particular experiment.

The primary reason for growing alkalide and electride films by physical vapor deposition is to obtain quantitative optical data. Several factors can still be changed that will allow us to achieve this goal. Most of these initial experiments were primarily concerned with isolating and solving practical problems, such as the decomposition or evaporation of previously deposited films,

and the effect of deposition parameters such as the evaporation rates, the pressure and temperature of deposition, the substrate material and the stoichiometry of films. In fact, one major problem that will soon be resolved is the method used to control the thickness, and hence the stoichiometry of the materials. The use of only one rate monitor meant that the rates were often difficult to control so that the stoichiometries tended to deviate slightly from the desired ratio. Finally, the experiment requires that the total thickness of films be estimated from the deposition rates and times, since independent measurements of film thickness are not feasible for these reactive materials. It is possible that there are errors in the estimation of these thicknesses. A few observations of the deposition rates in the central co-deposition position compared to the rates measured directly over the sources, indicate that the rates in the center are lower than expected on the basis of geometry alone. This means that the thickness estimated for the co-deposition syntheses may have larger errors than those for the layered syntheses. In the future, the rates in the central position should always be carefully checked for each film grown by co-deposition.

The data that have been presented so far were used to estimate the oscillator strength of the absorption of $Na^+C222\cdot Na^-$. Because of the differences between the

-118-

various experiments, such as the temperature of deposition, the peak widths, and the amount of scattering present, it was expected that the results would not be entirely consistent. One other film of Na⁺C222·Na⁻, produced by layering, was also analyzed. This film is described in detail later in this chapter. The oscillator strengths were estimated by using the experimentally measured values of the absorbances to calculate the absorption coefficient, K = (2.303A)/t (in which t is the film thickness in centimeters). The oscillator strength is related to the area under the curve of $K(\overline{v})$ vs. \overline{v} by Equation [28] in Chapter IV. The constants in this equation, including the appropriate unit conversion factors can be simplified by the following expression: $f = 4.33 \times 10^{-9} C^{-1} \int K(\overline{v}) d\overline{v}$. where C is the concentration of Na⁺C222.Na⁻ and is equal to 2.52 M. The integrals were estimated by weighing the areas under the curves. Because the data were not collected into the ultraviolet region of the spectrum, the curves had to be extrapolated for wavenumbers above 20,000 cm⁻¹. The results are shown in Table 7. It is not surprising that the values are different. Some films gave oscillator strengths near 2 but others gave values of only 1 or less. It should be noted that the values for f were always low for the co-deposited films, and the layered film f values increased with time. This is probably due to the incomplete reaction of the metal and

Film	Oscillator Strength
Layered V	
3 2 1	2.0 ± .1* 1.7 ± .09* 1.2
Co-Deposit II	
5 4 3	1.08 ± .09* 1.03 ± .01* 0.8
Co-Deposit III	
2 1	1.14 1.54
Co-Deposit IV	
3 2 1	0.47 0.78 0.71

Table 7. Estimated Oscillator Strengths for Films of Na⁺C222 Na⁻ Produced Both by Co-Deposition and Layering.

* Spectra used to calculate the optical constant, k.

cryptand. It may be very important to allow enough time for this reaction to proceed in order to obtain reliable values of f in the future. In addition, the values for f for different thicknesses of the same film were not self-consistent. This could be because of errors incurred in the estimation of the thicknesses and also because of the problems encountered with the high baseline. However, there were two encouraging results. First, the oscillator strengths were all close to the expected value of 2 as obtained for Na in solution (39). Second, the lineshapes of most spectra were very reproducible. The irreproducibility of lineshapes was one of the major problems encountered in films formed by solvent evapora-The non-uniform thickness of solvent evaporated tion. films was directly related to the irreproducibility of the lineshapes (32).

Recent attempts were made to grow another film, and to measure the optical spectra at several thicknesses with the intention of producing better quantitative data for a fully reacted film with reproducible lineshapes. These measurements were not successful, and in the interests of time the experiment was temporarily abandoned. The failure was caused by a persistent drift in the detector readings with time. Since the optical spectra were measured with a single beam technique, it was necessary for the baseline to be constant. It is not yet known what caused the detector to fail but it is possible that it may have been affected either by the exposure to vacuum or by exposure to room light, or both. The problem is mentioned here because the same problem may have existed in earlier measurements, and may account for some of the differences in the estimated oscillator strengths.

Four of the original spectra of Na⁺C222'Na⁻ were used to estimate the optical constants $k(\lambda)$. These four spectra were chosen because of their very similar lineshapes. They were Spectra 3 and 2 of the layered film V. and Spectra 5 and 4 of the co-deposited film II. The values for the absorption coefficients for these films were scaled by multiplication by the ratio of the expected oscillator strength of 2 to the measured oscillator strengths. The molar decadic absorption coefficients, $\alpha(\lambda)$, were calculated for each film and the averages were taken to produce a composite curve. This curve is shown in Figure 15, in which α is plotted against the energy in electron volts. The average value of α at the maximum wavenumber, $15.34 \times 10^3 \text{ cm}^{-1}$, was equal to $7.05 \pm .52 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. which is close to the value in solution of 8.2 \pm .3 x 10⁴ M^{-1} cm⁻¹ (39). Finally, the optical constant, $k(\lambda)$, was calculated from the average values of $\alpha(\lambda)$, where $\alpha = 4\pi k/\lambda$ (Fig. 16). This expression is derived from the absorption coefficient obtained from the natural logarithm so the





expression must be suitably scaled by 2.303. The average values for $\alpha(\lambda)$, and $k(\lambda)$, are shown in Table 8.

In conclusion, it has now been possible to use vapor deposited films to obtain reproducible lineshapes for Na⁺C222·Na⁻. These optical bands have also been used to estimate the values of the oscillator strength of the transition. The results were not very consistent but were at least reasonably close to the expected value of 2. The absorbances were also used with the expected value of the oscillator strength to calculate the molar decadic absorption coefficient as a function of wavelength, and hence the optical constant, $k(\lambda)$. Thus, in the future it will be possible to combine the transmittance data, with reflectance data from thin films, to calculate the optical constant, n. Finally, n and k together can be used to calculate both the real and imaginary parts of the complex dielectric constant for Na⁺C222·Na⁻. The results presented here obviously still suffer from the experimental difficulties described in this section, but they indicate that it should be possible to obtain good quantitative data in the near future.

1.(b) Layered Films of Na⁺C222.Na⁻

Most of the data collected so far in the study of vapor deposited layered films have been of a preliminary nature, so that no quantitative analysis was done on the

-124-

	$\alpha(\lambda) \pm sdx 10^{-4}$			$\alpha(\lambda) \pm sdx 10^{-4}$	
λ(nm)	$(M^{-1} \cdot cm^{-1})$	k(λ)	λ(nm)	$(M^{-1} \cdot cm^{-1})$	k(λ)
345	.31±.09	.05	702	3.81±.32	1.24
357	.53±.10	.09	719	3.02±.33	1.00
370	.78±.11	.13	735	2.56±.33	0.87
385	1.01±.09	.18	752	2.28±.31	•79
400	1.26±.10	.23	769	2.04±.33	.72
417	1.49±.08	.29	786	1.83±.28	.66
435	1.76±.08	•35	802	1.66±.26	.61
455	1.93±.20	.41	819	1.54±.24	•58
467	2.18±.20	•47	836	1.42±.19	• 55
484	2.38±.12	•53	853	1.36±.17	•54
501	2.67±.17	.62	870	1.30±.12	.52
517	2.77±.16	.66	886	1.21±.10	.50
534	2.93±.12	.72	903	1.14±.10	.48
551	3.10±.12	•79	920	1.12±.09	.48
568	3.40±.11	.89	1000	0.89±.06	.41
584	3.80±.15	1.02	1111	0.68±.05	•35
601	4.55±.30	1.26	1250	0.50±.04	.29
618	5.61±.30	1.60	1429	0.32±.02	.21
635	6.61±.34	1.94	1667	0.14±.03	.11
652	7.05±.52	2.12			
668	6.45±.52	1.99			
685	5.11±.35	1.62			

Table 8. Average Values of the Molar Decadic Absorption Coefficient $\alpha(\lambda)$, and the Optical Constant $k(\lambda)$ Obtained from Four Composite Films of Na⁺C222Na⁻.





films of $Na^+C222 \cdot Na^-$ produced by layering. The reason for this is primarily that we desired to investigate films of several other systems to ascertain the general behavior rather than to carry out a more detailed analysis of only one or two systems. Thus, these materials will be discussed in a qualitative manner.

The first of these experiments involves the synthesis of Na⁺C222·Na⁻ films by the layering technique. The layering method requires the alternate deposition of metal layers and cryptand layers as is fully discussed in Chapter III. The thickness and number of layers can be chosen at will. The first layered film, Film I, was made at a substrate temperature of -20°C and consisted of only two layers, that is, one layer of C222 and one layer of Na. The layers were deposited for 5.5 minutes at rates of 154 Å/min for C222 and 21 Å/min for Na. Therefore, the individual layers were very thick, giving a total film thickness of 945 Å. The experimental parameters for this film and for all the layered films of $Na^+C222 \cdot Na^-$ are given in Table 9. The spectrum of this film was markedly different from those of films made by the co-deposition method, since there was no strong Na peak but only a broad featureless absorption that changed very little with time (see Figure 17). It was thought that perhaps the addition of more layers would result in the normal spectrum of Na⁺C222·Na⁻ so one additional layer each of Na

Exp	p.	Film T (°C)	M/C	# Layers	Tot. Th. (Å)	Layer Th. (Å)	Time Delay (hr)
I.	1. 2.	-20 -14	2.02	1 C222 1 Na	945	830 113	0 1
II.	1. 2. 3. 4.	-43 -50 -41 -27	1.77	2 C222 2 Na	1900	830 113 873 90	0 1 1.6 2.2
III	.1. 2. 3.	-79 -109 -44	2.22	1 C222 1 Na	1296	1296 168	0 1.8 4.5
IV.	1. 2. 3.	-99 -46 -29	1.99	2 C222 2 Na	2286	152 Na 1062 C222 117 Na 955 C222	0 2.4 10.0
ν.	1.	-43	1.99	5 C222 5 Na	875	154 C222 21 Na	0
	2.	- 50	2.23	8 C222 8 Na	1400	155 C222 21 Na	0
	3.	-49	2.58	11 C222 11 Na	1994	156 C222 25	0

Table 9. Layered Films of Na⁺·C222·Na⁻ Deposition Parameters.



Figure 17. Unnormalized absorbance vs. wavenumber for layered films I, II, III of Na⁺C222·Na⁻.
and C222 was added to the same film. This is Film II in Figure 17. The spectrum changed slightly but still did not show the characteristic peak of Na⁻ at 15.5 x 10^3 cm⁻¹. Instead, the spectrum (shown in Figure 17) had two peaks. The first peak or shoulder occurred at about 15.3 x 10^3 cm⁻¹ (654 nm) and the second peak at 11.7 x 10^3 cm⁻¹ (855 nm). This is seen in spectrum 1 which was taken immediately after the film was grown. With time, the Na⁻ shoulder grew slightly and shifted to 15.5 x 10^3 cm^{-1} (645 nm). The second peak decreased slightly and shifted to $12.5 \times 10^3 \text{ cm}^{-1}$ (800 nm) after about two hours. The low energy peak was assumed to be caused by the presence of trapped electrons, although the reason for this high concentration of trapped electrons was not clear. The trapped electron peak was also at much higher energies than is usual. This peak is more often found between 7.0 x 10^3 and 8.0 x 10^3 cm⁻¹. This behavior is somewhat reminiscent of many earlier observations of films produced by solvent evaporation, in which the presence of the Na peak caused the e peak to shift to higher energies compared to the energy of the e peak in the absence of the metal anion peak.

Film III was made in the same way, in order to determine whether this behavior was reproducible. The film was made with 2 layers, 1 of Na and 1 of C222. The results are shown in Figure 17. It can be seen that the film degraded with time. That is, the spectral features have nearly disappeared in Spectrum 3, which was taken 4.5 hours after the film was made. However, the initial results were the same as those for films I and II. The Na⁻ appears only as a weak shoulder at about 15.4 x 10^3 cm⁻¹ and the main peak is the very high energy trapped electron peak. The trapped electron peak in this film is at a slightly lower energy (11.0 x 10^3 cm⁻¹ or 910 nm) than the peak in Film II. The only significant difference between the films was the temperature of deposition. Film II was grown at an average temperature of -33° C whereas Film III was grown at an average temperature of -93° C.

It was thought that the reason the Na⁻ peak did not grow appreciably while the trapped electron peak decreased, was that the kinetics of the solid state reaction were slow. The films had only been monitored for 2 to 4 hours, so Film IV was grown with the intention of allowing enough time for the reaction between the Na metal and the cryptand to proceed to completion. It was thought that this would produce the usual spectrum of Na⁺C222·Na⁻. The film was grown with 4 layers at an average temperature of -53° C. The film was monitored for 10 hours and was kept below -30° C for the entire time. The results are shown in Figure 18. It can be seen that the spectrum underwent very little change. In addition,



Figure 18. Layered Na⁺C222·Na⁻ Film IV. Unnormalized absorbance <u>vs</u>. wavenumber.

the Na⁻ shoulder at 15.4 x 10^3 cm⁻¹ did not grow but remained almost unchanged. The main peak was still the trapped electron peak. This peak is only partially seen since the wavelengths that were accessible at the time that the film was made did not go below 920 nm. However, the e⁻ band seems to peak between 10.5 x 10^3 cm⁻¹ and 11.0 x 10^3 cm⁻¹.

The results of this experiment seem to indicate that the kinetics of the reaction was not enough to explain the fact that the Na peak was not the major feature in the spectrum. Instead, the following explanation was proposed. It should first be noted that all four films of layered Na⁺C222·Na⁻ had relatively few layers (2-4) each of which was quite thick. The Ma layers were all on the order of 150 Å and the C222 layers were on the order of 1000 Å. It is therefore possible that the observed spectrum resulted from a partial reaction that occurs at the interfaces of these thick layers to produce Na(s) + C222 \rightarrow Na⁺C222 + e⁻. The trapped electron produced in this way is then able to react with the sodium metal to produce the metal anion: $Na(s) + e^- \rightarrow Na^-$. This, however, may create an intermediate layer, consisting of the complexed cation and the trapped electron on the cryptand rich side, and the metal anion on the metal rich side, which may inhibit the further production of Na. This would explain both the presence of the large

-133-

trapped electron peak and the failure of the Na shoulder to grow. It was thought that if a layered film were grown with many, very thin layers, the complete formation of Na would perhaps be favored. Film V was grown in this way. The individual layers were reduced by about 85% to thicknesses of 20 Å for Na and 150 Å for C222, and were deposited at an average temperature of -54°C. The spectra in Figure 19 show the results for several depositions of these thin layers, from 5 layers each, to 8 each, to the final total of 11 layers each. The optical spectra show that the film formed pure Na⁺C222·Na⁻ with no evidence for the formation of trapped electrons. This suggests that the layered growth of films requires the use of many thin layers so that the intimate mixture of components can lead to the formation of the desired material. This observation may be important when mixed films that contain three components are made.

2. <u>Na⁺C222[·]e⁻</u>

The study of vapor deposited films of Na⁺C222[•]e⁻ is rudimentary but is very encouraging. This electride is a system that has never been isolated in either the powdered or crystalline form, but has only been observed in either solvent evaporated films (31) or vapor deposited films (during the feasibility study Ref. 33). In both of these studies the trapped electron peak occurred at rather low



Figure 19. Layered Na⁺C222·Na⁻. Unnormalized absorbance \underline{vs} wavenumber for Film V.

energies, near 8.6 x 10^3 cm⁻¹. However, in the case of films evaporated from NH3, a second peak for Na was also present which caused a slight blue shift of the e⁻ peak as has been mentioned previously. The vapor deposited films showed no Na. The films produced in this study by vapor deposition show two peaks. In fact, many attempts to grow Na⁺C222·e⁻ films were unsuccessful. A film which was grown by co-deposition led to the production of Na⁺C222.Na⁻ even though the mole ratio of metal to cryptand was kept well below 2.00. The spectrum was virtually identical to Na⁺C222·Na⁻ films with a mole ratio of 2, except that the band was broader than usual, with a width at half height of 3.5 x 10^3 cm⁻¹ as opposed to the usual value of 2×10^3 cm⁻¹. So far, the only moderately successful attempts to grow films of Na⁺C222.e⁻ have both used the layered technique. This is not to suggest that co-deposition cannot result in good quality electride films, but rather that the tendency of the system to form Na is very favorable if any excess sodium metal is present. Therefore, it is thought that the codeposition synthesis of the sodium electride will require the use of more and better rate monitors as will be discussed in Chapter VI.

The first partially successful layered film of Na^+ -C222·e⁻ is shown in Figure 20. It was formed from 6 layers each of C222 and Na with average thicknesses of



Figure 20. Layered film of Na⁺C222·e⁻. Unnormalized absorbance <u>vs</u>. wavenumber for Film I. Spectrum 1 = 0 hr; Spectrum 2 = 1.5 hr; Spectrum 3 = 5.5 hr.

180 Å for C222 and 17 Å for Na. at a substrate temperature of -100°C. The total film thickness was 1200 Å and the metal to cryptand mole ratio was 1.4. Spectrum 1 shows the result immediately after the film was made. The spectrum still obviously contains a large amount of Na⁻ as indicated by the main peak at 15.4 x 10^3 cm⁻¹, but there is a fairly high concentration of trapped electrons as seen in the shoulder at about $12 \times 10^3 \text{ cm}^{-1}$. However, the e shoulder decreased with time as seen in the progression from spectrum 1 to Spectra 2 and 3. The second film of Na⁺C222[•]e⁻ is shown in Figure 21. The initial spectra are substantially different from Film I. Film II was grown at -115°C and consisted of six layers each of C222 and Na with average thicknesses of 330 Å for C222 and 19 Å for Na. The total film thickness was 2100 Å and the metal to cryptand mole ratio was 0.86. in contrast to the thinner Film I which also had a higher mole ratio. A qualitative difference could also be seen between the two films, since Film I had the typical very bright blue color characteristic of the sodide, whereas Film II was very black or blue-black in appearance. Spectrum 1 was taken immediately after the film was made, and does not indicate the presence of Na, but has a broad e^{-} peak at 12.5 x 10³ cm⁻¹. However, over a period of 4.5 hours the spectrum gradually changed to produce a small Na⁻¹ peak at 15 x 10³ cm⁻¹. The e⁻¹ peak decreased,



Figure 21. Layered film of Na⁺C222·e⁻. Unnormalized absorbance vs. wavenumber for Film II. Spectrum 1 = 0 hr; 2 = 2 hr; 3 = 3.5 hr. and 4 = 4.5 hr.

and became a plateau and finally a shoulder. This spectral shape is similar to that of the very thick layered films of Na⁺C222·Na⁻. The significant difference is that the thick layered films did not change with time but maintained both the trapped electron peak and the Na⁻ peak. It is less well understood why films which were nominally electrides evolved so rapidly to form Na⁻, even when a large excess of C222 was present as, for example, in Film II. This indicates that the reaction

 $2Na^+C222 \cdot e^- \rightarrow Na^+C222 \cdot Na^- + C222$

is favored. It is probable that the situation was complicated by the use of the layered technique itself. Pure sodium electride films may be formed only by a carefully controlled co-deposition synthesis.

3. к⁺с222•к⁻

The alkalide film $K^+C222 \cdot K^-$ was studied relatively little in this work and has only been grown by the codeposition method. Figure 22 shows the spectrum for the first film that was measured over the full wavelength range. The film was grown at -126°C with a total thickness of 1980 Å and a mole ratio of M/C = 1.80. Spectra 1-3 are very similar to the spectra obtained for dry films evaporated from ammonia (31). In both cases, one



Figure 22. Co-deposition film of $K^+C222 \cdot K^-$. Unnormalized absorbance vs. wavenumber. Spectrum 1 = 0 hr; 2 = 1.5 hr; and 3 = 2.5 hrs + warming to -60°C.

can see the presence of the K⁻ peak at $11.6 \times 10^3 \text{ cm}^{-1}$ as well as a shoulder or plateau between $7 \times 10^3 \text{ cm}^{-1}$ to $9 \times 10^3 \text{ cm}^{-1}$, which was probably due to the presence of trapped electrons. The vapor deposited film changed very markedly after warming to -60° C, as is seen in Spectrum 3, most likely as a result of decomposition. A careful quantitative study of this material has not yet been carried out, but the preliminary results indicate that these films can be grown by vapor deposition and do not differ from those produced by solvent evaporation.

4. <u>K⁺C222·e⁻</u>

Numerous attempts to grow $K^+C222 \cdot e^-$ films resulted in films which decomposed before any measurements had been Therefore, the results for only two successful taken. films can be reported, the first made by the layered method, and the second by the co-deposition method. The optical spectra of both films are quite similar and are shown together in Figure 23. Film I, formed by layering, consisted of 10 layers each of C222 and K. The individual layers had average thicknesses of 200 Å for C222 and 20 Å for K giving a total thickness of 2230 Å. The layers were deposited at a substrate temperature of -100°C and the mole ratio was M/C = 0.83. The film was kept below $-60^{\circ}C$ during the time that the optical spectra were measured, and it was monitored for 2 hours. Spectra 1-4 show a



Figure 23. Unnormalized absorbance vs. wavenumber for (a) Film I of layered K⁺C222·e⁻ and (b) Film II of co-deposited K⁺C222·e⁻.

strong time dependence. The spectra taken immediately after the film was made and 45 minutes later are almost identical to the spectra obtained previously for $K^+C222 K^-$. That is, there is a strong K⁻ peak at 11.5 x 10^3 cm⁻¹ followed by a shoulder between 7-9 x 10^3 cm⁻¹ due to the trapped electrons. However, unlike the alkalide case, the K⁻ peak has nearly disappeared in the later spectra and the e⁻ peak shows a rising absorption towards the infrared. This spectral shape is beginning to approximate the plasma-edge absorption seen in solvent evaporated films of $K^+C222 \cdot e^-$ crystals (see Chapter V). The behavior of the film is essentially identical to that observed in films of $K^+C222 \cdot e^-$ evaporated from ammonia (31) in which the initial dry film showed both a K peak and e shoulder, and the annealed dry film had no K peak and had an e peak which had increased significantly. Film II which was formed by the co-deposition method, shows very similar results. The film was very dark black in appearance. The spectra shown in the figure were taken after two different depositions. Spectra 1 and 2 were taken after the first deposition in which the mole ratio was 1.05, the total thickness was 1500 Å and the deposition temperature was -110°C. Spectrum 1 was taken immediately after the film was made and shows a single very broad peak at about 11 x 10^3 cm⁻¹. Spectrum 2 was taken 2 hours later. The K peak has completely disappeared and a

rising absorption of the trapped electrons has appeared at lower energies. An additional deposition of material was made on top of this layer. The second deposition was made at a substrate temperature of -90° C and resulted in a total thickness of 2700 Å and a mole ratio of 0.99. Spectrum 3 was taken immediately after this film and the K⁻ peak can be seen again, although there is still a strong e⁻ absorption. Finally, spectrum 4 was taken 35 minutes later, and already the spectrum has altered to be nearly identical to spectrum 2, in which the K⁻ peak has disappeared.

5. Discussion

It is obvious that the study of $Na^+C222 \cdot e^-$, $K^+C222 \cdot K^-$, and $K^+C222 \cdot e^-$, is still incomplete. The results for the sodium electride are puzzling, especially because of the difficulty in producing pure electride films that do not contain Na⁻, as was done in the vapor deposition feasibility study. Even in Film II in which the initial spectrum showed only one broad absorption for e^- the spectrum changed within three hours to show a considerable amount of Na⁻ absorption. The results, however, may be complicated by the fact that the only successful sodium electride films grown so far have been made by the layered method. In addition, every sodium film containing trapped electrons had an e^- peak at higher energies than had been previously observed in solvent evaporated films. This may indicate that the nature of the material is strongly influenced by the technique of physical vapor deposition. That is, the method itself may be responsible for the production of the high energy trapping potentials for the electrons. Finally, it should be noted that the sodium electride system is inherently nebulous since this material has never been isolated as crystals or as a microcrystalline powder, and has only been observed in films.

The potassium electride, $K^+C222 \cdot e^-$, is also a difficult system for study largely because of its extreme temperature sensitivity. Crystals of this material are known to decompose at -45°C (see Chapter V), and this reactivity may have led to the difficulty in growing and characterizing films of this material. Although both solvent evaporated films and vapor deposited films of $K^+C222 \cdot e^-$ show an initial K^- peak which disappears with time, this observation does not explain the reason for this annealing process. Finally, since the trapped $e^$ peak occurs at very low energy, it would be necessary to extend the accessible spectral range to determine whether the peak is localized or is a true plasma absorption.

The results, however, are pleasing for a number of reasons. First, it has been possible to demonstrate for

four different systems that the method of physical vapor deposition produces films that are qualitatively identical to those films produced by solvent evaporation from solutions of crystals. This means that the method holds concrete promise for the ability to produce qualitative spectra of many different systems in the near future. Secondly, some of the unique results for films produced by vapor deposition are intriguing, and suggest that the technique itself may allow us to create materials in these films that are different than the materials which are grown as bulk crystals. This may be especially true in the case of films grown by the layering technique. The results which were found for films consisting of only one alkali metal, may well be repeated in films consisting of two different alkali metals. It is even possible to conjecture that the order in which layers are deposited could have an effect on the nature of the resultant material. This is, of course, highly speculative, but the investigation of this possibility would be informative whether or not the effect is seen.

IV.E. Electrical Measurements on Vapor Deposited Films

The study of the electrical properties of alkalides and electrides in thin films promises to be a useful way of pursuing these measurements. It is thought that this technique will allow two new measurements of the properties of the films to be made. First, the conductivity of some films may be quite different from the conductivity measured in powdered samples. This would be the case because of the ability that the vapor deposition technique provides to control the stoichiometry of materials, and thus to control the amount of doping by electrons. Secondly, it will be possible to determine whether photoconductivity occurs in these materials, since the design of the <u>in situ</u> optical and electrical measurements is admirably suited to measure the effect of light quanta on the conductivity.

Feasibility experiments were made in this study of the d.c. conductivity of Na⁺C222·Na⁻. This system was chosen because of its remarkable thermal stability, and because it was the best characterized material that had been made by vapor deposition. Relatively few attempts were made to implement these experiments, primarily because the main emphasis of this work was on optical measurements rather than electrical measurements. In addition, several technical problems made the collection of good data quite difficult. For example, in the early experiments, silver metal was used as the electrode material. This worked quite well in the case of longitudinal conductivity measurements, in which the parallelstrip electrodes were deposited before the alkalide film

-148-

was grown. However, in the case of transverse conductivity, in which the electrodes sandwiched the alkalide film, it was found that the high temperature ($\sim 1000^{\circ}$ C) necessary to evaporate silver tended to completely decompose the alkalide film during the deposition of the top electrode. It was therefore necessary to use another electrode material. Sodium metal itself was used when the alkalide film, Na⁺C222·Na⁻, was made. Presumably K metal would be an appropriate electrode material when the corresponding K⁺C222·K⁻ salt is studied. This is not expected to be a satisfactory solution to the problem when electride films are measured, since the alkali metal electrodes may produce local concentrations of alkalide rather than electride, and may thus affect the electrical properties of the film.

The second problem encountered in making these measurements was failure to make good contacts between the thin film electrodes and the indium solder spots. In addition, the electrodes frequently shorted across each other in the transverse conductivity configuration. The success of this experiment was very sensitive to the proper alignment of the electrodes and the film masks. A simple guiding mechanism for the substrate support block would eliminate this problem entirely, and a possible design for this mechanism is discussed in Chapter VI.

In spite of these experimental difficulties, the

-149-

results from two conductivity measurements are discussed here. The results indicate that only a few improvements in the experimental design would allow the collection of good data on several films. The first experiment was a longitudinal measurement of Na⁺C222·Na⁻ in which Ag electrodes were used. The second, also of Na⁺C222·Na⁻. was a transverse conductivity measurement in which Na electrodes were used. The temperature was controlled in slightly different ways in the two experiments. The first method, used in the measurement of the longitudinal conductivity, cooled the substrate block by flowing liquid nitrogen through the cooling coils. In this case, it was noted that the temperatures were better controlled during the subsequent slow warming rather than during this rapid cooling process. This is borne out by the results for the temperature dependence of the resistance. In the second case, the temperature was controlled by monitoring the flow rate of N_2 gas, which passed through a liquid nitrogen bath before entering the substrate block. In this case it was found that the temperatures were better controlled during the cooling process.

In the longitudinal measurement the Ohm's Law behavior, at -30°C, was tested only for positive polarity, but was found to be very well behaved. The temperature dependence was measured at 4.00 volts. The film was made at -40°C, and the optical spectrum was also measured, giving the typical spectrum for Na⁺C222·Na⁻. The temperature dependence of the resistance was then measured, first going down in temperature and then going up in temperature. The temperature results are good only below -30°C since upon warming to 0°C a sharp decrease was found in the currents measured, and the optical spectrum showed the loss of the Na⁻ peak. Even so, the data shifted between the two runs and the two sets of data were fitted separately using the non-linear fitting program KINFIT IV. In both cases the results gave apparent band gaps of Eg = 0.05 ± 0.0008 eV, and I_∞ = $2.77 \pm 0.08 \times 10^{-9}$ amp, for a film which was 790 Å thick and had an area of 1.9 x 1.3 cm. The voltage was imposed across the shorter distance of 1.3 cm.

The history of the measurement of the film by transverse conductivity was slightly more complicated. The film and the sodium electrodes were all deposited at +15°C, since it had been discovered that Na⁺C222·Na⁻ films are stable up to room temperature if they are grown at ambient temperatures. Thus, the temperature range available for the resistivity measurements was much larger than for films grown at low temperatures. The bottom Na electrode was 3900 Å thick. The alkalide film was 11,400 Å thick and the thickness of the top electrode was 3500 Å. Ohm's Law behavior at + 21°C was tested for both positive and negative voltages, and it was found that strong polarization effects were present at a voltage of 2.0. The temperature dependence was first measured at + 1.00 volts. The data were very poorly behaved in this measurement. The signals were very noisy during the attempt to measure Ohm's Law. The data for the temperature dependence were also very poor, especially for the uncontrolled warming cycle, but even the data for the more controlled cooling cycle were unreliable, and showed a change in the slope of lnR vs. 1/T at about $-3^{\circ}C$. It was thought at first that the experiment was meaningless but approximately one hour later the Ohm's Law behavior was rechecked and the temperature dependence of the resistance was measured a second time at + 1.00 volt. There was still a polarization effect that was evident at about 2.5 to 3 volts, and the resistance of the film had increased slightly, from 5.5 x $10^9\Omega$ at -20°C to 9.1 x $10^{9}\Omega$ also at -20°C. However, the measurements were found to be much less noisy, and although the temperature dependence for warming was completely random, the data for the cooling cycle seemed to be good enough to fit them to the expected exponential relation

$$I = I_{\omega} e^{-E_g/2k_BT}$$
 [31]

The film was preserved overnight under vacuum, and all the measurements were repeated the following day. The

resistance had increased further to $1.3 \times 10^{11}\Omega$ at -20° C, and the V <u>vs</u>. I curves still showed polarization effects at 3 volts. The temperature dependence of the resistance for both warming and cooling was relatively stable in this measurement. However, a better fit was found for the data from the cooling cycle. The temperature dependence was measured at + 0.50 volts. The dimensions of the film were 3.9 x 1.4 cm. The results from the fitting program for the longitudinal measurement, the second transverse measurement, and the third transverse measurement that was made on the second day, are shown in Table 10.

It would be a mistake to place too much weight on these data. First, it is clear that a better method of temperature regulation must be used, since the present method produces temperatures that are not stable enough to allow the measurement of the vel small currents that are found in typical alkalide films. This is undoubtedly the reason for the random data collected during the warming cycle for the transverse conductivity measurement. Second, the polarization effect seen in the transverse conductivity case means that the quantitative treatment of these data may not be justified. In fact, the results are not readily explained. For example, the second measurement of the transverse conductivity has a much smaller band gap than the third measurement that was made on the second day. This would lead to the assumption that the

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Experiment	I _∞ ± std dev (amps)	E _g ± std dev (eV)	ρ _∞ (Ω-cm)
Longitudinal up or down in temp.	2.77 x 10 ⁻⁹ ± 0.06 x 10 ⁻⁹	0.05 ± 0.0008	6.0x10 ⁴
Transverse #2 cooling cycle	1.0 x 10 ⁻⁶ ± 0.4 x 10 ⁻⁶	0.39 ± 0.02	1.6 x 10 ¹
Transverse #3 cooling cycle	12.9 ± 0.08	1.06 ± 0.03	6.2 x 10 ³

Table 10. Conductivity Parameters for Thin Films of Na⁺C222 Na⁻. Results from KINFIT IV.

material measured the first day was more highly doped with electrons and that with time the electron traps annealed to produce the less doped film on day 2. However, the trend of the extrapolated values of ρ_{ϖ} do not bear this out. The more highly doped film would be expected to have a smaller value for ρ_{m} than the less highly doped film, judging by typical curves of resistivity vs. 1/T for doped semiconductors (see Figure 9) and assuming that the trap depths for both highly doped and lightly doped films are the same. This is exactly opposite to the observed behavior. It is possible to speculate that the films with the smaller band gap and larger value of ρ_{ϖ} are more highly doped with electrons that are in shallower traps on the average than the lightly doped films with the larger band gaps and smaller value of ρ_{∞} . That is, the slope of the ρ vs. 1/T curves may be different for the different concentrations of trapped electrons so that the extrapolated values of ρ_{ϖ} may be different than expected. Finally, it should be noted that the parameters E_{g} and I_{∞} (and thus $\rho_{\infty})$ were found by a fit to data that assumed that the resistance at each temperature point measured was in fact equal to the ratio of the applied voltage to the measured current. However, because of the measured polarization of the sample, these resistances may actually be substantially different. Future measurements, when polarization is

present, should involve the measurement of a complete Ohm's Law plot at each temperature point to give a slope that would correspond to a single point of the data from which E_g and ρ_{∞} would be found. This would, of course, require good control of the temperature in order to allow enough time for the Ohm's Law behavior to be measured.

The polarization that was observed in the transverse conductivity measurement is probably due to several factors. First, thin films in general often show non-Ohmic behavior. This is due to the fact that they are microcrystalline in nature, and the boundaries between the individual grains can have a large effect on the electrical properties of the materials. Secondly, polarization effects have recently been observed in our laboratories in single crystals of Na⁺C222·Na⁻. In this case, there is good evidence that the conductivity of the single crystal is due to both ionic and electronic carriers (41). In this case, the polarization in the presence of the applied voltage is probably due to the formation of two depletion layers, one consisting of a layer of sodium electride that has been postulated to form at one electrode, and the other of sodium metal that forms at the other electrode. The present evidence suggests that Na⁺ cations are the carriers rather than Na⁻ anions (41). It is not yet known whether a similar effect exists in thin films of Na⁺C222[·]Na⁻. However, it is possible to speculate that

-156-

there is some ionic conductivity present in films. For example, the transverse film #2 with a resistance at -20° C of 5.5 x $10^{9}\Omega$ may have had both ionic and electronic carriers.

Film #3, measured the following day, had a resistance of 1.3 x $10^{11}\Omega$ at -20°C. This increase may have been due to the total or partial loss of the electronic conductivity, so that only the ionic carriers contributed to the conductivity. Alternatively, the film may have partially decomposed, although this was thought to be less likely since the film was protected from the vacuum-space atmosphere by the sodium electrodes that sandwiched it.

The longitudinal measurement of a film of Na⁺C222·Na⁻ showed Ohmic behavior and, thus, the data might be expected to be more reliable. However, the data give an extremely small value for the band gap, that is, 0.05 eV as compared to the value for powdered samples of Na⁺C222·Na⁻ of 2.5 eV. The value for ρ_{∞} in this case is within the expected range for an extrinsic semiconductor. Nevertheless, the band gap is surprisingly small. However, it may be the case that the film contained a very high concentration of trapped electrons. In fact, the band gaps indicate that there was a substantial amount of electron doping in all the films. It may be generally true that alkalide film are always highly doped with electrons. Even crystalline alkalides grown from solution have substantial amounts of trapped electrons. Pressed powder d.c. conductivity measurements of alkalides very often exhibit extrinsic behavior. This implies that the measurements of thin film conductivities are best suited for electrides rather than alkalides. This may be especially true of the longitudinal measurements, for which the currents are expected to be low when measuring alkalides. This configuration may only be reliable when it is used to measure electride films which have larger conductivities.

In summary, it should be re-emphasized that the discussion of the electrical characteristics of thin films has been based entirely on two experiments that were done only with the intention to test the method itself. The results are therefore very preliminary and may not necessarily reflect the results that would be obtained from a comprehensive study.

-158-

CHAPTER V.

CRYPTATE ELECTRIDES

This chapter will present the results found in this work on crystals of the electrides $K^+C222 \cdot e^-$ and $Rb^+C222 \cdot e^-$, together with some recent measurements on the newly synthesized crystalline system of $Li^+C211 \cdot e^-$. Since all three of these electrides had previously been at least partially investigated in the form of solvent evaporated films or powders, this chapter will first present a summary of the earlier work before describing the synthesis and characterization of the crystalline electrides.

V.A. Introduction

The electrides $K^+C222 \cdot e^-$ and $Rb^+C222 \cdot e^-$ were studied primarily by M. G. DaGue (42), although some optical spectra of these systems were also measured by J. S. Landers (32). In fact, the $Rb^+C222 \cdot e^-$ system was only isolated as films evaporated from liquid ammonia solutions that contained a one-to-one mole ratio of the metal and cryptand. Potassium cryptand electride samples were isolated both as films for the measurement of optical spectra, and also as blue powders. These powders were

-159-

found to be extremely temperature sensitive, and it was difficult to prepare samples that were large enough to make certain types of measurements. This was particularly true since in order to produce larger amounts of powder, it was necessary to increase the amount of solvent used and to increase the time for evaporation. This increased the chance of solution decomposition. If the solutions did not decompose, the blue powders that were isolated often contained small amounts of white decomposition products (42). Nevertheless, some intriguing results came from these difficult experiments.

First, the optical spectra of the two electrides, but especially the potassium electride, were somewhat different from the usual trapped electron peak. DaGue observed a time dependence in a film formed from an ammonia solution that contained a nominal mole ratio of metal to cryptand of 1.05, in which the freshly formed film showed both a K⁻ peak at 11,000 cm⁻¹ and an e⁻ peak at 5600 cm⁻¹. However, with time the K⁻ peak reduced to a shoulder and finally disappeared in the annealed film. The final spectrum had an electron absorption peak that was highly absorbing into the infrared. This shape was reminiscent of the plasma-edge absorption of concentrated metal ammonia solutions. This indicated that the nature of the electrons in this material might be that of itinerant rather than localized electrons. The $Rb^+C222 \cdot e^-$ spectra showed a slightly more localized e⁻ peak at 6740 cm⁻¹, in addition to a small Rb^- shoulder at 10200 cm⁻¹.

An attempt was made to measure the static magnetic susceptibility of $K^+C222 \cdot e^-$, but the magnitude of the signal was below the detection limit of the instrument. However, this gave an upper limit to the susceptibility and allowed some speculations to be made on the phenomenon that could have produced such a small paramagnetic susceptibility. It was thought that if the decomposition of the sample was not the cause, then it was likely that the susceptibility was due to the weak Pauli paramagnetism of conduction electrons. The other possibility was that the susceptibility was actually diamagnetic due to extensive spin-pairing of the electrons. However, microwave conductivity measurements were done on this compound and it was found to be highly conducting, which was another indication that the electride might be nearly metallic in nature.

Finally, some ESR experiments were done on $K^+C222 \cdot e^-$. For powdered samples that had nominal mole ratios of 0.84, the spectrum gave a single narrow line at a g value of 2.0023. However, samples that had excess potassium had usually three lines below 77 K that reversibly merged to a single line at higher temperatures (42). There was some difficulty experienced in measuring the ESR of these

-161-

samples, since it was impossible to tune the cavity except at very low powers with very small samples. This is typical of the behavior of metallic samples that absorb a great deal of microwave power. The ratio of the low field to the high field lobe amplitudes was found to be asymmetric, which is also typical of the ESR of conduction electrons (42).

V.B. Synthesis and Properties of Crystalline K⁺C222·e⁻ and Rb⁺C222·e⁻

1. Synthesis

The possibility that the $K^+C222 \cdot e^-$ system might be nearly metallic, and the elusive nature of the $Rb^+C222 \cdot e^$ system, pointed to the need to grow crystals of these electrides for further investigation. In spite of the new crystallization techniques that had been developed in our laboratories, it was found to be extremely difficult to crystallize the potassium electride system, and numerous failures occurred in the process. The first successful synthesis of a crystalline material was from a solution of methylamine and the solvent of crystallization, diethylether. Lithium metal was also used since it had been previously discovered that lithium tended to stabilize electride solutions, as described in Chapter II. However, it was later found to be better to use the dimethylether and trimethylamine solvent system also described in Chapter II. The crystals of $K^+C222 \cdot e^-$ were extremely black with shiny, reflective crystal faces.

The first successful synthesis of $Rb^+C222 \cdot e^-$ was slightly easier to achieve, probably because of the experience gained from the synthesis of $K^+C222 \cdot e^-$. $Rb^+C222 \cdot e^$ was also harvested from dimethylether, but was crystallized with diethylether since the crystals were appreciably soluble in trimethylamine. However, this electride was also slightly soluble in diethylether, and was therefore often difficult to harvest. The crystals were also very black, but had almost reddish reflectances. Although both compounds have been successfully crystallized they remain as some of the most difficult systems to handle, largely because of their temperature sensitivity. The potassium electride is especially reactive and can decompose at temperatures as low as $-45^{\circ}C$.

2. Optical Spectra

Optical absorption measurements were made on films formed by solvent evaporation of $K^+C222 \cdot e^-$ or $Rb^+C222 \cdot e^$ in dimethylether. The spectra obtained for $K^+C222 \cdot e^$ were time and temperature independent. The spectral shape shown in Figure 24 was essentially identical to the earlier results, in which a plasma-edge type of

-163-





absorption that suggests the presence of conduction electrons is seen. The spectra for $Rb^+C222 \cdot e^-$, shown in Figure 25, were also time and temperature independent. The absorption band was very broad and the absorption dropped significantly at lower energies. The peak maximum was at 6700 cm⁻¹. The spectral shape is reminiscent of the so-called "wet" films from the earlier work (42), which had been left damp with NH₃ by not freezing the bulk solution in liquid nitrogen. However, the film was dry in the present work and yet shows a broad band which could be a combination of a localized electron peak and a plasma-edge absorption.

3. D.C. Conductivity

The standard method of measuring pressed powder d.c. conductivities was unsuccessful for both the rubidium and potassium electrides. Both electrides appear to be highly conductive. Rb⁺C222·e⁻ was found to have currents that were too high to measure with the picoammeter even at the lowest voltage setting. An attempt was made to measure the Ohm's Law behavior with a Fluke Model 8020 B Multimeter and the system was found to be nearly Ohmic, with a very slight curvature of the line. However, the attempt to use the multimeter to measure the temperature dependence of the currents was unsuccessful. The data did not obey the expected exponential law. The resistance of


Figure 25. Normalized absorbance \underline{vs} . wavenumber from a solution of Rb⁺C222·e⁻ crystals in dimethyl-ether.

the packed powder sample was also measured directly, using the multimeter, and a plot of ln R vs. 1/T for these data was completely different from the previous results. It was obvious that the multimeter was insufficiently accurate to make these readings. It is also probable that a two-probe d.c. measurement of such a conductive powder is unsatisfactory. This failure of the experimental technique was even more evident in the measurements of the conductivity of $K^+C222 \cdot e^-$. In this case, the current readings were on the scale of the picoammeter, but it was impossible to make any measurements. The currents showed no dependence on the applied voltages, and when the scale settings of the picoammeter were changed the polarity of the current changed also. In one case, the sample was finally left to decompose overnight. The following day the completely decomposed sample was measured. The sample obeyed Ohm's Law, and also showed a decreasing conductivity with decreasing temperature. This has been seen previously for decomposed samples, and was reassuring since the measuring circuit could not then be blamed for the unusual behavior of the good sample. Instead, the method of measurement was simply not suitable for the investigation of the electrical properties of this material. It is interesting to note that recent observations have been made of a chargeable battery behavior of single crvstals of Na⁺C222·Na⁻. That is, when single crystals

of the sodide have been charged, they have been found to produce a voltage of 2 volts for several hours, with a current on the order of 10^{-9} amps (41). It may be possible that a similar effect can exist in the electride system.

Better results could be obtained in several ways. First, if a four probe technique were used, the effect of contact resistance would be eliminated. The resistance of the contacts can become significant when the sample being measured is quite conductive. Second, the use of high frequency a.c. measurements of packed powders would help to eliminate the resistances that exist at the contacts (or grain boundaries) between the individual crystallites, which are also more significant in conductive materials. Finally, the use of single crystals would probably be the most suitable method of measuring the electrical properties of electrides. The four-probe technique should be used with either a.c. or d.c. voltages. The one advantage of a.c. measurements would be that the production of decomposition products at the electrode surfaces, which can occur in these reactive systems, would be minimized.

4. Magnetic Susceptibilities

The static magnetic susceptibilities of numerous samples from many different preparations of both $K^+C222 \cdot e^-$

-168-

and Rb⁺C222·e⁻ were measured using the S.H.E. SQUID Susceptometer described in Chapter II. The results were pleasingly reproducible, although in some cases the absolute values of the susceptibilities varied slightly. This variation probably occurred because the samples had small but varying amounts of decomposition products mixed with the undecomposed material. It was virtually impossible to completely avoid some decomposition when these very temperature sensitive compounds were loaded into the SQUID. All the measurements for these electrides were taken for both increasing and decreasing temperatures.

The susceptibility for both the potassium and the rubidium electrides showed a very weak paramagnetism with a Curie tail at low temperatures. Particularly in the case of $K^+C222 \cdot e^-$, the susceptibility at temperatures above the Curie tail (that is, above 20 K), was nearly constant (see Figure 26). In fact, in some cases the susceptibility of $K^+C222 \cdot e^-$ seemed to show a slight increase at the highest temperatures measured (see Figure 27). The susceptibility versus temperature curves of the rubidium electride more closely followed the Curie-Weiss behavior since the susceptibility data show a decrease with temperature over the temperature range observed (Figure 28), and a plot of the reciprocal susceptibility <u>vs</u>. temperature shows a fairly good linear relationship (see Figure 29).

-169-









Reciprocal molar susceptibility <u>vs</u>. temperature of Rb⁺C222.e⁻ crystals in a Delrin bucket. Sample mass = 0.0355 g. Figure 29.

The near temperature independence of the susceptibility of $K^+C222 \cdot e^-$ and the plasma-edge type of optical absorbance raised the interesting possibility that the magnetic susceptibility might be a combination of a small Curie-Weiss paramagnetism and a conduction electron paramagnetism. The paramagnetism of conduction electrons is in general very weak and is temperature independent. The theory that is most commonly used to describe it is due to Pauli (43). The general expression for this Pauli susceptibility is (9)

$$\chi_{\rm p} = \mu_{\rm B}^2 g(E_{\rm F})$$
 [32]

where μ_B = the Bohr magneton = efi/2mc, and $g(E_F)$ is the density of levels at the Fermi energy of the metal. By using the appropriate expression for the free electron approximation to $g(E_F)$ the susceptibility can be written as

$$x_{p} = \frac{4\mu_{B}^{2}m}{h^{2}} \left(\frac{3\pi^{2}N}{V}\right)^{1/3}$$
[33]

(where N/V is the conduction electron density) which can be rewritten in a Curie law form

$$\chi_{\rm p} = \frac{3\mu_{\rm B}^2(N/V)}{2k_{\rm B} T_{\rm F}}$$
[34]

by the appropriate definition of the constant Fermi temperature, $T_{\rm F}$. In these expressions h is Planck's constant and $\boldsymbol{k}_{\mathsf{R}}$ is Boltzmann's constant. This spin paramagnetism of conduction electrons is due to the interaction of the electron spins with the applied field. The simplest model of this effect is as follows (see Reference 25). The conduction electrons can be pictured as two groups of electrons with opposite spins. In the absence of an applied magnetic field there is an equal number of each spin set. When the magnetic field is applied a nonequilibrium situation is set up in which there is an energy difference, ΔE , between the two spin sets which are now parallel and antiparallel to the field. Equilibrium is reached when the two subsystems obtain the same Fermi level, that is, when both sets are filled to the same energy level. This occurs when some electrons change their spin directions. However, because the energy difference, ΔE , is very small compared to the Fermi energy, only the very few electrons near the Fermi level change their spins. This accounts for the small magnetism associated with metallic samples.

However, conduction electrons also have a diamagnetism due to an orbital motion of the electrons that is induced by the application of the applied field (9). This Landau diamagnetism is (in the free electron approximation) equal to 1/3 of the spin paramagnetism. Thus, the total bulk susceptibility that is measured is actually a combination of the Pauli paramagnetism and the Landau diamagnetism. The measurement of Pauli susceptibilities alone must be made indirectly. For example, the Pauli susceptibilities of the alkali metals have been measured by the use of NMR to measure the Knight shifts of the metals (44). An expression has been developed for the sum of the Landau diamagnetism and Pauli paramagnetism in which the mass of the free electron has been replaced by the effective mass, m*, in the diamagnetic expression. The equation is taken from Reference 45.

$$\chi = \frac{4\mu_B^2 m^*}{n^2} (3\pi^2 \frac{N}{V})^{1/3} (1 - \frac{m^2}{3m^{*2}})$$
[35]

Essentially, the effective mass, which can be either larger or smaller than the free electron mass, reflects the way in which electrons in a crystal behave in the presence of an applied field (or force). That is, the energy of the electrons in a real system can be found from the relation between the acceleration and the applied force if the electrons are assumed to have an effective mass, m* (47). The effective mass is proportional to the inverse of the second derivative of the energy with respect to the wavevector, k, and as such, is inversely related to the curvature of the energy bands in k space. Thus, when the band is highly curved the effective mass will be small. When there is very slight curvature the effective mass will be large. At the top of the bands the effective mass can even be negative, since the curvature is downward (47).

Because the materials $K^+C222 \cdot e^-$ and $Rb^+C222 \cdot e^-$ did exhibit slight Curie tails at low temperatures, the data were fit to a Curie-Weiss law expression, given below, that also included a term, B, that is typically intended to account for any temperature independent susceptibilities which can be either diamagnetic or paramagnetic. For example, in the case of electrides, the B term is often used to account for any diamagnetic decomposition products that might be present.

The results that are presented in Table 11 are from the data sets that had the highest values of the susceptibilities (and therefore had the least decomposition) and also that gave the best fits. The table reports values for the fraction of electrons that contributed to the Curie-Weiss paramagnetism relative to one mole of these electrons. This is done by comparing the value found for C to the value of the Curie constant for one mole of free electrons. This value is 0.376. It can be seen that the Curie-Weiss contribution is very small in both cases; the rubidium electride is larger and is about 4% of all the spins in the sample, whereas the potassium electride has only 1% of Curie spins out of

Parameter	к ⁺ С222 е ⁻	Rb ⁺ C222 e ⁻
C ± std dev	0.0036 ± 0.0004	0.013 ± .008
θ ± std dev	+1.5 ± 0.5	-3 ± 4
B ± std dev	+5.0 x 10^{-7} ± .2 x 10^{-7}	+0.8 x 10^{-6} ±3 x 10^{-6}
Ave χ high temp	+6.3 x 10 ⁻⁷ ± 1 x 10 ⁻⁷	+1.1 x 10 ⁻⁶ ± .3 x 10 ⁻⁶
% of 1 mole non- interacting electrons	0.96	3.5

Table 11. Parameters from a fit to Curie-Weiss Paramagnetism.

all the spins in the sample. This means that the majority of the electron spins in both electrides are contributing in some other way. At this point it is interesting to note the results for the B parameter. In both cases the final fitted values were positive, indicating that the socalled correction term to the Curie-Weiss law was paramagnetic rather than diamagnetic. In fact, the values of the B term were found to be nearly equal to the average value of the high temperature susceptibilities taken above the Curie tails. These values are also shown in the table.

The intriguing possibility that the potassium and rubidium electrides might contain electrons that behaved in a nearly free-electron manner naturally suggested that it might be instructive to use the Pauli susceptibility expression in order to estimate the conduction electron density in these materials. It was realized that a certain amount of error would be unavoidable in using the measured bulk susceptibilities of the electrides in this equation, because the total susceptibility would actually be a combination of Pauli paramagnetism, Landau diamagnetism and a Curie paramagnetism. In addition, the Pauli equation suffers from intrinsic faults as well. That is, since it relies on the completely free electron approximation the effects of long and short-range electronelectron interactions, which do exist, are ignored. As a result, the Pauli expression when used to calculate the susceptibility for well known systems such as the alkali metals gives values that are lower than the experimental numbers. The results for K and Rb metal are shown in Table 12. This table gives the experimental susceptibilities of the metals, and compares them to the values obtained from the calculated Pauli susceptibility. In addition, the table presents the calculated values from another theoretical expression due to Pines (46). In the Pines expression the electron-electron correlations and effective mass are taken into account, and it can be seen that the susceptibilities are improved although they are still lower than the experimental values measured by Kraeck (44). Conversely, when the Pauli susceptibility equation is used with the experimental values of the susceptibility for K and Rb, it results in values of the conduction electron density that are too large. This is shown in Table 13. Table 13 also gives the conduction electron densities for the two electrides. The results give electron densities of 1.2 x 10^{22} for K⁺C222·e⁻ and 4.8 x 10^{22} for Rb⁺C222^{·e⁻}. These results are thought to be rather high, since they are almost the same as the electron densities for the metals themselves.

The nature of the crystalline electrides, in which the positive ionic lattice consists of large complexed cations, suggests that the conduction electron density of these

-180-

Metal	* X _{Kraeck}	** X _{Pines}	*** X _{Pauli}
K	.84 x 10 ⁻⁶	.61 x 10 ⁻⁶	.53 x 10 ⁻⁶
Rb	.80 x 10 ⁻⁶	.53 x 10 ⁻⁶	.50 x 10 ⁻⁶

Table 12. Experimental and Calculated Values for the Pauli Susceptibilities of K and Rb Metals. Units are cgs Volume Units.

* From Reference 44, experimental measurements from Knight shift data.

** From Reference 46, Pines susceptibility.

*** Calculated from Pauli susceptibility Eqn. 33.

Material	N/V(cm ⁻³) expt'l [*]	N/V(cm ⁻³) calc'd ^{**}	N/V(cm ⁻³) est.
К	1.4 x 10 ²²	5.5 x 10^{22}	
Rb	1.15 x 10 ²²	4.8 x 10 ²²	
К ⁺ С222 е ⁻		1.2 x 10 ²²	1.1 x 10 ²¹
Rb ⁺ C222 e ⁻		4.8 x 10 ²²	9.6 x 10 ²⁰

Table 13. Conduction Electron Densities (N/V).

* From Reference 9 crystal structure data.

** Using experimental values for $\boldsymbol{\chi}$ in Pauli expression.

*** Estimated using the volume arguments.

electrides should be reduced from the density of the metals by at least the same factor as the volume is increased. Thus, the relative volumes of $K^+C222 \cdot e^-$ and K(s) and $Rb^+C222 \cdot e^-$ and Rb(s) were compared. The atomic radii of K and Rb are 2.35 Å and 2.48 Å. These radii correspond to volumes of 54 Å³ and 64 Å³, respectively. On the other hand, a simple calculation for the electrides using their respective molecular weights, and assuming that each has a density of 1.0 g-cm⁻³ results in volumes of 700 Å³ for K⁺C222 \cdot e⁻ and 770 Å³ for Rb⁺C222 \cdot e⁻. These volumes compare very well with the volume of Na⁺C222 · Na⁻ from crystal structure data. The volume per molecule in the sodide crystals is 660 Å³/molecule (20).

It is at least likely that the volumes calculated for the electrides are maximum values, so that the conduction electron densities inferred from this represent a lower limit of the true value. The assumption that the densities are both equal to 1.0 is not unreasonable, since the cryptand alkalide Na⁺C222·Na⁻ was found from the crystal structure data to have a density of 1.064 g-cm⁻³ (20). Thus, the conduction electron densities for the potassium and rubidium electrides should be reduced by factors of 13 and 12 from the electron densities of the metals. The results, shown in Table 13, give electron densities of 1.1 x 10^{21} cm⁻³ and 9.6 x 10^{20} cm⁻³ for the two electrides. These values, as lower limits, compare well with the average value of the conduction electron densities of the alkali metal hexammines which are about 5 x 10^{21} (6). They are also comparable to the conduction electron densities of the semimetals which are as low as 3×10^{17} cm⁻³ for Bi to 2×10^{20} cm⁻³ for As (9). It is even reasonable that $K^+C222 \cdot e^-$ should have the slightly higher electron density since it seems to show a greater tendency to be metallic. It is possible to speculate on the cause of the large discrepancy between these estimated electron densities and the conduction electron densities calculated from the Pauli expression. First, it is not likely that the free electron approximations are at all accurate in the electride systems in which the electrons may have strong interactions with each other and with the ionic lattice. For example, one error could result from the use of the free electron mass. It is probable that the effective masses, m*, of the electrons in the electride systems are not equal to the free electron mass, m. The estimated values of (N/V) were used in Equations [33] and [35] to estimate the effective masses of the two electrides. It was found that the effective mass of $K^+C222 \cdot e^-$ is $m^* = \sqrt{2}m$, whereas for $Rb^+C222 \cdot e^- m^* = \sqrt{4}m$. These are rather high effective masses but they are certainly not without precedent. For example, the b.c.c. solid phase I of the expanded metal compound Li $(NH_3)_{\parallel}$ has an effective mass of m*=1.83 m,

and the lower temperature solid phase II has an effective mass of m* = 3.0 m. Both mass ratios were found from treatment of magnetic susceptibility data by the Pauli theory (4). In fact, these values are even fairly low in comparison to the effective mass ratios of the dband or transition metals, in which the ratios can be as high as $m^*/m = 43$ (for Pd), $m^*/m = 28$ (for Ni), or $m^*/m = 12$ (for α -Fe) (47). Large effective masses are expected for the d-band metals since the calculation of their band structure indicated that the d-band lies high in the conduction band and in fact includes the Fermi energy. Thus the d bands are narrow and have a higher density of levels than the free electron density of levels (9). The effective mass is proportional to the density of levels (47) so that this can account for the high values. Even larger effective masses can be expected when there is very little overlap between the electronic wavefunctions on neighboring atoms. This occurs, for example, for the 4f electrons of the rare earth metals (48).

It should be noted that even for the metals potassium and rubidium, when Equation [33] is used with the experimentally determined values for N/V and the susceptibilities, the effective masses for both metals are found to be about 1.6 m, so that the values found for the electrides are very reasonable in comparison to the values for the pure alkali metals. These large effective masses are in contrast to the effective masses of the semimetals Bi, As, and Sb, which are smaller than the free electron mass (9) although their conduction electron densities are similar to those estimated for the electrides. The semimetals, however, have a small density of levels at the Fermi energy.

V.C. Conclusions

Much of the preceding discussion on the magnetism of the cryptate electrides has been highly conjectural due to the lack of other data that would be necessary to substantiate it. These data would include direct experimental measurements of the conduction electron densities and effective masses, and measurements of the conductivities, and the Hall effect. Single crystal structural data would be extremely desirable. However, it is encouraging that the results found in this fashion are comparable to the results of similar systems, in particular the expanded metal compound Li $(NH_3)_4$. Thus, the effective masses of $K^+C222 \cdot e^-$ and $Rb^+C222 \cdot e^-$ are estimated to be about 2 m and 4 m respectively, whereas the effective mass of Li $(NH_3)_4$ is 1.83 m. In addition, the conduction electron densities of the hexammine compounds are about 5 x 10^{21} cm⁻³ which are comparable to the estimated values for the K and Rb electrides of 1.1 x 10^{21} cm⁻³ and 9.6 x 10^{20} cm⁻³. One reason for the interest in the effective mass ratios of materials is that they can give some insight into the nature of the Fermi surface of the The Fermi surface is simply the constant energy metal. surface in k space. In the free electron gas model this surface is a perfect sphere which separates the occupied from the unoccupied levels. In real systems, the surface may no longer be a perfect sphere but in some cases, such as Al metal, it may be only slightly distorted. However, in other cases, such as the transition metals, the Fermi surface may not be a distortion of the sphere at all, but may be very different (9). Glaunsinger et al.(51) made some conjectures on the nature of the Fermi surface in Li $(NH_3)_4$. Unfortunately, they assumed that the crystal structure of the lithium compound was f.c.c., although it is now known to be b.c.c. (3) so that the conclusions that they drew may be in error. However, the substance of their arguments illustrates the use of the effective masses. Essentially, since the $Li(NH_3)_4$ molecules were presumed to contribute one electron each to the conduction band, and since there is one molecule per primitive cell, then the first Brillouin zone (the primitive cell of the reciprocal lattice) is one half filled with one electron. Therefore, the volume of the Fermi sphere is equal to one half of the volume of the Brillouin zone. Thus, the Fermi sphere is completely inside the zone.

Since the reciprocal lattice cell of f.c.c. is b.c.c. it was found that the distance of closest approach to the zone faces from the center of the zone was along the <lll> direction. This implied that the real Fermi surface was probably a distorted free electron sphere that bulged in the <lll> direction. Glaunsinger <u>et al</u> were able to use reciprocal mass arguments to estimate the amount of the distortion, in order to give a picture of the band structure of this material.

Obviously, similar considerations cannot be discussed for the electrides without a knowledge of their crystal structures. However, this certainly adds interest to the attempt to obtain structural data as well as measurements of the electron masses.

Finally, as has not been mentioned previously, the slight increase of susceptibility with increasing temperature at temperatures above 60 K that was observed in $K^+C222 \cdot e^-$, is also similar to the behavior of $Li(NH_3)_4$. In the liquid state, that is at temperatures above 90 K, the susceptibility of the lithium compound was found to obey the same equation as Equation [35] of this work (51). However, Glaunsinger <u>et al</u> also observed a small positive temperatures. They were able to attribute this variation of the susceptibility to the change in the bandwidth as the volume expanded with increasing temperature (51).

It may be the case that a similar situation exists in the electride.

Finally, the measurement of the electron spin resonance of $K^+C222 \cdot e^-$ and $Rb^+C222 \cdot e^-$ would be desirable. Until now, difficulties very similar to those encountered in the study of the powdered samples (42) have been encountered. That is, it has been found impossible to tune the cavity even at the lowest microwave powers unless the samples were partially decomposed. In this latter case, the line shape results would be unreliable. One attempt was made to measure the ESR on a sample of $K^{\dagger}C222 \cdot e^{-}$ that appeared to be no larger than a single grain (although there was no direct evidence that it was actually a single crystal). Even in this case, it was not possible to tune the cavity. In the future it would probably be necessary to measure very small single crystals at very low microwave powers. Apparently, similar difficulties have been encountered in the ESR studies of doped polyacetylene polymers (52). These polymers have two ESR lines, one of which is attributed to the conduction electrons, and exhibits a Pauli-like susceptibility. However, it was found necessary to cut the samples into extremely small needles in order to perform these measure-It has also been found possible to measure the ments. ESR of highly microwave conducting materials, such as the polyacetylene polymers, using the method of Schumacher

-189-

and Slichter (53). This method also allows the Pauli paramagnetism to be measured. The technique uses very small fields and measures the electron spin resonance and the nuclear magnetic resonance of the same sample using the same instrument. The ESR is measured first at a typical static central field of about 5 gauss. The static magnetic field is then changed to about 10,000 gauss and the NMR is measured. The ratio of the two areas is equal to the ratio of the conduction electron susceptibility to the nuclear static susceptibility. The nuclear static susceptibility can be calculated, so that the ratio of the areas can be used to measure the Pauli paramagnetism of the sample (53).

V.D. Li C211 Electride

The electride Li⁺C2ll·e⁻ has been extensively studied by J. S. Landers (32,49). Landers studied various nominal mole ratios of dark blue powders of this material which were prepared by the evaporation of ammonia from solutions of the starting materials. No crystalline materials were formed, but the optical spectra, ESR spectra and static magnetic susceptibilities of the powders were measured. The samples for the various measurements were all prepared in a single quartz apparatus that contained many sidearms so that the samples would not have to be transferred. The optical transmission spectra showed a dependence on the mole ratio of the material. For mole ratios of metal to cryptand up to 1.0 the broad band showed a slight shoulder at about 12,000 cm⁻¹ and two peaks very close together at about 5,000 cm⁻¹. The double peak suggested that the electrons were trapped in sites with different energies. For mole ratios from 1.0 to 2.0 the spectra gradually took on the appearance of the plasma-edge absorption.

The static magnetic susceptibilities were measured by using the Faraday method. The total susceptibility was corrected for the diamagnetism present by subtracting the values for the decomposed sample and bucket in the same way that has been described in this work. The results showed that there was again a dependence on the mole ratio. A sample with a mole ratio of 1.57 had Curie-Weiss behavior at high temperatures, a maximum susceptibility at about 20 K, and a susceptibility that decreased towards zero at lower temperatures. In contrast to this, a sample with a mole ratio of 1.0 had a much smaller susceptibility and had a broader peak. The temperature for the maximum susceptibility was about 70 K. The spin susceptibilities from the ESR measurements also approached zero at low temperatures. Thus, it was concluded that although there was a substantial amount of spin-pairing occurring at lower temperatures the system could not be regarded as a true antiferromagnet, in which the

susceptibility would not drop to zero, but would drop to a value equal to two thirds of the maximum. However, the data for the sample of mole ratio 1.57 were in fair agreement with an expression for single pair interactions developed by Wojciechowski (50). The expression used to fit the data also included a variable parameter, f, that was intended to account for partial decomposition of the system, or inhomogeneities in the sample. In the equation for the susceptibility, given below, the term J is the exchange energy for the interacting pairs, and was found to be negative.

$$\chi = \frac{N_{av}g^2 \mu_B^2 f}{k_B T [3 + exp(-J/k_B T)]}$$
[36]

However, even this equation did not fit the data until two different exchange energies were used, with two different values for f (32).

Because of the intriguing nature of this electride, and the inconsistencies and unanswered questions that remained, possibly as a result of the inhomogeneities of the powder samples, a successful attempt was made in this work to grow crystalline samples of Li⁺C2ll·e⁻. The high cost of the liquid cryptand prohibited the use of large amounts of material, so that the resultant samples were very small. This meant that there was not enough material from any of the three syntheses to perform a stoichiometric analysis.

The method used to synthesize these crystals differed slightly from the usual procedure. The preparation of the apparatus is described in Chapter II. The materials were dissolved in methylamine and the solution was kept at -40° C for four hours. This was done to ensure that the Li⁺ ion had been completely encryptated, since Li metal dissolves in methylamine in the absence of any complexing agent. This procedure was based on the work of Landers (32), in which he found that the lithium ions were completely complexed only after at least two hours at -40° C. The methylamine was almost completely evaporated away from the solution, leaving only a very thick, dark blue liquid material. A mixture of dimethylether and diethylether was added to the apparatus. The thick blue liquid dissolved, and a few small crystals were often seen at this point. The temperature was then reduced to -78° C and the solution was left for several hours. When the crystals were harvested they were extremely black and shiny. In spite of their small size, it was possible to see crystal facets. Three different syntheses were done. Two were made with starting mole ratios of 1.0, but the last synthesis had twice as much Li, with a mole ratio of 2.0. These crystals looked the same as the crystals with a mole ratio of 1.0 but there was no obvious

-193-

precipitated Li metal present. However, without a stoichiometric analysis it is not known whether the crystals actually contained a 2 to 1 ratio of metal to cryptand, or whether the excess lithium was present as finely divided particles mixed with crystals containing a 1 to 1 mole ratio.

As mentioned previously, the amount of crystals obtained from each synthesis was very small. The only measurements that were made, therefore, were of the static magnetic susceptibilities. The results are qualitatively similar to the results obtained for the powders, and are shown in Figures 30 and 31. The significant difference is that the material which showed the largest susceptibility and a maximum at 20 K (figure 30), had a nominal mole ratio of 1.0, whereas the equivalent material in the powders had a mole ratio of 1.57. Again, the material with a nominal mole ratio of 2.0 showed a very small susceptibility (Figure 31) and an indistinct peak at 60 K, whereas the equivalent powder had a mole ratio of 1.0. Finally, it should be noted that both of the crystalline materials show a distinct hysteresis between the data taken from low to high temperatures, and that taken going back down in temperature. In fact, not only did the susceptibility of sample 1 (shown in Figure 30) decrease, but the temperature of maximum susceptibility shifted to 10 K from 20 K.







It is possible that the hysteresis was due to partial decomposition of the sample especially since in the first case the sample was heated to -30° C and may have cycled to a higher temperature during the thermal equilibration of the susceptometer. The striking difference between the susceptibilities of the samples with different mole ratios is less well understood. It should be mentioned that the same behavior for the one-to-one material was observed twice, for samples from two different syntheses, and that the behavior of the two-to-one material was also observed for two different samples, which, however, were from the same synthesis. There is therefore a possibility that samples from this synthesis may have undergone decomposition. The other possibility is that the two-to-one material may indeed have Li⁺ ions incorporated in interstitial holes in the lattice. Tt would then have extra electrons donated to the system. It is possible to speculate that the very small susceptibility (note the scale change between Figures 30 and 31) may be due to conduction electron paramagnetism. Certainly, the temperature dependence is not very marked. However, the powder samples showed this behavior for the one-to-one ratio, so in that case it is not possible to use the same argument, except to point out that in both studies, two sorts of samples were isolated, of which one had a much smaller susceptibility. However, since the

materials used in the earlier studies were not crystallized, their mole ratios may not correspond well to the mole ratios of the crystalline materials.

The molar susceptibilities for sample 1 (mole ratio = 1.0) were fitted to the Wojciechowski equation using one value for J. The data for increasing and decreasing temperatures were fitted separately because of the hysteresis that was observed. An attempt was also made to fit the data for sample 2 (mole ratio = 2), but this was unsuccessful. The fitted parameters for sample 1, together with the results for the equivalent powder sample from Reference 49 are shown in Table 14. The substantially lower value for the fraction of electrons contributing to the spin-pairing may indicate that the crystalline sample had already partially decomposed before the highest temperatures were reached. Even the value of the maximum molar susceptibility is much smaller for the crystalline sample, being about 8×10^{-4} as compared to the value of 5.4 x 10^{-3} for the powdered sample B. Alternatively, the crystalline materials may be quite different in nature from the solvent evaporated powders, which may be very inhomogeneous. That is, electrons may be trapped in energy states in the powders that are not present in the crystalline electrides.

Now that it is possible to obtain crystalline Li C2ll.e⁻ it is obviously necessary to greatly extend

-198-

Sample	Nominal Mole Ratio Li/C2ll	\pm^{f} std dev	J ± std dev (joule/mol)
Powdered Sample B *	1.57	0.646 ±.006	-364 ±5
Crystalline Sample l Up in Temp	1.0	0.088 ±.005	-283 ±18
Crystalline Sample l Down in Temp	1.0	0.055 ±.005	-193 ±18

Table 14.	Values of	Fitted	Parameters	for	Wojciechowski's
	Equation.				

* From Reference 49, Table 1.

the characterization of this electride. The influence of the mole ratio of the metal to cryptand on the properties of this material must be thoroughly investigated. The static magnetic susceptibilities should be re-measured, and compared to the results for ESR. The conductivity of this electride, in common with all electrides, may be important to measure. Finally, the optical transmission spectra should be examined. In fact, this material is a good candidate for study in the vacuum evaporator in the thin film form, especially since good success has already been found in evaporating lithium metal using a stainless steel evaporation source. This technique would be ideally suited to investigate the properties of the material for a wide range of mole ratios.

CHAPTER VI

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

A. Summary

1. Crystalline Electrides

Crystals of two electrides, $K^+C222 \cdot e^-$ and $Rb^+C222 \cdot e^$ were synthesized for the first time. In previous studies, these electrides were isolated only as films or powders. The optical transmission spectra of films of these crystals formed from solutions of dimethylether agreed with the earlier results. The potassium electride showed a plasmaedge type of absorption similar to that observed for solvated conduction electrons in concentrated metal ammonia solutions. The rubidium electride showed a slightly more localized trapped electron band, that nevertheless was very broad. This suggested that the band resulted from a combination of localized absorption and a plasma-edge type of absorption.

A thorough investigation of the static magnetic susceptibility of both electride systems was performed. In both cases, the total paramagnetic electronic susceptibilities were very small. Curie tails were observed

-201-
at temperatures below 20 K. However, for K⁺C222'e⁻ the electronic contribution to the susceptibility was nearly independent of temperature, and this behavior suggested that the majority of the electrons in this electride exhibited the Pauli paramagnetism of conduction electrons. The temperature dependence of the electronic contribution to the susceptibility of $Rb^+C222 \cdot e^-$ appeared to have a Curie-Weiss paramagnetism. However, when the data for both the potassium and rubidium electrides were fitted to a Curie-Weiss expression that was modified by a B term in order to account for any temperature independent magnetism that might be present, the results for both systems were quite similar. In both cases the fitted value for B was positive. For most electrides, the B terms are negative and are usually used to account for small amounts of decomposition products. In addition, the values for the Curie constants showed that the fraction of electrons in the samples that contributed to the Curie behavior was very small: the values were 1% for $K^+C222 \cdot e^-$ and 4%for $Rb^+C222 \cdot e^-$. This indicated that the large positive values for the B terms were significant. In fact, these values were approximately equal to the average values of the susceptibilities at higher temperatures. Thus, in both electrides, the majority of electrons may well be in conduction bands and may contribute to the weak paramagnetism typical of metallic systems. The nearly

-202-

metallic behavior of $K^+C222 \cdot e^-$ has been suspected previously. For example, the microwave conductivity had been found to be very large (42). The abortive attempts in this work to measure the d.c. conductivities of both $K^+C22 \cdot e^$ and $Rb^+C222 \cdot e^-$ also suggested that both electrides are very conductive. Finally, the plasma-edge type of optical absorption spectra also help to support this concept of the nature of these systems.

Crystals of the electride, Li⁺C2ll·e⁻ were synthesized for the first time. This electride had also been studied before rather extensively, but only in the form of microcrystalline powders prepared by solvent evaporation. A qualitative agreement between the static magnetic susceptibilities for the crystals and the powder samples was found. In both cases, the system appears to undergo a spin-pairing process below 20 K. Finally, both studies indicated that this system may crystallize in two different stoichiometries, that is, one with two moles of lithium for every one mole of cryptand, and the other with a oneto-one mole ratio.

2. Thin Film Deposition

The major emphasis of this work was the design and construction of an apparatus for the physical vapor deposition of thin solid films of alkalides and electrides. This apparatus was installed in an Ultek high vacuum

-203-

evaporator. The experimental design included a homebuilt optical spectrometer that was designed to measure the optical transmission spectra of these films. In addition, a masking technique was developed to measure both the longitudinal and transverse d.c. conductivity of the films.

The completed system was used to demonstrate the ability of the method of vapor deposition to successfully grow uniform films of the alkalides and electrides. Four different systems were grown, including $Na^+C222 \cdot Na^-$, $Na^+C222 \cdot$ e^- , $K^+C222 \cdot K^-$, and $K^+C222 \cdot e^-$. The qualitative optical spectra of these films were measured, and were found to be in good agreement with the results obtained previously from films of these materials grown by flash evaporation from solution.

Finally, the data for several films of Na⁺C222·Na⁻ were used to estimate the oscillator strength and the optical constants $k(\lambda)$, of the material. Four films were chosen for this quantitative study because of their reproducible lineshapes. Two gave oscillator strengths of 2.00 and 1.76, but the other two were only 1.08 and 1.03. These latter values were only half of the expected value for the transition. The absorption coefficients were calculated from the absorbances, and were multiplied by the ratio of the expected oscillator strength of the transition (that was assumed to be equal to 2) to the

oscillator strength measured for each film. The averages of the four values for the molar decadic absorption coefficients were then used to calculate the optical constant k as a function of wavelength. The average value for the absorption coefficient at the 652 nm maximum was 7.0 \pm .5 x 10⁴ M⁻¹ cm⁻¹, which compares fairly well with the value obtained for Na⁻ in solution of 8.2 \pm .3 x 10⁴ M^{-1} cm⁻¹. Since these data gave results that were close to those expected on the basis of solution studies, it is thought that new data obtained from an improved experimental arrangement will result in even more reliable measurements. These transmission spectra and the values of the optical constant, k, should be used with reflectance spectra on the same film to obtain the optical constant, $n(\lambda)$. It would then be possible to calculate the complex dielectric constant for the film materials.

B. Suggestions for Future Work

1. Crystalline Electrides

A concerted effort to grow good single crystals of all three electride systems would be beneficial for several reasons. First, it would then be possible to obtain crystal structures by single crystal x-ray diffraction. In fact, a major goal of the research on alkalides and electrides is to obtain structures for as many of these

-205-

compounds as possible. While the electrides $K^+C222 \cdot e^$ and $Rb^+C222 \cdot e^-$ are not ideal candidates for the earliest structural determinations because of their extreme reactivity, it is hoped that with time their structures will be elucidated.

Second, if sufficiently large crystals were grown, the study of the electrical properties of the electrides would be greatly helped. Because of the difficulties encountered in the attempt to measure the d.c. conductivities of the electrides, a new effort should be made to measure the a.c. conductivities of these conductive materials, perhaps with a four probe technique. However, these measurements would be more reliable if they were performed on single crystals, in order to avoid the effects of the packing of polycrystalline samples.

The far infrared spectra of these materials might be worthwhile to measure. This would be especially true in the case of $K^+C222 \cdot e^-$ and $Li^+C211 \cdot e^-$ which both have plasma-edge type of absorptions. If the optical spectra were extended further into the infrared, it would be possible to better determine the nature of these absorptions.

Finally, it would be possible to measure the solid state Magic Angle Sample Spinning NMR spectrum of the Li C211 electride. The use of ⁷Li NMR should provide the definitive information on the nature of the cation and

-206-

anion present in the electride. If this compound can in fact crystallize with varying amounts of lithium metal in the lattice, the chemical shifts of the lithium cations might be different. In addition, the NMR technique can provide information on the percentage of atomic character of the electrons. This information can help to augment structural studies in order to determine the nature of the trapped electron in electrides.

2. Thin Film Studies

Several design improvements should be made on the vapor deposition system, and in fact, many of these modifications are already being made by J. Skowyra under the direction of Professors J. L. Dye and W. Pratt, Jr. The ion pumps and titanium sublimation pumps will be replaced by a cryopump. It is thought that this change will greatly decrease the time that is needed to bring the system from atmospheric pressure to high vacuum. This has become an increasingly serious problem, as the ion pumps and titanium pumps have aged.

A cooling system for the introduction of crown ethers to the vacuum system is also necessary. The present plan is to use thermoelectric coolers, which will themselves be cooled by a water-cooled heat sink, to keep the volatile crown ethers at a sufficiently low temperature that they do not vaporize in an uncontrolled fashion. Two additional quartz crystal oscillators have been purchased and will be installed in the vacuum system. They will be permanently mounted in the vapor streams of the metal and the complexing agent respectively. This will provide a means to continuously monitor the rate of deposition of the materials, which will then be much better controlled. In addition, the rate monitors should eventually be interfaced with a computer system. The computer could then be programmed to set the desired evaporation rates, monitor the rates, and determine whether the heater currents should be increased or decreased, in order to keep the rates at the correct value.

The present optical system is insecurely mounted on tables and laboratory jacks. This often results in difficulties with maintaining the alignment of the optical system. However, an optical table with a magnetic skin will be installed. In fact, the entire vacuum system, with the cryopump attached below, will be mounted on this table, so that the apparatus will be a single stable unit.

Finally, a support mechanism for the substrate block should be incorporated in the system. The precise alignment of the substrate over the evaporation sources is especially important in the conductivity experiments. The front of the substrate block could be supported by a track that would run along the front of the platform. It would then be possible to position the substrate

-208-

exactly in the center of the evaporation sources by using appropriate markers in the track itself.

In addition to these straightforward changes in the design of the apparatus, several new experiments should be done. When crown ethers can be used, many alkalide and electride systems can be made which have not yet been studied in thin film form. It will also be necessary to use the remaining alkali metals, Rb and Cs. Finally, quantitative measurements should be made on all of these systems, to yield the oscillator strengths of the transitions, and to determine the optical constants, $k(\lambda)$, for each material studied.

The reflectance spectroscopy of the films should also be measured. Some preliminary designs have been made for this endeavor. The purpose of the experiment would be to obtain simultaneous transmission and reflectance spectra of the same film. This would in turn provide the necessary data to determine both optical constants for the material under study. It is thought that the light beam could be moved between the film itself and a reflectance standard (both supported on the same substrate), by using a rocking mirror. The reflected light from the standard and from the film would be monitored by one detector, and the transmitted light would be monitored by a second detector. The data would then, ideally, be processed by a computer to yield the desired information.

-209-

The conductivity measurements of films should be continued. As suggested in Chapter IV, these results may provide interesting information on the nature of alkalides and electrides when these compounds are synthesized by the vapor deposition method. However, it would also be possible to determine whether photoconductivity occurs in these materials. The ease with which the simultaneous measurements of the optical spectra and the conductivities could be done, would make these measurements quite feasible.

Finally, a long term goal would be to design a way to remove suitably protected films from the vacuum system. Most importantly, this would enable the films to be studied with electron microscopy, using the Field Emission Scanning Transmission Electron Microscope located in the Physics Department at M.S.U. This would give information not only on the morphology of the films, but also on the structural, compositional, and electronic properties of these films. LIST OF REFERENCES

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