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# OPTICAL AND ELECTRICAL PROPERTIES OF VAPOR DEPOSITED THIN FILMS OF A SODIDE AND AN ELECTRIDE

by

James Erik Hendrickson

### A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Physics and Astronomy

1994

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### ABSTRACT

## OPTICAL AND ELECTRICAL PROPERTIES OF VAPOR DEPOSITED THIN FILMS OF A SODIDE AND AN ELECTRIDE

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The optical and electrical properties of vapor deposited Na+C222Na<sup>-</sup> and K+C222e<sup>-</sup> films were explored. Alkalides and electrides are ionic salts in which the cations are macrocyclic complexed alkali metal cations and the anions are alkali metal anions and trapped electrons, respectively. A vapor deposition apparatus was extensively modified. The accuracy and control of the film temperature and stoichiometry were improved and a fiber optic spectrophotometer was integrated into the deposition system. Electronic circuits were included to allow thin film conductivity measurements.

The optical and electrical properties of the best-characterized alkalide, Na+C222Na<sup>-</sup>, were studied, including a temperature study of the absorbance peak. The temperature dependence of the peak parameters demonstrated thermal broadening effects on the absorbance. The results clarified the previous band-like picture of

this sod presence produce to be du electron photoen Th electride absorba decayed Iwo-an of stable lower tr pì crì.21 electric mechar Conduci band-li domina A to char; ethers precurs radical in the A this sodide. Photobleaching with intense laser pulses showed the presence of new electronic states in absorbance, presumably produced by exciton-exciton interactions. The new absorbers appear to be due to the presence of substantial concentrations of trapped electrons. A conductivity study showed the presence of photoemission, not photoconductivity.

The optical and electrical properties of the most conducting electride, K+C222e<sup>-</sup>, were studied. The shape of the stable optical absorbance spectrum was found to be a broad plasma edge, which decayed irreversibly above -30 °C as the electride film decomposed. Two- and four-probe conductivity studies found apparent band gaps of stable films to be  $57 \pm 17$  and  $62 \pm 20$  meV, respectively, slightly lower than previous measurements on powdered samples prepared by crystallization from solution. The combination of the optical and electrical properties indicated that annealing and decomposition mechanisms may introduce defects that lead to increased conductivity prior to massive decomposition above -30 °C. Several band-like models are proposed, but apparently defects play a dominant role in the conductivity of K+C222e<sup>-</sup>.

A potpourri of other compounds was studied briefly in order to characterize new complexing agents such as aza-analogs of crown ethers and large organic globular electron acceptor (LOGEA) precursors. Surprisingly, Na<sup>-</sup> is apparently formed along with radical anions. Their optical and electrical properties are cataloged in the Appendix. To my parents (all of them).

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Ιw Electronic for their Shop guy Sam Jack Muns) De repaired apparatus go out to Jeffers, J electrode (xenon fla I w Physics. A Jacques, S almighty. administr. paperwor dedicated problem a I w roommate <sup>Fejzic</sup>, Gar learn almo and my ec I wol Wisconsin I would like to thank Marty Raab and the Chemistry Electronics Shop guys (Ron Haas, Tom Clarke and Scott Sanderson) for their electronic expertise. I would also like to thank the Machine Shop guys from both the Chemistry (Russ Geyer, Dick Menke and Sam Jackson) and Physics (Tom Palazzolo, Tom Hudson and Jim Muns) Departments for all of the equipment they have built and repaired for me. I would have never been able to keep my apparatus running without all of these talented people. Thanks also go out to several others who helped me with equipment: Mr. George Jeffers, Jr., and Dr. Michael Dubson (deposition of the gold electrodes), Dr. Mark Olson (He-Ne laser) and Dr. Mike Atamian (xenon flash lamp).

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LIST OF FI L Intro I.A. I.B. I.C. I.D. I.E. IL Expe I.A. II.B. I.C. II.D. II.E. II. Na+C I.A.

## TABLE OF CONTENTS

LIST	OF FIGU	JRES	x
I.	Introd	uction and Background	1
	I.A.	The Study of Alkalides and Electrides	1
	I.B.	Materials and Structures	4
	I.C.	Historical Background	12
		1. Alkalides and Electrides	12
		2. Thin Film Optical Studies	19
		3. Conductivity Studies	24
		4. General Theoretical Models for Electrides	25
	I.D.	Theory of Basic Optical Properties of Materials	31
	I.E.	Rationale	35
II.	Experi	mental: Vapor Deposition Apparatus	37
	II.A.	Vacuum Chamber and System	37
	II.B.	Evaporation System	40
	II.C.	Optical Absorbance Measurement System .	54
	II.D.	Photobleaching Set-up	59
	II.E.	Conductivity Measurement System	61
		1. Two-Probe	65
		2. Four-Probe	69
III.	Na+C2	22Na	71
	III.A.	Introduction	71

III.B. III.C. III.D. III.E. III.F. N. K+C2 N.A. N.B. N.C. N.D. V. Conc ľ. V.B. APPENDIX LIST OF RE

	III.B.	Temperature Optical At	Deper osorba	idenc nce S	e of t pectr	he a.	•	•	80
	III.C.	Photobleachir	ng Stu	dy	•	•	•	•	109
	III.D.	Stoichiometry	' Study	y.	•	•	•	•	121
	III.E.	Conductivity	Study	•	•	•	•	•	129
	III.F.	Conclusions	•	•	•	•	•	•	132
IV.	K+C22	2e⁻	•	•	•	•	•	•	135
	IV.A.	Introduction	•	•	•	•	•	•	135
	IV.B.	Absorbance S	pectra	•	•	•	•	•	140
	IV.C.	Conductivity	Study	•	•	•	•	•	163
	IV.D.	Conclusions	•	•	٠	•	•	•	183
V.	Conclu	isions and Futu	re Wo	rk	•	•	•	•	185
	V.A.	Conclusions	•	•	•	•	•	•	185
	V.B.	Future Work	•	•	•	•	•	•	188
APPE	ENDIX .	• •	•	•	•	•	•	•	192
LIST	OF REFI	ERENCES .	•	•	•	•	•	•	210

1. ( 2. ł 3. \ i c i 4. ( i ( ( t 1 t 5. S ( 6. 8. 4 9. 4

## LIST OF FIGURES

1.	Representative complexants: a). Top, cryptand[2.2.2]; b). Middle, 18-crown-6; c). Bottom, hexamethyl hexacyclen	5
2.	Packing of Na+C222 and Na <sup>-</sup> (solid circles) in the crystalline sodide Na+C222Na <sup>-</sup>	7
3.	View down c-axis of the complexed cation packing in the electride K+C222e <sup>-</sup> . A single K+C222 unit is outlined. The hexagonal holes represent channels in the c-direction of diameter $\approx 4$ Å. The cutaway views through A and B are shown in Figure 4.	9
4.	Cutaway views down the b-axis of the channels in K+C222e <sup>-</sup> : Top, View A, through the centers of the c-axis channels, which form the hexagonal openings in Figure 3; Bottom, View B, through the center of one set of a-axis channels. View B is displaced by $\approx$ 1.5 Å along the b-axis from that shown in View A.	10
5.	Schematic, three-dimensional representations of the channels in K+C222e <sup>-</sup> without the complexed cations: Top, view down b-axis; Bottom, view down c-axis. Thanks to Tibor Nagy and Gregor Overney	11
6.	Apparatus for the preparation of crystalline and powdered alkalides and electrides	18
7.	Apparatus for obtaining thin film optical spectra by solvent evaporation.	20
8.	Apparatus for preparation of alkalides and electrides by vapor deposition.	22

9. Sch vac 10. Dia On 11. Sou 12. Vie ori 13. Ter (T<sub>s</sub> cor hol site 14. Vie nev sho 15. Ter (T<sub>s</sub> cor hol situ 16. Sch ana mo 17. Dia fee nev 18. Sch lase exp hor per <sup>19</sup>. Diag

9.	Schematic diagram of the Ultek MX-14 vacuum system	•	38
10.	Diagram of the sample preparation chamber. Only one of the three metal ovens is shown.	•	41
11.	Source boats for resistive heating	•	42
12.	View of the bottom of the copper block with the original substrate holder (flexible metal clips).	•	45
13.	Temperature of the center of the substrate $(T_s)$ plotted versus the temperature of the copper block $(T_b)$ with the original substrate holder. The straight line represents the ideal situation $(T_s = T_b)$ .	•	47
14.	View of the bottom of the copper block with the new substrate holder. Small metal clips (not shown) hold the sapphire substrate in place.	•	49
15.	Temperature of the center of the substrate $(T_s)$ plotted versus the temperature of the copper block $(T_b)$ with the new substrate holder. The straight line represents the ideal situation $(T_s = T_b)$ .		50
16.	Schematic diagram of the original optical analysis system. A PbS detector is used to monitor the signal.	•	55
17.	Diagram of the home-made vacuum feedthrough for the fiber optic cable of the new optical analysis system	•	58
18.	Schematic diagram of the placement of the Nd:YAG laser and front-surface mirrors for the bleaching experiments. The dashed line represents a horizontal beam path which actually travels perpendicular to the plane of the page.		62
19.	Diagram of the two-probe, comb electrodes on the		

	sapphire substrate. The Samtacs are epoxied to the substrate and the wires plug into them. A fine gold wire connects the large Samtacs to the chrome/gold electrodes. The places where the flexible metal clip hold the substrate are shown.	e 1 d ps	64
20.	Diagram of the chrome/gold electrodes on the substrate for two-probe measurements with two		
	different conducting path lengths	•	66
21.	Schematic representation of the electronic circuit for the measurement of two-probe conductivity		
	as described in the text	•	67
22.	Diagram of the sapphire substrate with the chrome/gold electrodes for four-probe		
	conductivity measurements	•	70
23.	Optical absorbance (broad) and luminescence (narrow) spectra of a solvent-evaporated		
	Na+C222Na <sup>-</sup> film at 10 K	•	75
24.	Schematic representation of the decay scheme		77
25.	Typical Na+C222Na <sup>-</sup> absorbance spectrum from a thin film synthesized in the vapor deposition system. This particular film was 930 Å thick and was codeposited at 25 °C. The vertical line represents the position of the luminescence	•	
	peak at 10 K	•	79
26.	Absorbance (top) and normalized absorbance (bottom) spectra of a Na+C222Na <sup>-</sup> film which demonstrate how the spectral shape changes with temperature. Notice how the low energy edge of the absorbance spectrum moves toward the 10 K luminescence peak position (vertical lines) as the temperature is lowered.		82
27.	Oscillator strength versus film temperature for a Na+C222Na <sup>-</sup> film. Diamonds and circles		

	rep ten
28.	Exp abs find in t
29.	Pea Na rep ten
30.	Na for stu pre
31.	Pea Na- rep ten
32.	Ful hal film dec tem
33.	Hall hall film and side rep: and
34.	Hig! Plus Spec Na+( decr

	represent decreasing and increasing temperature, respectively.		83
28.	Expanded view of the main Na+C222Na <sup>-</sup> absorbance peak. The coordinates used to find the parameters of the peak are described in the text are shown.		85
29.	Peak position versus temperature for a Na+C222Na <sup>-</sup> film. Diamonds and plus signs represent decreasing and increasing temperature, respectively.		86
30.	Na+C222Na <sup>-</sup> peak position versus temperature for both a codeposited thin film from the present study and a solvent-evaporated thin film from a previous study.		88
31.	Peak absorbance versus temperature for a Na+C222Na <sup>-</sup> film. Diamonds and plus signs represent decreasing and increasing temperature, respectively.		89
32.	Full-width of the main absorption peak at half-height versus temperature for a Na+C222Na <sup>-</sup> film. Diamonds and plus signs represent decreasing and increasing temperature, respectively.		91
33.	Half-widths of the main absorption peak at half-height versus temperature for a Na+C222Na <sup>-</sup> film. The low energy side of the peak (circles and crosses) is narrower than the high energy side (diamonds and plus signs). Circles and diamond represent decreasing temperature and plus signs and crosses represent increasing temperature.	ds	92
34.	High (diamonds and crosses) and low (circles and plus signs) energy positions of the absorbance spectra at half-height versus temperature for a Na+C222Na <sup>-</sup> film. Circles and diamonds represent decreasing temperature and plus signs and crosses		

reg 35. Gr pe pe fit 36. Gr str da ex 37. Gr pe an 38. Ro Na 39. No fil 40. Sc va a) th at b, in 41. F-di is di er 42. Pe te sr 43. A at

	represent increasing temperature	•	94
35.	Graph showing the decrease in the Na+C222Na <sup>-</sup> peak absorbance value over an eight day period. The solid line represents an exponential fit to the data.		97
36.	Graph showing the decrease in the oscillator strength of a Na+C222Na <sup>-</sup> film over an eight day period. The solid line represents an exponential fit to the data.		98
37.	Graph showing the change in the absorbance peak position of a Na+C222Na <sup>-</sup> film over an eight day period.	•	99
38.	Room temperature absorbance spectra of a Na+C222Na <sup>-</sup> film taken over eight days.	•	100
39.	Normalized absorbance spectra of a Na+C222Na- film taken over eight days at room temperature.	•	101
40.	Schematic representation of transitions between valence and conduction bands in k space: a). direct optical transition, the excitation of the electron is drawn vertically because the absorbed photon has a very small wavevector; b). indirect optical transition, the excitation involves both a photon and a phonon		103
41.	F-center optical absorbance spectra at three different temperatures for KCl. Temperature is increasing from solid line to dotted line to dashed line. Notice that increasing photon energy is plotted from right to left.	•	105
42.	Peak position and width at half-height versus temperature of the F-center optical absorbance spectra for KCl (top) and NaCl (bottom).	•	106
43.	A four-gaussian fit (solid line) to the optical absorbance spectra of a Na+C222Na <sup>-</sup> film		

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	show
44.	Abso
	(bott
	Na+(
	h) or
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49	abs abs (do (lar · Ab- 21( ter 2 -
49	- 4366 abs (do (lar - Ab 21( ten 2 = an

	(dots). The individual gaussian peaks are shown as broken lines.	•	108
44.	Absorbance (top) and normalized absorbance (bottom) spectra of a solvent-evaporated Na+C222Na <sup>-</sup> film taken during a bleaching experiment of DeBacker, <i>et. al.</i> : a). initial spectra; b). spectra immediately after a 15 ns pulse from a 605 nm dye laser; c). spectra one second after the pulse.		110
45.	Absorbance spectra of a 1300 Å codeposited Na+C222Na <sup>-</sup> film before (diamonds) and after (circles) a 7 ns pulse from a 532 nm Nd:YAG laser. Film temperature = -60 °C.		114
46.	Normalized absorbance spectra of a 1300 Å codeposited Na+C222Na <sup>-</sup> film before (diamonds) and after (circles) a 7 ns pulse from a 532 nm Nd:YAG laser. Film temperature = -60 °C.	•	115
47.	Peak absorbance value of a 1000 Å Na+C222Na- film versus 532 nm Nd:YAG pulse number. Shows the bleaching process becomes saturated after repeated pulses. Film temperature = $-10$ °C. The solid curve represents a double exponential fit to the data.		116
48.	Absorbance spectra of a 1000 Å Na+C222Na <sup>-</sup> film: Top, spectra taken before (solid line) and after (dashed line) a 7 ns pulse from a 532 nm Nd:YAG laser; Bottom, spectra of fraction of "true" sodide absorbance subtracted from the dashed line above (dot-dashed line) and remaining absorbing species (large dashed line).		122
49.	Absorbance spectra of a sequentially deposited 2100 Å Na+C222e <sup>-</sup> film deposited by Faber. Film temperature = -100 °C. Spectrum 1 = Initial, $2 = 2$ hours after deposition, $3 = 3.5$ hours		
	and $4 = 4.5$ hours	•	124

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50.	Absorbance spectra of a sequentially deposited 1020 Å Na+C222Na <sup>-</sup> film at -40 °C: Diamonds = initial spectrum; circles = 30 minutes after deposition.	•	125
51.	Absorbance (top) and normalized absorbance (bottom) spectra of a codeposited 1200 Å Na+C222Na <sup>-</sup> film with Na:C222 = 2:1.1: Crosses and diamonds = initial spectrum at -20 °C; circles = spectrum after 20 hours at room temperature.	•	127
52.	Absorbance spectrum of a codeposited 1200 Å $K^+C222K^-$ film at -60 °C. This type of spectrum was only seen once.	•	141
53.	Absorbance spectrum of a codeposited 1400 Å K+C222K <sup>-</sup> film at -60 °C. Notice the extra absorbance "bumps" at 14000 and 18000 cm <sup>-1</sup> .	•	143
54.	Absorbance spectrum of a codeposited 1400 Å K+C222e <sup>-</sup> film at -40 °C. Notice the trapped electron peak at 8000 cm <sup>-1</sup> on the plasma edge-shaped spectrum.	•	144
55.	Evolution of the absorbance spectra of a codeposited 1350 Å K+C222e <sup>-</sup> film at approximately -60 °C: plus signs = initial spectrum; crosses = one hour after deposition; squares = two hours after deposition; circles = three hours after deposition. Notice the isosbestic point at 7000 cm <sup>-1</sup> .	•	146
56.	Evolution of the absorbance spectra of a codeposited 1800 Å K+C222e <sup>-</sup> film at -60 °C: solid line = initial spectrum; dotted line = one hour after deposition; dashed line = 1.5 hours after deposition; dot-dashed line = two hours after deposition. Notice the rough isosbestic point at 7000 cm <sup>-1</sup> .	_	147
57.	Absorbance spectrum of a 2750 Å		

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	off-stoichiometry K/C222 film at -60 °C. K:C222 = 1.5:1. Notice the extra absorbance "bumps" at 14000 and 18000 cm <sup>-1</sup> .	151
58.	Absorbance spectrum of a 500 Å K metal film at -60 °C. These peaks were time and temperature dependent.	153
59.	Absorbance spectrum of a codeposited $1800 \text{ \AA}$ K+C222e <sup>-</sup> film at -60 °C (dots). The solid line represents the fit to a plasma edge absorbance plus a potasside peak.	156
60.	Schematic representation of several simple band-like models as described in the text.	159
61.	Beer's Law plot for the absorbance value at 8000 cm <sup>-1</sup> of many K+C222e <sup>-</sup> spectra	160
62.	Two-probe ln(p) versus time for the codeposited K+C222K <sup>-</sup> film shown in Figure 52	164
63.	Two-probe $ln(\rho)$ versus inverse temperature for a codeposited 1400 Å K+C222e <sup>-</sup> film after the film has been annealed.	167
64.	Two-probe $ln(\rho)$ versus inverse temperature for a codeposited 1800 Å K+C222e <sup>-</sup> film which shows an increase in the resistivity upon annealing.	169
65.	A typical two-probe I-V plot for a K+C222e <sup>-</sup> conductivity experiment. The output voltage of the amplification circuit is proportional to the current.	171
66.	Two-probe $ln(\rho)$ versus inverse temperature for a codeposited 1650 Å K+C222e <sup>-</sup> film. The substrate with electrodes having two different path lengths was used in this experiment. The two lines represent the data from the wide (solid) and narrow (dashed) path lengths.	172

67. S a 68. F C T d b a t d d 69. S n c 70. F d s 71. A 0 72. A 0 73. A 0 74. A a 75. A fi 76. A fi 77. A

67.	Schematic diagram of the resistances of a sample and two resistive sample/electrode interfaces.	174
68.	Four-probe $ln(\rho)$ versus inverse temperature for a codeposited 2400 Å K+C222e <sup>-</sup> film after annealing. The solid line represents a llinear fit to the diamond-shaped data points. The typical apparent band gap is 62 meV. The circles show the decrease and then increase in resistivity as described in the text. The dashed line represents an extension of the data of Moeggenborg, <i>et. al.</i> (gap = 86 meV).	176
69.	Schematic representation of a possible decomposition mechanism in K+C222e <sup>-</sup> . Two electrons attack the cryptand molecule and an ethylene molecule is ejected into the vacuum.	180
70.	Four-probe ln(ρ) versus thickness of a K+C222e <sup>-</sup> film during deposition at -60 °C. Notice the resistivity settles down at a relatively small thickness.	182
71.	Absorbance spectrum of a 2000 Å codeposited film of Na:TETMCY = 2:1 at -50 °C	194
72.	Absorbance spectrum of a 2500 Å codeposited film of Na:PMPCY = 2:1 at -60 °C	195
73.	Absorbance spectrum of a 2550 Å codeposited film of Na:TMTACM = 2:1 at -60 °C.	196
74.	Absorbance spectrum of 50 Å of Na deposited onto a film of supertriptycene at 25 °C.	198
75.	Absorbance spectrum of a 500 Å codeposited film of Na:tris(2,6-dimethoxyphenyl)methyl radical = 2:1 at -60 °C.	199
76.	Absorbance spectrum of a 200 Å codeposited film of Na:tris(2,6-dimethoxyphenyl)methyl radical = 2.5:1 at -60 °C.	200
77.	Absorbance spectrum of 50 Å	

of Y tis 78. Abs cod Na: 79. Abs of Y 80. Abs of Y 81. Abs of Y 82. Abs of Y

	of Na deposited onto a film of tris(2,6-dimethoxyphenyl)borane at -60 °C	202
78.	Absorbance spectrum of a 2250 Å codeposited film of Na:tris(2,6-dimethoxyphenyl)amine = 1:1 at -60 °C	203
79.	Absorbance spectrum of a 1450 Å codeposited film of Na:phenanthrene = $1.2:1$ at $-25$ °C	205
80.	Absorbance spectrum of a 1200 Å codeposited film of Na:triphenylene = $1:1$ at $-30$ °C.	206
81.	Absorbance spectrum of a 1300 Å codeposited film of Na:triptycene = 2:1 at -40 °C	207
82.	Absorbance spectrum of a 1000 Å codeposited film of Na:anthracene = $1:1$ at $-35$ °C.	208
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This th synthesis and deposited thi known as alka the cations ar anions are alk formula M+Ln may or may <sup>complexing</sup> m requires one <sup>cation</sup>). Elec <sup>complexed</sup> a apped elec formula M+1 Alkali due not onl which the 1 <sup>shape</sup> and s A in diamet nolecules pa <sup>over</sup> 30 alkalı varient of struc

#### I. INTRODUCTION AND BACKGROUND

# I.A. The Study of Alkalides and Electrides

This thesis will present the results of research involving the synthesis and the optical and electrical characterization of vapor deposited thin films of two new classes of solid state compounds known as alkalides and electrides. Alkalides are ionic salts in which the cations are macrocyclic complexed alkali metal cations and the anions are alkali metal anions. These compounds have the general formula  $M^+L_nN^-$ , where M and N are alkali metal atoms (M and N may or may not be the same alkali metal) and L is an organic complexing molecule where n = 1 or 2 (depending on whether it requires one or two molecules to encapsulate each alkali metal cation). Electrides are also ionic salts and they have the same complexed alkali metal cations as the alkalides but they have trapped electrons as their anions. The electrides have the general formula  $M^+L_ne^-$ .

Alkalides and electrides have interesting physical properties due not only to their unusual anions, but also due to the manner in which the molecules stack together into a crystal structure. The shape and size of the large complexing molecules (on the order of 10 Å in diameter) usually dominate the overall mechanics of how the molecules pack together. Single crystal X-ray diffraction studies of over 30 alkalides and 5 electrides demonstrate an extremely wide variety of structures. Some are relatively simple, in which the alkali

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metal anion or trapped electron is relatively isolated in a single cavity of the structure. This type of structure does not allow the anion or electron to couple strongly with the other trapped anions or electrons. Other structures are very complex, where the anion or electron is trapped in a cavity that is connected by a variety of channels to other cavities that contain anions or electrons. This type of structure allows interesting interactions between the anions or the trapped electrons. In some electrides, this complex interconnected structure can create a nearly free electron lattice gas. The study of alkalides and electrides is then the study of how alkali metal anions or trapped electrons interact with each other through a range of connectivities (from nearly no connection between cavities, to electron pairs connected by two dimensional channels, to sixmembered electron rings connected by three dimensional channels).

Several review papers present the *tour de force* of characterizations performed on alkalides and electrides in much more detail than will be presented here.<sup>1,2</sup> These characterizations include: single crystal and powder X-ray diffraction, magnetic susceptibility, differential scanning calorimetry, solution and magic angle spinning nuclear magnetic resonance, electron paramagnetic resonance, photoluminescence spectroscopy, reflectivity, pressed powder and single crystal electrical conductivity and optical absorbance on solvent-evaporated and vapor deposited thin films. The present work concentrates on the optical and electrical properties of thin films of an alkalide and an electride prepared by codeposition of an alkali metal and a complexant in an evacuated bell jar.

The or opportunity i photons exc energetically and 6 for N seen). The peaks revea bound-to-bou each anion. Electric correlation I electrical con range of con in the electri one cavity to two cavities <sup>channel)</sup>, ar semiconduct properties of <sup>electron</sup> inte Electric <sup>theoretical</sup> n <sup>is an</sup> elemen <sup>coul</sup>d be use <sup>COUrse</sup>, in re <sup>the electride</sup> <sup>and each</sup> of t The optical absorbance properties of alkalides provide an opportunity to study localized bound-to-bound transitions. Incident photons excite the outer *s* electrons of the anions into an energetically higher *p* state in an  $ns^2$  to nsnp transition (n = 3, 4, 5 and 6 for Na<sup>-</sup>, K<sup>-</sup>, Rb<sup>-</sup> and Cs<sup>-</sup>, respectively; Li<sup>-</sup> has never been seen). The position and shape of the corresponding absorbance peaks reveal information regarding not only the nature of the bound-to-bound transition, but also of the environment surrounding each anion.

Electrides present an interesting opportunity to study the correlation between crystal structures, optical absorbances and electrical conductivities. As was stated above, the structures show a range of connectivities between the cavities that trap the electrons in the electrides. Depending on how much interaction there is from one cavity to another (which depends on the distance between the two cavities and on the cross-sectional size of the connecting channel), an electride could behave as a metal, a semi-metal, a semiconductor or an insulator. Studying the optical and electrical properties of electrides helps determine the nature of the electronelectron interactions.

Electrides also present an opportunity to compare a variety of theoretical models with experimental results. The particle in a box is an elementary quantum mechanics problem. A model such as this could be used on a completely isolated and localized electride. Of course, in reality the potential energies associated with the walls of the electride "box" are not infinite in height nor spherical in shape, and each of the known electrides has some channel structure. Other,

more comple how the spec assist in predi conducting el LB. <u>Materials</u> Alkalide organic compl K, Rb and Cs, 1 complexing ag crown ethers a are three-dime to an Americar cryptand[2.2.2 <sup>employ</sup> a diffe strands that con <sup>(211)</sup>. Crown an example of <sup>employ</sup> either and 12C4). Aza the previously <sup>replace</sup> each of <sup>the</sup> aza anal<sub>Og</sub> (EV:HCY). The two c <sup>are the</sup> alkalide more complex models, though, could assist in the understanding of how the specifics of the channels affect the electride properties or assist in predicting what type of organic molecules may lead to more conducting electrides.

#### I.B. Materials and Structures

Alkalides and electrides are composed of alkali metals and organic complexing molecules. The alkali metals used include Li, Na, K. Rb and Cs. but not the radioactive Fr. The most frequently used complexing agents fall into three different categories: cryptands, crown ethers and aza analog cryptands and crown ethers. Cryptands are three-dimensional cage-like polyethers that have a shape similar to an American football. Figure 1a shows an example of a cryptand: cryptand[2.2.2] (commonly referred to as C222). Other cryptands employ a different number of oxygen atoms in one or more of the strands that connect the two nitrogen atoms (such as C322, C221 and C211). Crown ethers are cyclic, planar polyethers. Figure 1b shows an example of a crown ether: 18-Crown-6 (18C6). Other crowns employ either larger or smaller rings (such as 30C10, 21C7, 15C5 and 12C4). Aza analogs of cryptands and crown ethers are similar to the previously described compounds, but nitrogen-methyl groups replace each of the oxygen atoms. Figure 1c shows an example of the aza analog to the 18C6 crown ether: hexamethyl hexacyclen (HMHCY).

The two compounds that the present research concentrates on are the alkalide Na+C222Na<sup>-</sup> and the electride K+C222e<sup>-</sup> (pronounced



Figure 1. Representative complexants: a). Top, cryptand[2.2.2]; b). Middle, 18-crown-6; c). Bottom, hexamethyl hexacyclen.

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sodium C222 sodide and potassium C222 electride, respectively). The main reasons for studying Na+C222Na<sup>-</sup> are that it is the bestcharacterized, the most stable and the easiest to synthesize in a defect-free state when compared to all of the other alkalides and electrides. The high level of sample stability and purity eliminates the worry regarding the condition of the samples changing drastically during characterization. The many previous characterizations also allow one to compare the new results presented here with the well-known behavior of the compound and to see if these new results fit into and add insight into the accepted model of Na+C222Na<sup>-</sup>. The main reasons for studying K+C222e<sup>-</sup> are that it is the most conducting (possibly metallic) alkalide or electride and that there is a discrepancy regarding its true optical absorbance spectrum. Furthering the characterizations of the only alkalide or electride that appears to be nearly metallic is important to assist in the understanding of what characteristics may make other compounds in this new class of materials conducting. Finally obtaining the true optical absorbance spectrum of K+C222e<sup>-</sup> would assist in describing the overall nature of this unique electride.

As already mentioned, crystal structures play a very important role in the interpretation of the characterization studies of alkalides and electrides. Figure 2 shows the packing of Na+C222Na<sup>-</sup> (each Na+ in the diagram is actually encapsulated by a C222 molecule and each black dot represents a Na<sup>-</sup> ion).<sup>1</sup> This sodide has a rhombohedral structure with parameters: a = 8.83 Å, c = 29.26 Å (space group R32, hexagonal setting).<sup>3</sup> The Na<sup>-</sup> ions are in pseudo-octahedral cavities formed by the packing of the cryptands and are



Figure 2. Packing of Na+C222 and Na<sup>-</sup> (solid circles) in the crystalline sodide Na+C222Na<sup>-</sup>.

rather isol packing pl a sodide i 11.0 Å. T Na+C222 correspon (although electride h Figur of K+C2226 centers of view also al course thro Figure 4 sh K+C222e-. dimensiona <sup>picture</sup> in F the bottom that look clo <sup>b</sup>axis. Ther <sup>out of the</sup> p With structu <sup>95.2</sup>°, Z = 8. <sup>Each large</sup> c With a 4 x 4 pair of trapp. <sup>(avities</sup> by rather isolated from each other. The sodides are 8.83 Å apart in the packing plane perpendicular to the threefold axis. The distance from a sodide in one plane to the nearest sodide in an adjacent plane is 11.0 Å. This anisotropy appears in the characteristic properties of Na+C222Na<sup>-</sup>. All attempts to synthesize single crystals of the corresponding electride, Na+C222e<sup>-</sup>, have been unsuccessful (although vapor deposited and solvent-evaporated films of this electride have been formed<sup>4,5,6</sup>).

Figure 3 shows a view down the *c*-axis of the crystal structure of K+C222e<sup>-,7,8</sup> Notice that this particular slice is taken through the centers of the C222 cages where the K<sup>+</sup> cations can be seen. This view also allows a look at a cross-section of the large channels which course through the structure. To see the channels in more detail, Figure 4 shows two views down the *b*-axis of the crystal structure of K+C222e<sup>-</sup>. The two views are necessary to show the open two dimensional channels that zig-zag through the structure. The top picture in Figure 4 shows the slice through Figure 3 labeled A and the bottom picture shows the slice labeled B. The alternate channels that look closed in this figure are open at different locations on the b-axis. There are no open channels in the third dimension (into and out of the page of Figure 4). The space group is monoclinic (C2/c)with structure parameters: a = 12.13 Å, b = 20.69 Å, c = 21.52 Å,  $\beta =$ 95.2°, Z = 8. Figure 5 shows a schematic view of the electron traps. Each large cavity (dumb-bell-shaped, approximately 4 x 6 x 12 Å with a 4 x 4 Å cross section at the center) presumably contains a pair of trapped electrons and is connected to four nearest neighbor cavities by channels (with minimum channel diameters of



<sup>Figure</sup> 3.



Figure 3. View down c-axis of the complexed cation packing in the electride K+C222e<sup>-</sup>. A single K+C222 unit is outlined. The hexagonal holes represent channels in the cdirection of diameter -4 Å. The cutaway views through A and B are shown in Figure 4.





Figure 4. Cutaway views down the b-axis of the channels in K+C222e<sup>\*</sup>: Top, View A, through the centers of the c-axis channels, which form the hexagonal openings in Figure 3; Bottom, View B, through the center of one set of a-axis channels. View B is displaced by ~ 1.5 Å along the b-axis from that shown in View A.

b

<sup>Figure</sup> 5.





Figure 5. Schematic, three-dimensional representations of the channels in K+C222e<sup>-</sup> without the complexed cations: Top, view down b-axis; Bottom, view down c-axis. Thanks to Tibor Nagy and Gregor Overney.

t F k P 9 e e a S a p tł ( Þ٥ di !( in cha approximately 2 Å along the *a*-axis and 4 Å along the *c*-axis). This type of open, interconnected structure naturally leads to thoughts of the possibility of a one- or two-dimensional metallic compound.

The crystal structure of the alkalide K+C222K<sup>-</sup> (pronounced potassium C222 potasside) is similar to that of K+C222e<sup>-</sup>, but of lower symmetry. The space group is triclinic (PI) and the structure parameters are: a = 12.30 Å, b = 12.42 Å, c = 11.47 Å,  $\alpha = 106.5^{\circ}$ ,  $\beta = 92.7^{\circ}$ ,  $\gamma = 62.0^{\circ}$ , Z= 2. The similarity between the potasside and the electride causes complications when trying to study either the pure electride or pure potasside. The electride is easily "doped" with K<sup>-</sup> and the potasside is easily "doped" with e<sup>-</sup>. The pure potasside is strongly insulating and has a typical localized alkalide-like optical absorbance spectrum. The fact that the alkalide and electride, when pure, have very dissimilar optical and electrical properties suggests that interesting behavior may occur when a mixture of the two (or a compound of either that is doped with the other) is prepared. These possibilities are examined in the K+C222e<sup>-</sup> chapter of this dissertation.

# I.C. Historical Background

# 1. Alkalides and Electrides

Dye and coworkers synthesized the first alkalide, Na+C222Na<sup>-</sup>, in 1973 and published its crystal structure and initial characterizations in 1974. This work evolved from the study of

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solvated electrons and alkali metal anions. The major steps of this evolution are described in this section.

The ability of liquid ammonia to dissolve alkali metals has been well known for over a century. Actually, it is now known that Sir Humphry Davy first observed the deep blue solution of potassium metal in ammonia in 1808.<sup>9</sup> The study of metal ammonia solutions became an active area of chemical research after W. Weyl's extensive, and first published, work<sup>10</sup> and a thirty-year study by C. A. Kraus which began in the early 1900's.<sup>11</sup>

All the alkali metals are very soluble in liquid ammonia. These solutions are blue when dilute (less than 3 mole percent metal) and metallic bronze at higher metal concentrations. The two major species present in dilute solutions are the solvated metal cation, M<sup>+</sup>, and the solvated electron, e<sup>-</sup>. The formation of these species follows the equation:

$$M_{(s)} + NH_3 \Rightarrow M^+_{solv} + e^-_{solv}$$

As the concentration increases, the cations and solvated electrons exist as associated ion pair species held together by the attractive Coulomb potential between the ions.<sup>12</sup> The optical absorption spectra of metal ammonia solutions explain the characteristic blue color. The main absorption is that of the solvated electron which is totally independent of the alkali metal used and which peaks at about 0.9 eV (1400 nm). The absorption band is asymmetric and the long tail which extends beyond 1.8 eV (700 nm) is responsible for the color.<sup>11</sup> As the metal concentration increases from 3 to 8

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mole percent metal, these solutions undergo a non-metal to metal transition. Above 8 mole percent metal, the solutions are good liquid metals with electrical conductivities generally >  $10^3 \Omega^{-1}$ cm<sup>-1</sup> (actually becoming higher than the conductivity of liquid mercury at room temperature).<sup>11</sup>

In contrast to ammonia, alkali metals are not very soluble in other solvents, such as amines. Dye's lab was one of the main experimental groups in the field of metal amine solutions. A variety of analytical techniques (including electron spin resonance<sup>13</sup> and optical absorbance spectroscopy<sup>14</sup>) helped characterize these solutions during the 1960's. These less polar solvents not only contained the ionic species seen in metal ammonia solutions, M<sup>+</sup><sub>solv</sub> and e<sup>-</sup><sub>solv</sub>, but they also contained solvated alkali metal anions, M<sup>-</sup>. The optical absorbance spectra for the various alkali metals showed strongly metal-dependent bands occurring at higher energies than the band for the solvated electrons. These bands were identified as arising from the solvated alkali metal anions<sup>15</sup> formed by the equilibrium reactions:

$$2e_{solv} + M^+ \Leftrightarrow M^-$$
$$M_{(s)} + e_{solv} \Leftrightarrow M^-.$$

Ultimately, the irrefutable evidence for the existence of M<sup>-</sup> in solution came from the solution NMR work.<sup>16</sup> The extremely narrow line for Na<sup>-</sup> at a chemical shift value nearly identical to that of Na<sup>-</sup> in the gas phase, with no solvent induced paramagnetic shift, indicated the presence of an anion with a filled 3s orbital.

in the respec alkali dissolu makes crypta agents and in experi contai and al C222) solven absort were M model Na+ a lifetim minute reason concen at low. <sup>cont</sup>ain ajiow.ei <sup>then</sup> re Pederson and Lehn developed two new classes of compounds in the late 1960's which they called crown ethers<sup>17</sup> and cryptands,<sup>18</sup> respectively. Both of these classes of compounds selectively complex alkali metal cations very strongly.<sup>17,19</sup> When an alkali metal is dissolved, this complexation frees the electrons in the solution which makes them available for solvation.

Dye and coworkers were the first to use crown ethers and cryptands in metal amine solutions. The use of these complexing agents enhanced the solubilities of the alkali metals in these solvents and increased the range of usable solvents.<sup>20,21</sup> Thus, in 1973, three experimental facts were used to devise a plan to prepare solids that contain complexed alkali metal cations,  $M^+L_n$ , trapped electrons, e<sup>-</sup>, and alkali metal anions, M<sup>-</sup>: (1) an appropriate cryptand (such as C222) helps create concentrated solutions of all the alkali metals in solvents (such as methylamine and ethylamine), (2) optical absorbance spectra demonstrated that the major species present were M<sup>-</sup> and complexed M<sup>+</sup>, and (3)  $^{23}$ Na NMR measurements on model salts showed that the rate of dissociation of Na+(C222) to yield Na<sup>+</sup> and C222 was relatively  $slow^{22}$  (the data suggested that lifetimes for Na<sup>+</sup> in the cryptand cage at low temperatures might be minutes to hours after removal of the solvent). The Dye group reasoned that by rapidly evaporating the solvent from a concentrated stoichiometric solution of Na and C222 in methylamine at low temperatures, it might be possible to synthesize a solid salt containing Na<sup>-</sup>. The rapid evaporation of the solvent would not allow enough time for the Na<sup>+</sup> to get out of the cryptand cage and then recombine with Na<sup>-</sup> to form the neutral metal and free

comple therm precip group solid a By car synthe of crys stoichi in the ] numbe permu the rac moleci new c charac I alkalid structu <sup>and</sup> el During Perfect and lo under and ele Vacuun complexant. Actually, the crystalline sodide salt proved to be thermodynamically stable to decomplexation and could be precipitated from solution without solvent evaporation. The Dye group reported the first characterization and crystal structure of a solid alkalide in 1974: a sodide (or natride) named Na+C222Na<sup>-</sup>.<sup>23</sup> By careful control of the stoichiometry, they were later able to synthesize Cs+(18C6)e<sup>-</sup>, which was the first member of a new series of crystalline compounds called electrides.<sup>24</sup> These compounds have stoichiometric amounts of trapped electrons that serve as the anions in the structure.

These discoveries opened up a whole new field of study. The number of possible compounds is immense: consider the number of permutations and combinations using all of the alkali metals (minus the radioactive Francium) and the enormous variety of complexing molecules (both known and yet to be synthesized). The search for new compounds (and their crystal structures) with unique characteristics was on.

Dye and coworkers published the next crystal structure of an alkalide or electride more than ten years after the Na+C222Na<sup>-</sup> structure. The main reason for this delay was the fact that alkalides and electrides are very air, temperature and moisture sensitive. During the late 1970's and early 1980's, the Dye group designed and perfected many new techniques for handling, storing, transferring and loading these reactive compounds at low temperatures and under inert atmosphere or vacuum conditions.<sup>25,26</sup> Several alkalides and electrides are stable at room temperature for a short time under vacuum. Usually, though, alkalides and electrides must be handled

at te (alth) comp stored an att tend ether smalle that a will d encap cation Sever synth increa offset decon of all descri nearly <sup>into</sup> a remov <sup>10-5</sup> 7 Retal <sub>20]</sub>...e1 at temperatures below -40 °C to avoid thermal decomposition (although the extent of thermal instability varies with each compound). For long term storage, most alkalides and electrides are stored at liquid nitrogen temperatures (77 K).

Aza analogs of cryptands<sup>27</sup> and crown ethers<sup>28</sup> were used in an attempt to synthesize more stable compounds. These aza analogs tend to be more resistant to reductive decomposition than crown ethers and cryptands.<sup>29</sup> Unfortunately, these compounds have smaller complexation constants for alkali metal cations, which means that alkalides and electrides made by using aza analog complexants will decomplex more quickly when warmed (in other words, the encapsulating aza analog molecules will release the alkali metal cations at lower temperatures than the crown ethers or cryptands). Several of these alkalides and electrides have recently been synthesized and characterized.<sup>30,31,32,33</sup> It appears that any increase in stability due to better resistance to decomposition is offset by a decrease in stability due to poorer resistance to decomplexation.<sup>32,33</sup>

A general detailed description of the wet chemistry synthesis of alkalides and electrides is given elsewhere.<sup>34,35</sup> A brief description is given here. The synthesis involves the introduction of nearly stoichiometric amounts of alkali metal(s) and complexant(s) into a reaction cell (Figure 6) in a helium-filled glove box. The cell is removed from the glove box and attached to a high vacuum line (1 x  $10^{-5}$  Torr). Proper application of a torch flame produces an alkali metal mirror in one part of the cell (bulb labeled B).<sup>36</sup> An added solvent dissolves the complexant in the bulb labeled A. This



Figure 6. Apparatus for the preparation of crystalline and powdered alkalides and electrides.

solver desire is har polar crysta cell an (labele sample carefu 2 C species the opt the alk. 950 nr Peaks c shape c the loc modera has an ; through Tł reaction <sup>One</sup> cha other is solvent/complexant solution then dissolves the alkali metal. The desired alkalide or electride, whose species are in solution in the cell, is harvested by removal of the solvent or by the addition of a less polar solvent which precipitates the crystalline compound. The crystals of the alkalide or electride are harvested by inverting the cell and sealing the material into the small glass or quartz ampoules (labeled Sample Fingers). The researchers then characterize the samples by opening the ampoules under guarded conditions and carefully loading the crystals into the appropriate apparatus.

#### 2. Thin Film Optical Studies

Optical studies are used to identify and study the anionic species in alkalides and electrides. The positions of the maxima in the optical absorbance spectra of the alkalides are unique for each of the alkali metal anions (approximately 650 nm, 820 nm, 880 nm and 950 nm for Na<sup>-</sup>, K<sup>-</sup>, Rb<sup>-</sup> and Cs<sup>-</sup>, respectively).<sup>1</sup> These localized peaks correspond to the *ns*<sup>2</sup> to *nsnp* optical transitions. The spectral shape of the absorbance of electrides contains information regarding the localization of the trapped electrons.  $Cs^+(18C6)_2e^-$  has a moderately sharp peak in the near-IR [localized] whereas K+C222e<sup>-</sup> has an absorbance spectrum that continually increases from the UV through the visible and into the IR [delocalized].

The first optical absorbance studies used specially modified reaction cells.<sup>4,5,37</sup> Figure 7 shows an example of one of these cells. One chamber of the cell is a rectangular quartz optical cell and the other is a storage bulb. The alkalide or electride crystals are loaded



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into the r cell is th solvent dissolves spectrum the optic electride by imme film of t optical a Sev absorba complete the films will be bu group de Sev when all introduct reactions reasoned <sup>form</sup> the A reactic <sup>solv</sup>ent-fi schematic metal are <sup>Ihe cell</sup> is
into the reaction cell inside a helium-filled glove box. The reaction cell is then connected to a high vacuum line and evacuated. A solvent is distilled into the cell and the alkalide or electride dissolves. If the solution is dilute enough, an optical absorbance spectrum is taken of the alkalide or electride and solvent solution in the optical cell. To take a spectrum of a thin film of the alkalide or electride, the solvent is quickly distilled away from the optical cell by immersing the storage bulb in liquid nitrogen. This leaves a thin film of the alkalide or electride on the walls of the optical cell for optical analysis.

Several questions arise regarding these thin film optical absorbance spectra. Are the films dry? If the films are not completely solvent-free, does the solvent affect the spectra? Are the films of uniform thickness? If the films are rough, the peaks will be broadened.<sup>38</sup> Are the films stoichiometrically correct? Dye's group designed a series of experiments to answer these questions.

Several observations of a deep blue product in reaction cells when alkali metals came in contact with complexants prior to introduction of the solvent suggested the feasibility of solid state reactions between the metal and the complexant.<sup>1,39</sup> It was reasoned that codeposition of metal and complexant vapors may form the alkalide or electride directly without the use of a solvent. A reaction cell was designed and constructed to synthesize a solvent-free thin film of an alkalide or electride.<sup>40</sup> Figure 8 schematically shows one of these cells. The complexant and alkali metal are introduced into the side arms in a helium-filled glove box. The cell is attached to a high vacuum line and evacuated ( $1 \times 10^{-5}$ 



Figure 8. Apparatus for preparation of alkalides and electrides by vapor deposition.

Torr). Indiwindings all the metal ar above the st vapor strear the confluer. deposited fil: apparatus m. of the optical lowered into variation of ti to be studied. The opti <sup>solvent</sup> evapor solvent effect <sup>Stoichiometric</sup> <sup>this</sup> feasibility <sup>could</sup> be synth Dye, Pra deposition appa <sup>is given</sup> in the <sup>apparatus</sup> uses <sup>allow</sup> stoichiom <sup>sapphire</sup> subst <sup>deposited</sup> films films.6 The re <sup>shapes</sup> of the va Torr). Individual control of the current to the Nichrome heater windings allows a rough control of the relative evaporation rates of the metal and complexant. The inner quartz optical cell was kept above the streams of vapor until a satisfactory ratio of the two vapor streams was achieved. The inner cell was then lowered into the confluence of the alkali metal and complexant streams. The deposited films were reasonably uniform, but the geometry of the apparatus made the complexant-to-metal ratio vary across the face of the optical cell. The inner cell, with the deposited film, was then lowered into the outer quartz optical cell for optical analysis. The variation of the relative rates allowed both alkalides and electrides to be studied.

The optical absorbance spectra of alkalides and electrides from solvent evaporation and vapor deposition were very similar.<sup>40</sup> Thus, solvent effects on the optical spectra appeared to be minimal. Stoichiometric control and film uniformity were still necessary, but this feasibility study demonstrated that alkalides and electrides could be synthesized via a solid state reaction.

Dye, Pratt and coworkers then built a high vacuum vapor deposition apparatus.<sup>41,42</sup> A complete description of this evaporator is given in the experimental chapter of this dissertation. The apparatus uses oscillating quartz crystal thickness monitors which allow stoichiometric deposition of uniform thin films onto a small sapphire substrate. Optical absorbance spectra from the vapor deposited films were very similar to the dry solvent evaporated films.<sup>6</sup> The researchers could quantitatively trust the spectral shapes of the vapor deposited films whereas the spectral shapes of the non-uniform solvent evaporated films were treated as only qualitatively correct.

# 3. Conductivity Studies

Ever since researchers saw the bright, gold-colored Na+C222Na<sup>-</sup> crystals in 1974, the search for a metallic alkalide or electride has been intense. Powder conductivities show that this first sodide behaves as a semiconductor with a bandgap of 2.4 eV.<sup>23,43,44</sup> Other alkalides appear to be extrinsic semiconductors (their linear logarithmic dependence of resistance with inverse temperature gives apparent bandgaps of 0.6 eV to 1.5 eV, but their optical absorbance spectra which show peaks at 1.2 eV to 2.0 eV indicate conduction bands at much higher energies<sup>1</sup>). It seems that trapped electrons at defect sites in the compounds cause the high conductances and low apparent bandgaps.

Powder conductivities of electrides show behaviors that range from localized to itinerant. It appears that the cavity-to-cavity distances and the size of the interconnecting channels play an important role in the electronic properties of electrides.<sup>45</sup> Electrides with localized electron cavities (such as  $Cs+(15C5)_2e^-$  and  $Cs+(18C6)_2e^-$ ) show semiconductor-like behavior and have low conductivities that are dominated by defect electrons.<sup>46,47</sup> The conductivity above 200 K appears to be mainly cationic conductivity. Pressed pellet conductivities of an itinerant electride, K+C222e<sup>-</sup>, show nearly metallic behavior (conductivities more than 10 orders of magnitude higher than those of the localized electrides mentioned above) and an apparent bandgap of only 0.086 eV.<sup>46</sup> This is the most conducting alkalide or electride to date with a resistivity not greater than 0.2  $\Omega$  cm at 130 K.

Four-probe single crystal conductivity studies on alkalides and electrides have not been successful due to the difficulties in attaching leads to the highly reactive and thermally unstable samples. Two-probe conductivity measurements on Na+C222Na<sup>-</sup>, which used a single crystal sandwiched between two parallel plates, demonstrated a temperature dependence at low voltages that gave the same apparent bandgap value as for powdered samples.<sup>44</sup>

Dye, Pratt and Faber conducted a preliminary thin film conductivity study on Na+C222Na<sup>-</sup> using the vapor deposition apparatus.<sup>6</sup> The study included both longitudinal and transverse measurements. Although they were not able to obtain quantitative results, the method was qualitatively shown to be promising for measuring the thin film conductivity of alkalides and electrides.

# 4. General Theoretical Models for Electrides

Until recently, most detailed theoretical calculations on electrides were impossible due to the very complex structures and large number of atoms per unit cell. Supercomputers have become more accessible of late and several groups have taken advantage of them. A general overview of the simple early theoretical models and of the most recent advances is given here.

One way to start thinking about the nature of electrides is to look at the basic building blocks and use them to construct a bigger

pict alka whe stay<sup>.</sup> ML toge elect by ti the (**M**+) evid of el the WCU infir close figu close four Jsir Tae Verj N.O.T aton desc picture.<sup>2</sup> The basic building block of electrides is the complexed alkali metal atom (ML or ML<sub>2</sub>). There are two possibilities regarding where the valence *s* electron will reside. If the valence electron stays on the metal atom inside the complexant molecule, then these ML or ML<sub>2</sub> molecules would stack together to form a solid held together by van der Waals forces. On the other hand, if the valence electron was removed from the metal atom when it is encapsulated by the complexant molecule, then the electron would reside outside the complexant, creating a metallic or ionic solid consisting of  $(M+L)e^-$  or  $(M+L_2)e^-$  molecules. Both theoretical and experimental evidence appear to agree that the latter description fits the behavior of electrides.

Another thought experiment involves looking more closely at the interactions within the (M+L) and  $(M+L_2)$  molecules and what would happen if these  $(M+L)e^-$  or  $(M+L_2)e^-$  molecules started at an infinite distance away from each other and were brought closer and closer together.<sup>2</sup> Inspection of the structure of the complexants (see figures above) shows that the most electronegative atoms are in closest contact with the encapsulated cations. A C222 molecule has four oxygen and two nitrogen atoms surrounding its cation and a pair of 18C6 molecules has 12 oxygen atoms surrounding its cation. The most electropositive atoms, hydrogens, are always around the very outside the complexant. This is the region where the electron would reside if it was ejected upon encapsulation of the alkali metal atom, keeping the entire molecule neutral. This scenario is described as an expanded atom.

ator (whe com Sinc addi shell pick Cavi of al As t elect elect Cavi meta elect Vaca dista Mair cent elect 1011 perm tapp allow electu What would happen if a large number of these expanded atoms were brought close together? In the case of an alkalide (where there are twice as many alkali metal atoms as there are complexant molecules) the answer seems fairly straightforward. Since alkali metal anions are intrinsically stable (due to the fact that adding one electron to each metal atom fills its outermost *s* orbital shell), as the expanded atoms are brought together the electrons are picked up by the metal atoms that become trapped in the periodic cavities that are created in the structure of the solid. The existence of alkali metal anions in solids is experimentally well-established.<sup>1</sup>

In the case of an electride, there are two possible scenarios. As the expanded atoms are brought closer together, the outer electrons will repel each other. In order to minimize the electronelectron repulsions, the electrons could either localize in the periodic cavities created in the structure of the solid or delocalize into a metallic state. Whether a localization or a delocalization of the electrons occurs, the distances between and the connectivities of the vacancies in the structure will be the determining factors. If the distances between trapping sites are large, the electrons may be mainly noninteracting by the formation of stoichiometric Fcenters.<sup>48</sup> F-centers in ordinary salts are usually viewed as electrons trapped in spherical wells of unit charge, they are normally found in very low concentrations and the interactions between trapped electrons are minimal. The distances between trapped electrons in the electrides, though, will be short enough to allow more than minimal interactions (especially since several of the electrides have open channels connecting the electron traps). Also,

since electrons cannot be treated classically (as anions can be treated), trapping-site-to-trapping-site mobility, similar to semiconductor behavior, and cooperative magnetic effects may be expected to occur. If the distances between the trapping sites are relatively short, the quantum mechanical wave functions of the electrons would begin to overlap strongly. This overlapping would induce cooperative behavior of the electrons and the band gap of the material would diminish. As the electron-electron overlap becomes large enough, the Mott criterion<sup>49,50</sup> may be achieved and the electride may become metallic. These compounds would be considered expanded metals since the electron-electron distances would still be larger than in normal metals.

Recently, Rencsok, Kaplan and Harrison constructed and studied a theoretical model of an isolated  $ML_2$  molecule in an attempt to gain some insight into the nature of electrides.<sup>51</sup> This model is basically a quantitative theory that simply describes the initial assumptions of the thought experiment above. A Cs+(18C6)<sub>2</sub>e<sup>-</sup> molecule was modeled by two uniformly charged spheres surrounding a Cs<sup>+</sup> ion. The electronegative oxygens were modeled by the inner sphere (radius equal to the average Cs-O distance and charge equal to -Qe). The electropositive hydrogens were modeled by the outer sphere (radius equal to the average Cs-H distance and charge equal to +Qe). The radial Schrödinger equation for the 6s wave function was solved by using numerical integration methods. The solution showed that as Q was increased from zero, the maximum in the electron wave function moved out from the center of the spheres. At a Q of only 3, the wave function maxima had moved out beyond the ring of hydrogens. This model was also applied to  $Cs^+(15C5)_2e^-$  and even better agreement with experimental values of the fractional atomic character of the compound was found. Thus, this rather crude model supports the qualitative picture described above that the electron resides outside the complexant like an expanded atom such as  $(M^+L_n)e^-$ .

Rencsok, Kaplan and Harrison also used *ab initio* Hartree-Fock calculations to model an isolated 9C3 molecule and two Li complexes  $(Li+9C3e^{-} \text{ and } Li+(9C3)_2e^{-}).^{51,52}$  As in the rather crude charged shell model, the calculations indicated that for the  $Li+(9C3)_2e^{-}$  system there is a considerable amount of negative charge on the oxygens and that the electronic wave function is expelled from the interior of the complexant. Thus, the theoretical treatments of the isolated  $(M+L_n)$  systems support the idea that the electrons are weakly bound and situated just outside the complexant in the form  $(M+L_n)e^{-}$ .

The use of supercomputers has allowed Singh, *et. al.*, to perform an *ab initio* self-consistent density-functional calculation of the electron distribution of the electride  $Cs^+(15C5)_2e^{-.53}$  The need for the supercomputer is obvious when considering the fact that the calculations were carried out by using 12,219 plane waves, 187 local basis functions and 100 occupied bands and that the unit cell contains 71 atoms. Interestingly, their calculations do not show the potential at the center of the trapped electron cavity to be a minimum (as might be expected) and it does not show any evidence for a potential barrier from the complexants that encapsulate the alkali metals (as described by Rencsok, Kaplan and Harrison above).

Actually, the calculations show a maximum in the potential at the centers of the cavities with a monotonical decrease towards the complexing molecules. How can an electron reside in a region where the potential is so repulsive? One reason given by Singh, *et. al.*, is the required orthogonality of the electronic state to the bonding molecular orbitals. This orthogonality forces the electronic state of the electride to attempt to reduce its kinetic energy by avoiding the regions of the material in the vicinity of the atoms where the potential is most attractive (near the complexants). In other words, the electron likes to stay in the very flat plateau region near the center of the cavity instead of sliding down into the potential wells near the complexants. The position atop the potential plateau would minimize its kinetic energy and, more importantly, its overall energy.

Singh, et. al., also invoke the Hubbard model to assist in their explanation of why  $Cs+(15C5)_2e^-$  is an insulator.<sup>53</sup> Their ab initio LDA calculations (above) show the electronic band to be very flat and narrow. This is analogous to the partially-filled narrow f bands in the rare-earth compounds which are also insulating. The Hubbard model, using the calculated band width and the experimentally measured antiferromagnetic coupling energy, indicates that the electride is probably insulating. I.D. Theory of Basic Optical Properties of Materials

The main optical property used in this research to characterize the alkalide and electride films is the absorbance, which is defined as:

$$ABS = -\log_{10}(I/I_{o})$$

where  $I_0$  is the intensity of the light incident upon the film and I is the intensity of the light that has passed through the film. The absorbance of a film is related to the optical constants of the material. A brief derivation of this relationship, adapted from Reference 54, will start with Maxwell's equations (in cgs units):

$$\nabla \cdot \mathbf{D} = 4\pi\rho_{\text{ext}}$$
$$\nabla \cdot \mathbf{B} = 0$$
$$\nabla \mathbf{X} \mathbf{E} = -(1/c) (\delta \mathbf{B}/\delta t)$$
$$\nabla \mathbf{X} \mathbf{H} = (1/c) (\delta \mathbf{D}/\delta t) + (4\pi/c) \mathbf{J}.$$

Assume that  $\mu = 1$  in the constitutive relation  $\mathbf{B} = \mu \mathbf{H}$  (which is appropriate for nonmagnetic materials). Recall that the other constitutive relation is  $\mathbf{D} = \varepsilon \mathbf{E}$ . Set  $\rho_{\text{ext}}$  and J to zero (this assumes the material is an insulator and there are no external sources of charge or current). Assume plane wave solutions of the form:

$$\mathbf{E} = \mathbf{E}_{o} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$$
$$\mathbf{H} = \mathbf{H}_{o} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)].$$

Substitution of these solutions into Maxwell's equations yields:

$$\epsilon \mathbf{k} \cdot \mathbf{E} = 0$$
$$\mathbf{k} \cdot \mathbf{H} = 0$$
$$\mathbf{k} \mathbf{X} \mathbf{E} = (\omega/c)\mathbf{H}$$
$$\mathbf{k} \mathbf{X} \mathbf{H} = -(\omega/c)\epsilon \mathbf{E}.$$

Use of the vector identity  $\mathbf{k} \times \mathbf{k} \times \mathbf{E} = \mathbf{k}(\mathbf{k} \cdot \mathbf{E}) - (\mathbf{k} \cdot \mathbf{k})\mathbf{E}$  and several substitutions yield a dispersion relation,  $\mathbf{k} \cdot \mathbf{k} = \mathbf{k}^2 = \varepsilon(\omega/c)^2$ , which relates the spatial variation of  $\mathbf{k}$  with the time variation of  $\omega$ . A complex index of refraction, n, is defined in terms of the magnitude of  $\mathbf{k}$ :  $\mathbf{n} = \mathbf{k}(c/\omega) = \mathbf{n}_1 + \mathbf{i}\mathbf{n}_2$ . Since  $\varepsilon$  and  $\mathbf{k}$  are, in general, complex, the dispersion relation can now be rewritten in the form:  $\varepsilon = \mathbf{n}^2 = (\mathbf{n}_1 + \mathbf{i}\mathbf{n}_2)^2$ . Thus, the real and imaginary parts of the dielectric function are:

$$\epsilon_1 = n_1^2 - n_2^2$$
  
 $\epsilon_2 = 2n_1n_2.$ 

The usefulness of the complex n is apparent when the spatial dependence of the fields is written in terms of  $n_1$  and  $n_2$ :

$$\exp(ikz) = \exp[i(\omega/c)n_1z] \exp[-(\omega/c)n_2z].$$

This shows that the real component of n determines the phase velocity and that the imaginary component determines the spatial decay of the wave.

The intensity loss of a wave propagating through a material is defined as the attenuation coefficient  $\alpha$ :

$$\alpha = -(1/I) (dI/dz)$$
  
or  
 $I(z) = I(0) e^{-\alpha z}$ .

Using the fact that the intensity depends on the square of the fields, it is found that  $\alpha = 2\omega n_2/c$ . It is now easy to see that the absorbance is related to the attenuation coefficient by:

$$ABS = \alpha z / 2.303$$

where z is the thickness of the material that the wave has propagated through.

Another quantity of interest is the reflectance, R, of a material. R is defined as the intensity of the reflected wave divided by the intensity of the incident wave at normal incidence. Examination of the continuity of the components of E and B at the boundary between the vacuum and the material and the realization that the intensity depends on the square of the fields gives:

$$R = E_{ref} * E_{ref} / E_{inc} * E_{inc} = [(n_1 - 1)^2 + n_2^2] / [(n_1 + 1)^2 + n_2^2].$$

It is possible to obtain  $n_2$  by measuring the attenuation coefficient (or absorbance, A). Then,  $n_1$  can be obtained by using  $n_2$  and the measured frequency dependent R. All other optical constants can then be determined from these two quantities.

Oscillator strengths also divulge information regarding the optical transitions in a material. Examination of a simple model will reveal some insight into the content of this information.<sup>54</sup> Consider a Lorentz (damped harmonic) oscillator. Electrons are bound to their cores by harmonic forces (force constant  $\gamma$ ) in an externally applied field, **E**. The equation of motion is given by:

$$m[(d^2\mathbf{r}/dt^2) + \gamma(d\mathbf{r}/dt) + \omega_0^2\mathbf{r}] = -e\mathbf{E}$$

where m and e are the mass and charge of a bound electron, respectively, and  $\omega_0$  is the natural oscillator frequency. Allowing E to vary harmonically in time with frequency  $\omega$  (E = E<sub>0</sub>e<sup>-i $\omega$ t</sup>) and solving for the displacement r with the form r = r<sub>0</sub>e<sup>-i $\omega$ t</sup>:

$$\mathbf{r} = -(\mathbf{e}\mathbf{E}/\mathbf{m}) / (\omega_0^2 - \omega^2 - i\gamma\omega).$$

To put this response in terms used in the definition of the oscillator strength, the polarization (P = erN/V, where N/V is the number of oscillators per unit volume), the susceptibility ( $P = \chi E$ ) and the relation between the dielectric constant and the susceptibility ( $\epsilon = 1 + 4\pi\chi$ ) are used to show:

$$\varepsilon = 1 + (4\pi e^2 N/mV) [1/(\omega_0^2 - \omega^2 - i\gamma \omega)].$$

Now, suppose that the N molecules per unit volume have Z electrons per molecule and that, instead of a single binding frequency for all, there are  $f_j$  electrons per molecule with binding frequency  $\omega_j$  and damping force constant  $\gamma_j$ , then the dielectric constant becomes

$$\epsilon = 1 + (4\pi Ne^2/mV) \Sigma_j f_j (\omega_j^2 - \omega^2 - i\omega\gamma_j)^{-1}$$

where the oscillator strengths  $f_j$  satisfy the sum rule  $\Sigma_j f_j = Z.^{55}$  Thus, if the total oscillator strength, f, could be calculated from the optical absorbance spectra, the number of electrons participating in the transition could be determined. The relationship that allows this calculation to be made is (in SI units):

$$f = (4mc\epsilon_0/Le^2) \tilde{A}$$

where L is Avagadro's number,  $\varepsilon_0$  is the permittivity of free space and  $\tilde{A}$  is the integrated absorbance coefficient ( $\tilde{A} = \int ABS(v) dv$  since the optical absorptions are spread over a range of frequencies).<sup>56</sup>

## I.E. Rationale

The main purpose of the research presented in this dissertation was to expand the amount of information known about the optical and electrical properties of an alkalide and an electride and try to use this information to improve our understanding of alkalides and electrides, in general. The alkalide, Na+C222Na<sup>-</sup> was

chosen because it is relatively stable and it is the best-characterized alkalide. The electride, K+C222e<sup>-</sup>, was chosen because it is the most conducting electride. Modifications to the existing vapor deposition apparatus were made to assist in the pursuit of the main purpose. This work presents a detailed description of the results and modifications.

The past results of thin film optical absorbance studies and thin film electrical conductivity measurements on alkalides and electrides indicated the need for a more detailed study of the optical and electrical properties of these unique compounds. Also apparent was the need for better measurement techniques and instrumentation. This work will focus on detailed studies of an alkalide (Na+C222Na<sup>-</sup>) and an electride (K+C222e<sup>-</sup>) which use improved and new measurement techniques. In the Appendix, an optical and electrical study on a series of pseudo-buckyball precursor compounds will be presented.

#### II. EXPERIMENTAL: VAPOR DEPOSITION APPARATUS

This chapter will detail the development and present status of the entire vapor deposition apparatus. The development of the apparatus prior to the present work was performed mainly by Margaret K. Faber, Joseph B. Skowyra and Dr. William P. Pratt, Jr.<sup>6,42</sup> The first two sections of the chapter describe the physical characteristics of the basic vacuum chamber and evaporation system. The last three sections explain how the different characterization experiments (optical absorbance, photobleaching and conductivity) were carried out. The following chapters will present the results and the discussions of the characterization experiments.

#### II.A. Vacuum Chamber and System

A Perkin-Elmer (Ultek Model MX-14) high vacuum system is the basis of the vapor deposition apparatus. The Ultek system consists of three main sections: the glass bell jar, the stainless steel feedthrough collar and the vacuum pumps (Figure 9). The top section of the system is a glass bell jar measuring 14 inches in diameter and standing 24 inches high. An aluminum screen-like shield protects the glass jar. The bell jar and screen lift off the middle section of the system, a stainless steel feedthrough collar, by use of a pulley system attached to the ceiling. The feedthrough collar section uses eight copper-gasketed, 2.75-inch conflat ports to





allow electrical, fluid and gaseous access into and out of the vacuum system. The feedthrough collar rests on a poppet valve assembly. The poppet valve separates the upper and lower portions of the **vacuum system.** This separation allows the upper chamber to be at a tmospheric pressure while maintaining a high vacuum in the lower **chamber.** The vacuum seals between the bell iar and feedthrough **collar** and between the feedthrough collar and poppet value are Viton L-boot gaskets. The bottom section of the system consists of two types of vacuum pumps. The rough pump is an Edwards direct**drive** mechanical pump (Model #5). A liquid nitrogen trap prevents oil from contaminating the high vacuum chamber. A Varian TC **vacuum** gauge (Type #0531) monitors the pressure during the roughing stage of evacuation. The rough pump evacuates the upper chamber down to a pressure between  $10^{-2}$  and  $10^{-3}$  Torr. The high vacuum pump is a CTI-Cryogenics cryopump system (ON-BOARD Model #8). A Varian ionization gauge (Model #880) monitors the pressure of the bell jar during the high vacuum stage of evacuation. The vacuum chamber consistently reaches pressures of 10-7 Torr.

Such low pressures are necessary for the thermal vapor deposition of materials. Once the materials are vaporized, long mean free paths and straight line geometries for the vapor molecules are essential. A long mean free path means that the molecules will not collide and react with any of the other molecules in the vacuum nor will they collide and change direction. The approximate mean free for air molecules in a vacuum of 10<sup>-7</sup> Torr at room temperature is Steater than 10 m.<sup>56</sup>

## II.B. Evaporation System

The core of the evaporation system is a multi-chambered oven assembly which allows the thermal evaporation of the alkali metals and a wide variety of organic complexants onto a cold substrate inside the vacuum system. Figure 10 shows a schematic diagram of the heart of the evaporation system: two of the four oven chambers and the rotatable LN2-cooled copper block that holds the substrate. Each oven contains an evaporation source boat at the bottom of the chamber and has several openings at the top of the chamber. The chambers are approximately 25 cm high. The source boats are made of tantalum and are from the R. D. Mathis Company. The boats used for evaporating the alkali metals are simple covered evaporation boats (Figure 11a). These boats evaporate the alkali metals when resistively heated by the passage of a large current through the thin metal boats. The boat used for evaporating the complexants is a baffled-box evaporator (Figure 11b). The baffling assures that no splattering of complexant onto the substrate occurs. The complexant boat sits on a thermoelectric cooler or TEC (Borg-Warner Thermoelectrics Model 930-71). A water-cooled copper block sits below the TEC and acts as a heat sink or source. The TEC cools the volatile complexants during evacuation of the chamber. This cooling assures that there is complexant remaining in the source boat after the vacuum system has brought the chamber down to base pressure. The TEC then heats and vaporizes the complexants during the evaporation process.

40



Figure 10. Diagram of the sample preparation chamber. Only one of the three metal ovens is shown.



a.) Resistively Heated Akali Metal Boat



b.) Baffled Complexant Boat

Figure 11. Source boats for resistive heating.

A Vacuum Atmospheres helium-filled glove box stores the alkali metals and organic complexants. The complexants are transferred from the glove box and loaded into the bell jar under atmospheric conditions. The complexant boat is then secured to the TEC. The metals are cut and loaded into the source boats inside the glove box. The metal is covered with purified octane while still inside the glove box. The octane protects the alkali metals during the transfer from the glove box to the bell jar under atmospheric conditions. The boats are secured into place in the resistive heaters and then the bell jar is lowered and the chamber is evacuated. The mechanical pump removes the octane quickly. This method works well for Li, Na, K and Rb. The reactivity of Cs requires a different method to be used to load pure Cs into the bell jar. A speciallymade boat cover allows the attachment of a Teflon tube. The Csfilled boat and special boat cover are enclosed in a resealable plastic bag inside an argon-filled glove box. The bag and its contents are transferred to the bell jar under atmospheric conditions. The Teflon tube protrudes from the bag. The tube is connected to an argon gas source that emanates from inside the bell jar and a slight flow is allowed to wash over the liquid Cs. The plastic bag is removed, the **boat** is placed in the resistive heater and then the bell jar is closed and roughed out. As the pressure decreases, the flow of argon is reduced until it is eventually shut off just before the high vacuum **poppet valve is opened.** Thus, all of the alkali metals (except for the radioactive one) are in the deposition system's arsenal.

The source boat temperatures are computer-controlled. Instructions entered into an IBM PC-XT vary the voltage to the TEC and the current to the resistively heated boats. There is a speciallydesigned attachment for the thermocouple on the bottom of the resistively heated boat which allows its temperature to be monitored during deposition.

An LN2-cooled copper block holds the substrate using flexible metal clips. A small amount of grease provides the thermal contact between the copper block and substrate. The block has a hole through it which allows light to pass. A mechanically rotatable feedthrough allows the copper block to rotate through an angle of approximately 260°. This rotation allows the positioning of the substrate over any of the source boats or into the light path for optical transmission. The substrate slides are cleaned with a suitable solvent in an ultrasonic cleaner.

The original substrate material was fused silica (Heraeus-Amersil, Inc.). These substrates were 1 inch by 3 inches by 2 mm in size (microscope slides). It was noticed during the early research of the present work that occasionally the reactive films would thermally decompose at temperatures that should have been cold enough to keep them alive. One possibility for this behavior is that the temperature of the copper block is not the same as the temperature of the film at the center of the substrate. There is no <sup>CO</sup>pper in thermal contact with the substrate directly behind the part of the film that is being optically studied (Figure 12). This means that the fused silica must transfer the heat from the film for <sup>Sev</sup>eral centimeters before dumping it into the grease film and <sup>CO</sup>pper block. Perhaps the heat was not being conducted away from the film quickly enough.



Figure 12. View of the bottom of the copper block with the original substrate holder (flexible metal clips).

A study of the effect of different thermally conducting greases was carried out. The greases studied were: Apiezon N, Apiezon H, Wakefield Thermal Compound and Corning High Vacuum Silicone Grease. An epoxy (Hardman Adhesives) made thermal contact between a thermocouple and the center of the substrate. The actual substrate temperature  $(T_s)$  was compared to the thermocouple reading from the side of the copper block  $(T_b)$ . Figure 13 shows a typical data set from this study (the grease used was Apiezon N for this example).  $T_s$  is always warmer than  $T_b$  and the deviation becomes enormous when cooled below -65 °C. Each grease had its own "breakaway" temperature. The range of "breakaway" values varied with the different greases from -50 °C to -70 °C. If the temperature is held constant at a value warmer than the "breakaway" temperature, eventually  $T_s$  will reach  $T_b$ . If the temperature is held constant at a value lower than the "breakaway" temperature, though,  $T_s$  never reaches  $T_b$  and sometimes  $T_s$  even begins to warm. The "breakaway" temperature of each of the greases was very close to each of their freezing or solidification temperatures. Most thermal greases are designed to behave properly (low outgassing and good thermal conductivity) at temperatures much higher than room temperature.

The problem appeared to be centered around the solidification of the grease. Two other factors seemed to contribute to the problem also: surface area and differential contraction. After the grease becomes a solid, the copper and fused silica continue to thermally contract as the temperature continues to decrease. The surface area of the grease-filled interface is relatively large (1 inch



Figure 13. Temperature of the center of the substrate  $(T_s)$  plotted versus the temperature of the copper block  $(T_b)$  with the original substrate holder. The straight line represents the ideal situation  $(T_s = T_b)$ .

by 3 inches of substrate minus the 1 cm by 3 cm hole in the copper block). The thermal expansion (or contraction) constants for the two materials are quite different (1.66 x 10<sup>-5</sup>/°C and 5.5 x 10<sup>-7</sup>/°C for Cu and fused silica, respectively<sup>57</sup>). Thus, the differential contraction of the two materials over such a large lateral distance may force the solid film of grease to separate from one of the two materials. This separation or loss of thermal contact would substantially decrease the amount of heat that the block could conduct away from the substrate and film.

The thermal grease study indicated that a new substrate was needed, not a new grease. A substrate with a much smaller lateral length would decrease the differential contraction problem, as would a much better thermally conducting substrate material. The small (0.5 inch by 0.5 inch by 1 mm) sapphire substrates were a gift from researchers in the Physics and Astronomy Department who use the department's ultra-high vacuum sputtering apparatus. Sapphire is a much better thermal conductor than fused silica (0.099 cal cm / cm<sup>2</sup> °C sec for the sapphire versus 0.0033 cal cm / cm<sup>2</sup> °C sec for the fused silica<sup>57</sup>). A new substrate holder was designed and built (Figure 14). The holder attaches to the bottom of the copper block and clips the new substrate underneath itself. The hole for optical measurements is 0.375 inch by 0.375 inch. Corning High Vacuum Grease provides the thermal contact to the copper holder. The  $T_s$ versus  $T_b$  study on this new set-up did show that  $T_s$  is still slightly warmer than  $T_b$ , but there was no large temperature difference breakaway even down to -100 °C (Figure 15). Also, when the temperature was held constant between 25 °C and -100 °C, T<sub>s</sub>



Figure 14. View of the bottom of the copper block with the new substrate holder. Small metal clips (not shown) hold the sapphire substrate in place.



Figure 15. Temperature of the center of the substrate  $(T_s)$  plotted versus the temperature of the copper block  $(T_b)$  with the new substrate holder. The straight line represents the ideal situation  $(T_s = T_b)$ .

always slowly cooled to  $T_b$ . Thus, the film temperatures reported in this dissertation refer to  $T_b$ , but unless otherwise noted they are assumed to be nearly equal to  $T_s$ .

A Temescal (Model #3000) quartz crystal film thickness monitor (FTM) samples the vapor stream from each oven and another is attached to the side of the substrate block (Figure 10). The cooled Temescal monitors measure the deposition rates (angstroms per second) of the streams of vapor as well as the total Having the FTM's at low temperature avoids thicknesses. inaccuracies due to the re-evaporation of molecules and atoms from the FTM's during deposition. Thermocouples constantly display the temperatures of each of the FTM's. The FTM at the substrate level calibrates the tooling factors for each of the FTM's in the ovens. The advantage of having the FTM's in the vapor streams is that the fluctuating deposition rates can be accurately monitored during the evaporation process instead of assuming that the rates remain constant. Deposition onto the substrate begins after the evaporation rate reaches a steady state. The thickness ratio desired to obtain the correct stoichiometry of the films is calculated using the following:

(Moles M/Moles C) =  $[A_M T_M \rho_M (MW_M)^{-1}]/[A_C T_C \rho_C (MW_C)^{-1}]$ or  $T_C/T_M = (Moles M/Moles C) \cdot (\rho_M MW_C/\rho_C MW_M)$ 

where T = film thickness,  $\rho$  = density, MW = g/mole, A = area of film (assumed to be the same for the metal and the complexant, A<sub>C</sub> = A<sub>M</sub>) and M and C represent the metal and the complexant, respectively.

There are two copper chimneys for the complexant oven (one each for the codeposition configuration and the sequential deposition configuration). The codeposition chimney is shown in Figure 10. The chimneys are attached to the FTM for the complexant oven. The thermal contact with the cooled FTM keeps the chimney cold during deposition. The chimney captures all of the complexant vapor that is not heading directly to either the substrate or the FTM. Thus, the volatile complexing molecules are not allowed to adsorb on other walls and then desorb from these walls and end up on the substrate or the FTM crystal (which would alter the measured deposition rate of complexant onto the substrate). Chimneys are not necessary for the metal ovens since any metal atoms that adsorb onto any wall will not desorb at room temperature.

During the early work of the present research, it was noticed that the oscillator strength of the absorbance spectra of films of Na+C222Na<sup>-</sup> was usually less than one (the value should be equal to 2.0). Examination of the complexant spot on the substrate suggested that the codeposition chimney was not aligned properly. The optical absorbance spectra were being taken on portions of the films that were not receiving the stoichiometric amount of complexant. A slight modification of the alignment of the chimney corrected this problem.

Film impurities formed during deposition from the partial pressures of  $H_2O$ ,  $N_2$  and  $O_2$  were kept to a minimum with low pressures and fast deposition rates. A residual gas analyzer showed that approximately 95% of the gaseous impurities are  $H_2O$ . Using simple ideal gas law calculations, it can be shown that the deposition

rate of impurity air molecules impinging on a surface at a pressure of 10<sup>-7</sup> Torr is approximately 0.044 monolayers/sec.<sup>58</sup> This calculation assumes that each impinging molecule sticks to the surface. A typical combined metal and complexant deposition rate of about 10 Å/sec would produce a 1000 Å film in less than 2 minutes. Thus, less than the equivalent of three or four monolayers of impurities would be distributed throughout the fairly thick film. The constancy of the absorbance spectra of the Na<sup>+</sup>C222Na<sup>-</sup> films after preparation suggests that the sticking probability coefficient of reactive molecules, such as H<sub>2</sub>O, is much lower than unity.

Two methods are used to synthesize alkalide and electride films: codeposition and sequential deposition. Codeposition uses two adjacent ovens (one metal and one complexant) where the wall between the ovens is partially cut away which allows the substrate to be positioned at the confluence of the two vapor streams. Sequential deposition alternately deposits layers of the metal and layers of the complexant until the film contains as many layers as desired. This layering is accomplished by moving the substrate back and forth between the various sources. The layering technique relies on the complexation reaction occurring between the layers in the solid state on the surface of the cooled substrate. This is in contrast to the codeposition synthesis where the solid state reaction takes place between the more intimately mixed and more thermodynamically active components.
### II.C. Optical Absorbance Measurement System

Faber and Dawes tried many times to remove the thin alkalide and electride films from the vapor deposition system for *ex situ* measurements.<sup>6</sup> They attempted to coat the films with two different materials, SiO and undyed paraffin wax, that would protect the reactive films from exposure to  $H_2O$  and  $O_2$ . The numerous attempts were mainly unsuccessful. The blackbody radiation from the SiO source boat (850 °C) decomposed the samples upon coating and the paraffin wax coating was too uneven (allowing penetration of  $H_2O$ and  $O_2$ ). A more successful attempt used a mechanical trapping device. A cover plate that pressed firmly against the substrate material made a vacuum seal with a Viton O-ring. Several of the films survived outside of the bell jar for one to two minutes before decomposing. Many mechanical difficulties prevented this method from becoming a standard procedure.

Steps were taken during this research to pursue the goal of *ex situ* measurements. A cylindrical glass jar and stainless steel top were purchased. Conflat feedthrough ports were attached to the steel top in hopes of designing an evacuable port that the films could somehow be brought into for removal from the vacuum chamber. The films could then be transferred under vacuum conditions into the helium-filled glove box for study. This method appears to be promising and should be pursued further.

The optical absorbance measurement system used during the early research presented in this dissertation for the *in situ* study of the thin films is shown in Figure 16. The light source is a 100 W





Aries Quartz Tungsten Halogen lamp in a Universal lamp housing (Model 40-130). A dc regulated power supply controls the lamp. An Optical Engineering attenuator chops the light beam and provides the source frequency for the lock-in amplifier. A Jarrell-Ash Model 82-000 series Ebert Scanning monochromator with an f number of 8.6 monochromates the light beam. Two Jarrell-Ash diffraction gratings (Model 980-28-20-22 with 1180 grooves/nm and Model 980-28-40-30 with 295 grooves/nm) are used to monitor wavelengths ranging from 450 nm to 2200 nm. The light enters the deposition system through a sapphire window conflat. An aluminum light pipe then directs the light up through the film, substrate and the hole in the copper block into a photodetector. The photodetector is a Kodak Ektron PbS detector housed in a vacuum can along with a self-zeroing pre-amplifier circuit. An instrumentation feedthrough transmits the signal from the pre-amplifier to the lock-in amplifier. Instructions entered into Labtech Notebook software on an IBM PC-XT start the monochromator's stepper motor and record the output voltages at preset wavelength step sizes into data files. A single scan of 150 data points from 450 nm to 2200 nm takes nearly 20 minutes to complete (this includes the time necessary to change the gratings at 900 nm). This long scan-time and the extreme reactivity of the films raised the question: Is the film the same film from beginning to end of the optical scan? Skowyra showed that at cold enough temperatures in the vacuum system the films were stable enough for reproducible scans.<sup>42</sup> The reference spectrum of the substrate is taken prior to the deposition of the film. These voltage versus wavelength values are defined and recorded as  $V_0$ . The

voltage versus wavelength values for the light passing through the deposited film and substrate are defined and recorded as  $V_i$ . The absorbance, ABS, of a particular film is then calculated for each wavelength using the two data files by ABS =  $-\log_{10}(V_i/V_0)$ . The known spectrum of a didymium oxide glass filter was used to calibrate the wavelengths. Neutral density filters calibrated the absorbances.

During the course of the present research, a new optical absorbance measurement system replaced the system described above. The Guided Wave Model 260 Spectrophotometer contains the tungsten lamp, the grating, the chopper, the lock-in amplifier and two photodetectors. Fiber optic cables carry the light out of and into the spectrophotometer. The bare fibers are 500  $\mu$ m in diameter. A vacuum feedthrough was designed for the fiber optic cables (Figure 17). Two thin stainless steel tubes were welded onto a conflat flange shaft. The fibers were then epoxied (Torr Seal<sup>®</sup> low vapor pressure resin) into the steel tubes. The epoxy also produces a vacuum seal around the fibers. A collimating lens at the end of one of the fibers inside the vacuum system directs the light through the film and substrate. Another collimating lens at the end of the other fiber collects the transmitted light and focuses it back down onto the fiber. The light then travels back outside the bell jar and into the spectrophotometer for analysis. An IBM-compatible 286 computer controls the spectrophotometer and stores the absorbance versus wavelength data files. A typical scan of 200 data points between 450 nm and 2200 nm takes approximately one minute. This short



Figure 17. Diagram of the home-made vacuum feedthrough for the fiber optic cable of the new optical analysis system.

scan-time would allow kinetic studies to be performed on these very reactive films at elevated temperatures, if desired.

Didymium oxide and holmium oxide filters calibrated the wavelengths of the Guided Wave system. Neutral density filters calibrated the absorbance spectra. Blank experiments (scan through the sapphire substrate only) demonstrated a slight temperature dependence of the background absorbance. As the substrate temperature decreases, the background absorbance increases slightly.

The older optical system was kept integrated into the system. Plans for photoemission studies and photoconductivity studies require its services. The Guided Wave sends white light through the fiber optic cables and film/substrate for analysis, whereas the monochromator system emits only a specific wavelength of light. A photoemission or photoconductivity study would look at the electron emission current or the conduction current, respectively, as a function of incident photon energy. These studies are not possible with the Guided Wave spectrophotometer. Of course, having both optical systems in the evaporator increases its versatility.

#### II.D. Photobleaching Set-up

A photobleaching experiment assisted in the analysis of the electronic structure of the alkalide, Na+C222Na<sup>-</sup>. This experiment used three different light sources and set-ups.

The first photobleaching light source is a small Uniphase (Model #155A) He-Ne laser (632 nm, 0.5 mW continuous,  $1.6 \times 10^{15}$ 

photons per second, 0.6 mW/mm<sup>2</sup>). Ring stands and clamps hold the laser horizontally outside the bell jar and direct the beam through the glass wall of the jar. A small aluminized mirror situated in the bottom of an unused oven chamber directs the laser beam vertically through the chamber and then through the film and substrate. The size of the laser beam is approximately 1 mm in diameter. The size of the optical analysis light beam is approximately 9.5 mm in diameter. To assure that a large enough portion of the film was affected by the laser beam for proper analysis, the laser was moved manually to produce a slow rastering motion of the beam across the film.

The second photobleaching light source is a home-made Xenon flash lamp (0.5 mJ/mm<sup>2</sup> per pulse, 17  $\mu$ s pulses, 1.4 x 10<sup>15</sup> photons per pulse, 15 W/mm<sup>2</sup> per pulse). The flash lamp is set up in approximately the same position as the He-Ne laser. The physical size of the flash lamp allows it to be situated directly on the floor and still have the beam aimed directly into the bell jar. Ring stands were not necessary as in the case of the He-Ne laser. A simple electronic circuit allows the production of single flashes of the lamp with a push of a button. The spot size of the Xenon flash is much larger than the size of the film on the substrate. Each flash illuminates the entire film.

The final photobleaching light source is a Spectra Physics Nd:YAG (Quanta-Ray Model #DCR-11) pulsed laser (3 W average at 10 Hz, 7 ns pulses, 7.5 mJ/mm<sup>2</sup> per pulse, 1 x  $10^{18}$  photons per Pulse, 10 MW/mm<sup>2</sup> per pulse). The laser is portable and resides on a large cart that allows variation of the vertical height of the laser.

The physical size of the laser and cart combination does not allow the laser beam to be aimed directly into the bell jar. A Newport front surface 45° mirror situated outside the bell jar directs the beam into the jar through the glass wall (Figure 18). An identical mirror is situated inside the bell jar at the bottom of an unused oven and directs the beam vertically through the chamber and then through the film and substrate. Pairs of the mirrors were purchased specifically for each of the Nd:YAG harmonic lines (355 nm, 532 nm and 1064 nm). The size of the laser spot is nearly identical to that of the analysis light beam. The laser has a low intensity, long pulse mode for aligning the beam (10 Hz, 75 ms pulses).

The photobleaching experiments usually consist of three main parts. First, a thin film of an alkalide or electride is produced on the substrate and then analyzed with the optical absorbance system. Second, the film is rotated until it is positioned in line with the interior mirror and then one of the three light sources applies a pulse or series of pulses to the film. Third, the film is analyzed with the optical absorbance system again. The second and third steps are repeated indefinitely (usually until the film is destroyed).

### II.E. Conductivity Measurement System

A new approach to measuring the conductivity of the **deposited** thin films of alkalides and electrides was developed due to the problems that Faber encountered.<sup>6</sup> Faber found that the **alignment** of the masks for *in situ* deposition of silver electrodes was **very** difficult. Many times the silver electrodes did not make good



Figure 18. Schematic diagram of the placement of the Nd:YAG laser and front-surface mirrors for the bleaching experiments. The dashed line represents a horizontal beam path which actually travels perpendicular to the plane of the page. electrical contact to the appropriate wires that were soldered onto the substrate in both the longitudinal and transverse experiments. Also, the deposition of the second silver electrode in the transverse experiments usually decomposed the alkalide or electride film due to the blackbody radiation from the extremely hot silver source boat.

For the present research, gold electrodes for longitudinal conductivity measurements were thermally deposited onto the sapphire substrates prior to use in the vapor deposition apparatus. The electrodes consisted of 50 Å of chrome and 200 Å of gold. The chrome was necessary since gold will not stick to the sapphire alone. The specific thickness of the gold was chosen to assure a continuous film while using a minimum amount of gold. Three different masks were designed (see detailed descriptions below). The masks were constructed out of thin pieces of stainless steel. Fine gold wires connect the electrodes to Samtac pin connectors (Figure 19). A silver conducting epoxy (Tra-Con BIPAX<sup>®</sup>) attached the fine gold wires to the electrodes and the Samtac pin connectors. Epoxy (Hardman Adhesives) held the pin connectors to the outside edges of the substrate. These pin connectors allowed easy attachment of the circuitry wires required for all of the electrical measurements.

The basic equation for the resistivity of a conducting material is  $\rho = R A / I$ , where R is the resistance of the material, A is the **Cross-sectional** area that the current is passing through and I is the **Conduction** path length. For a thin film, A becomes the thickness of **the** film (t<sub>f</sub>) times the width of the film (w<sub>g</sub>).



Figure 19. Diagram of the two-probe, comb electrodes on the sapphire substrate. The Samtacs are epoxied to the substrate and the wires plug into them. A fine gold wire connects the large Samtacs to the chrome/gold electrodes. The places where the flexible metal clips hold the substrate are shown.

### 1. Two-Probe

Two different two-probe masks and substrates were designed and made. Figures 19 and 20 show the designs of the different twoprobe electrodes.

The electrodes shown in Figure 19 have an intertwining comblike design. The conduction path is only 0.4 mm long at all points, but the width of this path is very wide (32 mm) and tortuous due to the interlaced comb teeth. The purpose of this design was to try to minimize the resistance of the sample and, thus, to maximize the amount of current through the sample. A small I and a large  $w_g$  (for a given  $\rho$ ) would give a smaller R and, for a specific voltage, would give a larger current. This would facilitate the measurement of the relatively large resistivities in the thin semiconductor-like films.

The electrodes shown in Figure 20 have two different path lengths, but similar widths (9 mm). The wide path length (0.8 mm) is twice the width of the narrow path length (0.4 mm). The purpose of this design was to look for resistive electrode/sample interface effects. The resistivity of the thin film should be the same over the entire electrode area, but the path length difference between the two sides should make the resistance of the wide side twice that of the narrow side.

Figure 21 shows the amplification circuit used in the twoprobe conductivity measurements. Two 15 V power supplies provide either positive or negative bias. A switch toggles between the two polarities. Another switch toggles between the bias voltage and ground. This allows the system to be calibrated periodically



Figure 20. Diagram of the chrome/gold electrodes on the substrate for two-probe measurements with two different conducting path lengths.



Figure 21. Schematic representation of the electronic circuit for the measurement of two-probe conductivity as described in the text.

during an experiment. A variable resistor regulates the bias voltage from 0 to 15 V. When electrodes with different path lengths are used, another switch toggles between the two sides. Only one side is biased at a time, but the switch allows the same voltage to be used on either side. This switch is not necessary when the comb-like electrodes are used since there is only one electrode to bias.

An instrumentation feedthrough brings the two bias voltage wires into the bell jar. Depending on which set of electrodes is being used, one wire is, or both of the wires are, attached to the pin connector, or connectors, on the substrate. Another wire is attached to the anode pin connector. This wire carries the current that passes through the sample due to the bias voltage to a simple current-tovoltage amplification circuit. The anode wire is kept as short as **possible** to avoid picking up and amplifying any background noise. The amplification circuit employs an operational amplifier (Model **#AD515AJ**) and several feedback resistors. One of the two feedback resistors (and, thus, one of the two amplifications) must be chosen **prior** to the start of the experiment. The  $10^6 \Omega$  and  $10^9 \Omega$  resistors **provide amplifications of 10^6 and 10^9, respectively.** For example, if the  $10^9 \Omega$  resistor was used and a current of 5 picoamperes was being measured, the output voltage of the amplification system would be 5 V. The output voltage was read with a voltmeter (Fluke <sup>80</sup>OOA digital multimeter) and recorded as a function of time with an XY recorder (Linseis Model #LY18100).

# 2. Four-Probe

Figure 22 shows the electrode design for the four-probe substrate. The distance between  $I_+$  and  $V_+$  and  $I_-$  and  $V_-$  is 0.25 mm and between  $V_+$  and  $V_-$  is 0.75 mm. The width of the long parts of the electrodes is 5 mm. A four-probe measurement eliminates the problem of electrode/sample interface resistance. The current is introduced into the sample through the outer electrodes and the inner electrodes only sample the voltage drop between them. The working current does not flow in or out of the voltage leads and, thus, the electrode/sample interface does not contribute to the measurement.

A 17 Hz conductance bridge (S.H.E. Model PCB clone) is used to **make** both four-probe and two-probe measurements with this **substrate**. An instrumentation feedthrough brings the four wires **into** the bell jar. The four wires are then connected to the pin **Connectors** on the substrate. In the four-probe mode, the current is **sent** in through I<sub>+</sub> and out through I<sub>-</sub>. V<sub>+</sub> and V<sub>-</sub> then measure the **vol**tage drop across the sample and the four-probe conductance (1/R) of the sample is displayed. The bridge also allows two-probe **Conductances** to be measured and displayed. Four different sets of **electrodes** can be chosen for two-probe measurements:  $I_+/V_+$ ,  $I_-/V_-$ ,  $V_+/V_-$  and  $I_+/I_-$ . For each of these sets, the voltage drop is **measured** across the same two electrodes where the current is being **introduced** into and removed from the sample. An XY recorder plots **the** conductance versus time during the experiment.



Figure 22. Diagram of the sapphire substrate with the chrome/gold electrodes for four-probe conductivity measurements.

III. Na+C222Na<sup>-</sup>

### III.A. Introduction

Na+C222Na<sup>-</sup> has been studied more than any other alkalide or electride. Not only was it the first member of this new class of compounds, but it is the most stable. Thin films of this sodide (or natride) survive for several weeks at room temperature in the evacuated vapor deposition system. The slow decay of its absorbance peak appears to be due to surface contamination that eventually propagates through the film. This contamination is presumably from the small residual partial pressure of water in the jar. Experiments on the films are normally performed before the degradation becomes significant. Most other alkalides and electrides irreversibly decompose at temperatures above -40 °C, even under Vacuum.

Every type of characterization used on alkalides and electrides has been used on Na+C222Na<sup>-</sup>. This sodide is the model for describing the "typical" alkalide, even though each new measurement seems to show how much more complicated the compound really is. Optical and electrical measurements have always been major contributors to the characterization of alkalides and electrides. These studies divulge information regarding the electronic structure of each of the materials.

The earliest optical absorbance spectra of Na<sup>-</sup> in solution showed a single peak at approximately 650 nm (1.9 eV,  $1.5 \times 10^4$ 

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cm<sup>-1</sup>).<sup>14</sup> Thi is a good com solution and ± 0.2 was of just what is its ground s Optica by solvent position as 1.9 x 104 c cm<sup>-1</sup>).37 Th Na<sup>-</sup> nor in c from powd eV. This ev <sup>being</sup> the r The p good stoic absorbance spectra.40 deposition <sup>were</sup> planı Fabe and nearly <sup>spectra</sup> ve evaporate <sup>spectra</sup> or <sup>small</sup> pea cm<sup>-1</sup>).<sup>14</sup> This peak was assigned to the  $3s^2$  to 3s3p transition. There is a good correlation between the absorbance peak position of M<sup>-</sup> in solution and that of the gaseous atom.<sup>1</sup> An oscillator strength of 1.9  $\pm$  0.2 was obtained for the Na<sup>-</sup> absorbance peak in solution (this is just what is expected for a species with two equivalent electrons in its ground state outer shell).<sup>59</sup>

Optical absorbance spectra of Na<sup>+</sup>C222Na<sup>-</sup> thin films prepared by solvent evaporation have a major peak at 650 nm (the same position as the Na<sup>-</sup> peak in solution), a shoulder at 530 nm (2.4 eV,  $1.9 \times 10^4 \text{ cm}^{-1}$ ) and a small peak at 410 nm (3.0 eV, 2.5 x 10<sup>4</sup> cm<sup>-1</sup>).<sup>37</sup> The latter two features are not seen in solution spectra of Na<sup>-</sup> nor in other sodide films. The band gap of Na<sup>+</sup>C222Na<sup>-</sup> obtained from powder<sup>23,60</sup> and 2-probe single crystal<sup>44</sup> conductivities is 2.4 eV. This evidence points to the possibility of the 530 nm shoulder being the result of a bound-to-continuum transition.

The first vapor deposited films of Na+C222Na<sup>-</sup> did not have good stoichiometrical control or uniformity, but their optical absorbance spectra were very similar to the solvent evaporated film spectra.<sup>40</sup> This feasibility study led to the construction of the vapor deposition apparatus. Detailed optical and electrical film studies were planned.

Faber constructed the bell jar system and showed that uniform and nearly stoichiometric thin films of Na+C222Na<sup>-</sup> had absorbance spectra very similar to the earlier vapor deposited films and solvent evaporated films.<sup>6</sup> The spectral range was limited, though. Most spectra only ran from 500 nm to 900 nm. Thus, the shoulder and small peak on the high energy side of the main peak could not be fully str smaller incomp accurat oscillat F conduc the tra contact to inco S film si Prelim both se study . and s depen The e tempe These meV i that r the g excite 1.835 the b

fully studied. Also, the calculated oscillator strength values were all smaller than the expected value of 2. It was assumed that an incomplete reaction of the Na and C222 and the inability to accurately measure the film thickness and stoichiometry led to the oscillator strength values of around 1.

Faber also studied both transverse and longitudinal conductivities of Na+C222Na<sup>-</sup>.<sup>6</sup> Problems with decomposition during the transverse conductivity synthesis and with poor electrical contact to the conductivity pads during both types of synthesis led to inconclusive results.

Skowyra's modifications to the jar allowed better control of the film stoichiometry and the study of a wider spectral range.<sup>42</sup> Preliminary studies of Na+C222Na<sup>-</sup> included a Beer's Law study for both sequential deposition and codeposition and a sodium migration study through the potasside K+C222K<sup>-</sup>.

The position of the photoluminescence peak of polycrystalline and single crystal Na+C222Na<sup>-</sup> samples showed a temperature dependence during studies at very low temperatures (7 to 80 K).<sup>61</sup> The emission peak position shifted toward lower energy as the temperature increased, with a shift of approximately -0.4 meV/K. These studies revealed that the ground state s band was only 40 meV in width at 10 K. The photoluminescence study also concluded that not only was there emission from the bottom of the p band to the ground state (1.860 eV), but there was also emission from an excited state that was slightly below the bottom of the p band and 1.835 eV above the ground state. The half-life of the emission from of the energy transfer from the bottom of the p band to the other excited state level is 2.5 ns, which then also decays to the ground state with a half-life of 5.0 ns. Photoluminescence studies at low temperatures also show that in a pure defect-free crystal, light absorption at energies below about 2.4 eV yields a Frenkel exciton.<sup>62</sup> The exciton can move rapidly by a diffusive process and is apparently an exciton-polariton. The mobile exciton-polariton converts to a photon at the edge of the crystal or can be trapped at an appropriate defect, such as a trapped electron at an anionic site. Thus, an increase in the concentration of defect electrons will essentially quench the fluorescence of the crystal. The shape of the emission band is explained very well by use of an Urbach-tail theory in conjunction with the exciton-polariton picture.<sup>62,63</sup> Earlier, Park, Solin and Dye had attempted to describe all of the experimental results with just an exciton-polariton theory.<sup>64,65</sup>

The absorbance spectra were also studied at low temperatures.<sup>61,63</sup> A comparison of the absorbance and emission spectra of a Na+C222Na<sup>-</sup> film is shown in Figure 23. Notice how narrow the emission spectrum is in comparison with the absorption spectrum. This shows that the ground state s band is very narrow (40 meV) and, thus, that the broad absorbance spectra is mapping out the approximate shape of the joint density of states in the excited p band and conduction band (it would be the true shape if the temperature were 0 K and if the film were completely uniform).

Photobleaching studies were performed on solvent evaporated In films of Na+C222Na<sup>-.66</sup> Short pulses (15 ns) of high intensity (1  $mJ/mm^2$ , 6.6 x 10<sup>4</sup> W/mm<sup>2</sup>, 3 x 10<sup>15</sup> photons per pulse) 605 nm dye

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ABS.

Figure



Figure 23. Optical absorbance (broad) and luminescence (narrow) spectra of a solvent-evaporated Na+C222Na<sup>-</sup> film at 10 K.

laser light bleached the Na<sup>-</sup> peak. The bleaching of the 650 nm absorbance peak was partially reversible, with a half-life of approximately 30 ms at 25 °C. A relative increase in the absorbance at 790 nm indicated that a long-lived transient appears to be the major reason that the main absorbance peak never fully recovers (a minor reason may be that some of the film has decomposed due to the intense laser blast). EPR results also showed evidence of a new paramagnetic species during steady state illumination by a 150 W tungsten lamp.

All of the experimental evidence described above can be used to develop an electronic band-like picture of Na+C222Na<sup>-</sup>. Figure 24 shows a schematic of this picture. The conductivity studies give the 2.4 eV gap from the ground state  $(3s^2)$  to the conduction band. The optical absorbance spectra assist in defining the shapes and positions of the excited state (3s3p band) and the conduction band. The photoluminescence studies give us the energy of the gaps from the bottom of the p band (labeled A) to the ground state, from the bottom of the p band to another excited state (labeled B) and from the excited state (B) to the ground state. The photobleaching studies describe how an intense overpopulation of the p band and conduction band may lead to new electron trapping sites in the regions below the p band and conduction band.

All of the previous studies set the stage for a detailed study of thin films of Na+C222Na<sup>-</sup> in the vapor deposition system. The present study will test and expand the band-like model discussed above. The rest of this chapter describes the Na+C222Na<sup>-</sup> studies performed during this research project: a temperature dependence





study of th stoichiomet In the thin films system was spectra was A typical sp values agre strengths of in the range deposited f layered film (only losing strength eac <sup>from</sup> the G film for an <sup>heating</sup> the <sup>photoly</sup>tic d <sup>tests</sup> descrit <sup>from</sup> the c <sup>Applying</sup> ap <sup>beam</sup> to the the substrate <sup>of the</sup> subst <sup>absorbed</sup> fro decompositio decompositio study of the optical absorbance peak, a photobleaching study, a stoichiometry study and a conductivity study.

In the present research, many preliminary runs of Na+C222Na<sup>-</sup> thin films were performed to assure that the vapor deposition system was operating properly. The overall shape of the absorbance spectra was identical to that of Skowrya and was very reproducible. A typical spectrum is shown in Figure 25. The peak absorbance values agreed well with Skowyra's Beer's Law plots. The oscillator strengths of the initial spectra of each of the codeposited films were in the range of 1.5 to 2, but were slightly lower for the sequentially deposited films (probably due to incomplete complexation in the layered films). The spectra were very stable at room temperature (only losing approximately 10 - 20% of the films' total oscillator strength each day). The spectra did decay slightly if the light beam from the Guided Wave spectrophotometer remained fixed on the film for an extended period of time. Is this decay from the light heating the sample to decomposition temperatures or from a photolytic decomposition process? During the substrate temperature tests described in Chapter II, it was found that heat was removed from the center of the sapphire substrate rather efficiently. Applying approximately the same amount of energy from the light beam to the substrate with a resistor increased the temperature of the substrate from -60 °C to only -57 °C. Thus, the thermal contact of the substrate to the copper block should remove the energy absorbed from the incident photons fast enough to prevent thermal decomposition of the cold films. It appears that a photolytic decomposition mechanism occurs when the sodide films are

Absorbance

Fig



Figure 25. Typical Na+C222Na<sup>-</sup> absorbance spectrum from a thin film synthesized in the vapor deposition system. This particular film was 930 Å thick and was codeposited at 25 °C. The vertical line represents the position of the luminescence peak at 10 K.

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III.B. <u>Temp</u>

A cor thin film op of the spe electronic t found that with the ter try to overc a tempera performed. <sup>the</sup> experim temperatur After <sup>the</sup> chamt <sup>codeposited</sup> <sup>was</sup> 930 Å. <sup>minute</sup> afte <sup>The</sup> film w spectrum w. down to -75 temperature

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continually illuminated by the Guided Wave light source. The films were always removed from the path of the analysis beam between optical absorbance scans to avoid this effect.

## III.B. Temperature Dependence of the Optical Absorbance Spectra

A concerted effort was made to describe mathematically the thin film optical absorbance spectra of Na+C222Na<sup>-</sup>. An analytical fit of the spectral shape would allow quantitative analysis of the electronic transition (for example, Kramers-Kronig analysis). It was found that the position and width of the major absorption peak vary with the temperature, though, which made a global fit difficult. To try to overcome this problem and find a universal fit to the spectra, a temperature study of the optical absorbance spectra was performed. The use of the newer substrate holder (as described in the experimental chapter) allowed accurate control of the film temperature.

After a normal loading of the Na and C222 from the glove box, the chamber was evacuated overnight before the film was codeposited at room temperature. The final thickness of the film was 930 Å. The absorbance spectrum taken approximately one minute after the completion of the deposition is shown in Figure 25. The film was then cooled to 15 °C where another absorbance spectrum was taken. This process was repeated at 5 °C increments down to -75 °C and back up to 10 °C. The film remained at room temperature in vacuum overnight. The next day, absorbance spectra were again taken (this time at 10 °C intervals) from room temperature down to -75 °C and back up to -35 °C. The film remained at room temperature and under vacuum for the next three days. Each day a single absorbance spectrum was taken. On the fifth day after deposition, absorbance spectra were taken at 10 °C intervals from room temperature down to -75 °C and back up to 15 °C. A final absorbance spectrum was taken eight days after the deposition. A small, typical Na+C222Na<sup>-</sup> spectrum remained.

A qualitative analysis of the plethora of optical absorbance spectra reveals several trends. The entire spectrum decreases with each day that the film sits at room temperature in the vacuum chamber. This is an irreversible process due to the small amount of impurities in the vacuum slowly degrading and decomposing the film. A decrease in temperature shifts the position of the absorbance maximum toward larger wavenumbers (higher energy), decreases the width of the absorbance peak and increases the value of the absorbance maximum (Figure 26). Upon increasing the temperature, these three phenomena are reversible. The normalized absorbance spectra show that the positions of the high energy side of the large absorbance peaks do not shift with temperature. This phenomenon, as will be shown later, greatly assists in the description of the electronic band structure of the sodide.

A quantitative analysis of the absorbance spectra was performed. The oscillator strength should remain constant during the temperature-dependent changes of the absorbance peak described above. The area under the absorbance versus wavenumbers curve was integrated and used to calculate the oscillator strength as a function of temperature (Figure 27). The

2.0-0.0 1.0 0.0 Figure



Figure 26. Absorbance (top) and normalized absorbance (bottom) spectra of a Na+C222Na<sup>-</sup> film which demonstrate how the spectral shape changes with temperature. Notice how the low energy edge of the absorbance spectrum moves toward the 10 K luminescence peak position (vertical lines) as the temperature is lowered.


Figure 27. Oscillator strength versus film temperature for a Na+C222Na<sup>-</sup> film. Diamonds and circles represent decreasing and increasing temperature, respectively.

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data are noisy, but fairly constant with both decreasing and increasing temperature, until the film is again warmed to approximately -20 °C where the oscillator strength decreases rapidly. Any water cryopumped onto the surface of the film at low temperatures might begin to react with the sodide at this temperature, causing a small amount of irreversible decomposition to occur.

A thorough quantitative analysis was performed on the temperature-dependent parameters of the main sodide absorption peak. Each absorbance spectrum was expanded around the major peak and shoulder and plotted on graph paper. A typical spectrum used in the analysis is plotted in Figure 28. Approximately twenty sets of ABS and wavenumber coordinates were found for each peak. These sets were used to define the skewed center line of the asymmetric peak. This center line was then used to find the true absorbance peak maximum value and position (this was necessary due to the step size of the spectrophotometer and the asymmetric peak). Once the peak maximum was known, then the full-width and half-widths at half-maximum could be determined.

The qualitative observations now had numbers to go with them. Figure 29 shows how the absorbance peak position changes linearly with temperature (both increasing and decreasing) for the spectra taken on the same day the film was deposited. The slopes of the lines that fit the data are  $-0.230 \pm 0.004$  meV/K and  $-0.225 \pm$ 0.005 meV/K for the decreasing and increasing temperature data sets, respectively. (Standard deviation estimates are given.) Only slightly different numbers were found for the spectra taken one day



Figure 28. Expanded view of the main Na+C222Na<sup>-</sup> absorbance peak. The coordinates used to find the parameters of the peak described in the text are shown.



Figure 29. Peak position versus temperature for a Na+C222Na<sup>-</sup> film. Diamonds and plus signs represent decreasing and increasing temperature, respectively.

after deposition (-0.206  $\pm$  0.005 meV/K and -0.186  $\pm$  0.019 meV/K) and taken five days after deposition (-0.177  $\pm$  0.005 meV/K and -0.194  $\pm$  0.011 meV/K).

The peak position of sodide films formed by solvent evaporation had previously been examined at low temperatures.<sup>63</sup> A comparison of the sodide peak position versus temperature at low temperatures from the earlier study and at higher temperatures from this study is shown in Figure 30. The peak position values and the trend are comparable, but displaced from one another.

Figure 31 shows the linear dependence of the maximum peak absorbance value with respect to temperature for the spectra taken on the same day the film was deposited. The slope of the least squares fit line through the decreasing temperature data is  $-0.00356/K \pm 0.00008/K$ . The peak absorbance value for the increasing temperature data breaks away from linearity strongly at about -20 °C. Similar slopes are seen for the decreasing temperature data for the second  $(-0.00276/K \pm 0.00010/K)$  and fifth day  $(-0.00357/K \pm 0.00008/K)$  spectra and the deviations from linearity during the increasing temperature data half-cycle are apparent. These deviations from a linear dependence and the sudden degradation of the oscillator strength shown in Figure 27 may be due to a small amount of water being cryopumped onto the film when it is cold, as mentioned earlier. Interestingly, not one of the other parameters seems to be affected by this phenomenon, except for the full- and half-widths of the increasing temperature data **Taken** five days after deposition (the absorbance spectra from the fifth day, though, are very small and noisy).



Figure 30. Na+C222Na<sup>-</sup> peak position versus temperature for both a codeposited thin film from the present study and a solvent-evaporated thin film from a previous study.



Figure 31. Peak absorbance versus temperature for a Na+C222Nafilm. Diamonds and plus signs represent decreasing and increasing temperature, respectively.

Figure 32 shows that the full-width at half-maximum (FWHM) also behaves linearly with temperature for the spectra taken on the same day the film was deposited. The slopes for the decreasing and increasing temperature data are  $0.568 \pm 0.009$  meV/K and  $0.604 \pm$ 0.014 meV/K, respectively. Similar slopes for the FWHM versus temperature spectra were found from the data taken on the second  $(0.585 \pm 0.009 \text{ meV/K} \text{ and } 0.645 \pm 0.035 \text{ meV/K})$  and fifth  $(0.650 \pm 0.005 \text{ meV/K})$ 0.033 meV/K and 1.01  $\pm$  0.059 meV/K) days. It appears that the peak is always wider and increasing in width faster as the temperature is being increased. The half-widths of the asymmetric peak also have a linear dependence with respect to temperature, as shown in Figure 33 (again, the data presented are from the spectra taken on the same day the film was deposited). Note that the halfwidth on the high energy side of the peak is always larger than the half-width on the low energy side. The decreasing temperature data have similar slopes for the high and low energy sides of the peak:  $0.265 \pm 0.007$  meV/K and  $0.303 \pm 0.011$  meV/K, respectively. The corresponding values for the increasing temperature data are nearly the same:  $0.303 \pm 0.008$  meV/K and  $0.301 \pm 0.015$  meV/K. It is interesting that there is a trend in these four slopes for the three sets of data. The slopes of the low energy side appear to be nearly the same no matter whether the temperature is decreasing or increasing  $(0.329 \pm 0.009 \text{ meV/K} \text{ for decreasing and } 0.323 \pm 0.014$ rneV/K for increasing temperatures for the data taken on the second day and 0.312  $\pm$  0.013 meV/K for decreasing and 0.367  $\pm$  0.022 meV/K for increasing temperatures for the data taken on the fifth day). The slopes of the high energy side, though, appear to always



Figure 32. Full-width of the main absorption peak at half-height versus temperature for a Na+C222Na<sup>-</sup> film. Diamonds and plus signs represent decreasing and increasing temperature, respectively.



Figure 33. Half-widths of the main absorption peak at half-height versus temperature for a Na+C222Na<sup>-</sup> film. The low energy side of the peak (circles and crosses) is narrower than the high energy side (diamonds and plus signs). Circles and diamonds represent decreasing temperature and plus signs and crosses represent increasing temperature.

increase significantly during the increasing temperature half-cycle compared to the decreasing half-cycle  $(0.254 \pm 0.009 \text{ meV/K} \text{ for})$  decreasing and  $0.347 \pm 0.029 \text{ meV/K}$  for increasing temperatures for the data taken on the second day and  $0.338 \pm 0.028 \text{ meV/K}$  for decreasing and  $0.646 \pm 0.082 \text{ meV/K}$  for increasing temperatures for the data taken on the fifth day).

One parameter that was not qualitatively thought about with respect to temperature was the actual frequency positions of the absorbance values at half-height. The temperature dependence of this parameter, though, probably reveals the most insight into the nature of the shifting absorbance peak. Figure 34 shows the positions at half-height for the low and high energy sides of the absorbance peak versus temperature for the spectra taken on the same day the film was deposited. The slopes for the decreasing and increasing temperature spectra from the low energy side are -0.533  $\pm$  0.009 and -0.526  $\pm$  0.014 meV/K, respectively. This is about an order of magnitude larger than the corresponding values for the high energy side  $(0.0350 \pm 0.0055 \text{ and } 0.0773 \pm 0.0059 \text{ meV/K})$ . The data from the second and fifth days are similar. The low energy side values for the second day are  $-0.536 \pm 0.012$  and  $-0.509 \pm 0.024$ meV/K for the decreasing and increasing temperature data and for the fifth day are  $-0.489 \pm 0.014$  and  $-0.550 \pm 0.020$  meV/K. The high energy side values for the second day are  $0.0474 \pm 0.0087$  and  $0.161 \pm 0.012$  meV/K for the decreasing and increasing temperature data and for the fifth day are  $0.162 \pm 0.026$  and  $0.452 \pm 0.084$ meV/K. Again, the data from the fifth day are quite noisy due to the small signal which remains. This information means that the



Figure 34. High (diamonds and crosses) and low (circles and plus signs) energy positions of the absorbance spectra at halfheight versus temperature for a Na+C222Na<sup>-</sup> film. Circles and diamonds represent decreasing temperature and plus signs and crosses represent increasing temperature.

decrease of the widths as the temperature is decreased is caused only by the movement of the low energy side to higher energies. The high energy side of the peak essentially does not move with a change in temperature (Figure 26). This evidence hints towards the contribution of low energy excitations (such as phonons) to the absorption process which will be discussed near the end of this section.

Do the peak parameters of the high energy absorbance shoulder and the small peak at 25000 cm<sup>-1</sup> have the same temperature dependence as the parameters of the main absorption peak at 15400 cm<sup>-1</sup> described above? The overlap of the main peak and the shoulder do not allow a detailed study of the shoulder. Figure 26 indicates that the width and position of the shoulder absorbance spectra do not change with respect to film temperature. This apparent shape conservation of the shoulder does not rule out that some of the temperature-dependent parameters of the main absorbance peak at low energies may arise from overlapping portions of the shoulder. Figure 26 does show that the 25000 cm<sup>-1</sup> peak qualitatively behaves in a manner similar to the main sodide absorption peak. As the temperature increases, the peak position shifts to lower energy and the low energy side of the peak becomes more broad.

Another interesting set of data from this experiment is the time dependent parameters at room temperature over eight days. A clearer picture emerges of the degradation of the film. This presumably results from reaction with the small amount of gaseous impurities in the system, although it could indicate the intrinsic decomposition rate. Figure 35 shows the decay of the absorbance maximum value as a function of time. The decay is approximately exponential, as demonstrated by the curve. The oscillator strength also shows a nearly exponential decay over the eight days (Figure 36). All of the other parameters, though, follow the example of the peak position versus time graph shown in Figure 37. The parameters remain fairly constant at their initial values until between the second and third days where they all begin to diverge rapidly. It is also at this point that the value of the peak maximum decreases below 50% of the original value. It appears that after more than 50% of the film has been degraded light scattering and other effects of inhomogeneity become important.

The room temperature optical absorbance spectra of the Na+C222Na<sup>-</sup> film taken over the eight days (Figure 38) demonstrate the decay that was shown in Figures 35 and 36. Does the overall shape of each spectrum change? The normalized absorbance spectra are plotted in Figure 39. It is apparent that the shape of the optical absorbance is conserved until somewhere between the spectrum taken at 49 hours and the spectrum taken at 72 hours. This is also where the value of the peak maximum decreases below 50% of its original value. At times greater than 49 hours after deposition, the three features remain, but their peak positions and widths change. Again, it is evident that after more than 50% of the film material has been degraded the spectral shape changes.

How do the above experimental results assist in describing the band-like picture of Na+C222Na-? The fact that the ground state s band is narrow implies that the breadth of the absorbance spectrum



Figure 35. Graph showing the decrease in the Na+C222Na<sup>-</sup> peak absorbance value over an eight day period. The solid line represents an exponential fit to the data.

**Oscillator Strength** 

Figu



Figure 36. Graph showing the decrease in the oscillator strength of a Na+C222Na<sup>-</sup> film over an eight day period. The solid line represents an exponential fit to the data.



Figure 37. Graph showing the change in the absorbance peak position of a Na+C222Na<sup>-</sup> film over an eight day period.



Figure 38. Room temperature absorbance spectra of a Na+C222Na<sup>-</sup> film taken over eight days.

Normalized Absorbance

Normalized Absorbance

Fig



Figure 39. Normalized absorbance spectra of a Na+C222Na<sup>-</sup> film taken over eight days at room temperature.

at static temperatures is due to the shape of the accessible excited states. At 0 K this spectrum would describe the joint density of states of the transitions. The reproducibility of the spectra of films made at different times attests to their uniformity. Due to the anisotropic crystalline structure of Na+C222Na<sup>-</sup>, the excited p band states will also be anisotropic. The anisotropy of the excited states will contribute to the breadth of the absorbance spectrum. Changing temperatures will alter the positions of the band edges, the shapes of the bands and the population of phonons. As the temperature increases, the bands will thermally broaden due to the lattice expansion or lattice "softening" of the sodide.<sup>67</sup> This broadening, which will also be anisotropic, lowers the amount of energy necessary to excite an electron from the ground state to an excited state. Thus, photons with lower energy will be absorbed due to these newly accessible excited states. Another way for a lower energy photon to be absorbed is an indirect optical transition. These absorptions, in contrast to direct transitions, are assisted by phonons (Figure 40). As the temperature increases, the population of phonons increases and the probability of an indirect transition is enhanced. The photoluminescence studies demonstrated that at low temperatures the energy difference between the bottom of the p band (state A) and a relaxed energy state below the p band (state B) was 25 meV (Figure 24). $^{61,63}$  This energy gap was shown to be temperature independent. The size of this energy gap is comparable to the energy of a phonon at approximately room temperature. Such an electronic excited state structure would allow lower energy photons to populate state A through state B (as shown in Figure 24)



Figure 40. Schematic representation of transitions between valence and conduction bands in k space: a). direct optical transition, the excitation of the electron is drawn vertically because the absorbed photon has a very small wavevector; b). indirect optical transition, the excitation involves both a photon and a phonon. with the help of a phonon. The new absorbances described above will expand the width of the absorbance peak on the low energy side and move the peak position to a lower energy. Since the oscillator strength must be (and was shown to be) conserved, the peak absorbance value has to decrease in order for the wider peak at higher temperatures to have the same integrated area under the absorbance curve. These same characteristics are seen in the Fcenters of alkali halides (Figure 41 for KCl).<sup>48</sup> The decrease in energy of the peak position and the increase in width of the optical absorbance spectra with increasing temperature are shown in Figure 42 for KCl and NaCl. Markham explains that the major factors for the broadening of the absorbance spectra at higher temperatures are the effect of the increase in interactions between the F-centers and the increase in the phonon population. These same factors lead to the broadening of the optical absorbance spectra of alkalides. The lattice vibrations will assist the lower energy photons in exciting electrons into the p-band and conduction band. This assistance by the phonons will again broaden the absorbance peaks on the low energy side and lead to absorbance peak maxima at lower energies and smaller maximum absorbance peak values. Of course, a direct analogy to F-centers for the sodide may not be appropriate. An Fcenter is basically an electron trapped in a cavity, whereas a sodide is an electron bound to a neutral Na atom.

The absorbance spectrum of the high energy shoulder does not appear to shift in position or change shape at different temperatures. The low energy side of this absorbance, though, is hidden under the large,  $15400 \text{ cm}^{-1}$  peak. If the bottom of the

<sup>Figure</sup> 41.



Figure 41. F-center optical absorbance spectra at three different temperatures for KCl. Temperature is increasing from solid line to dotted line to dashed line. Notice that increasing photon energy is plotted from right to left.





Figure 42. Peak position and width at half-height versus temperature of the F-center optical absorbance spectra for KCl (top) and NaCl (bottom).

conduction band were thermally broadened or if phonons assisted in the promotion of electrons into the bottom of the conduction band, the overlap of the absorbances from the excited p band state and the conduction band would make it appear as if only the excited state band was affected. However, the temperature independence of the shape of the shoulder absorbance that can be studied implies that the joint density of states between the ground and conduction bands is also temperature independent.

What is the origin of the small absorbance peak at 25000 cm<sup>-1</sup>? The peak position and shape of this peak have a temperature dependence similar to that of the 15400 cm<sup>-1</sup> peak. The correlation implies that these two transitions are related. Thus, the 25000 cm<sup>-1</sup> peak is probably not due to an impurity state (the 15400 and 25000) cm<sup>-1</sup> peaks appear to share the same ground state). For convenience in quantifying the spectra, the absorbance spectra were fit with four gaussian peaks: two for the 15400 cm<sup>-1</sup> peak, one for the shoulder (conduction band) and one for the 25000 cm<sup>-1</sup> peak (Figure 43). The conduction band gaussian did not change in shape or position with changing film temperature. This result implies that the joint density of states between the ground state and the conduction band is temperature independent. It should be noted, though, that conduction band absorbances are usually not gaussian-shaped.<sup>68</sup> The three other gaussians shifted and changed shape in a correlated manner with temperature. A qualitative picture that describes this scenario is that the two gaussians near 15400 cm<sup>-1</sup> represent an excited p band and the gaussian at  $25000 \text{ cm}^{-1}$  represents another, higher energy p band. Notice that the energy of this high energy



Figure 43. A four-gaussian fit (solid line) to the optical absorbance spectra of a Na<sup>+</sup>C222Na<sup>-</sup> film (dots). The individual gaussian peaks are shown as broken lines.

band (3.0 eV) is above the assumed vacuum level of 2.8 eV. This implies that the excited state may be a virtual state. A photoemission mechanism may also contribute to this high energy absorption. A peak in the photoemission spectrum is observed at approximately the same energy.<sup>67,69</sup>

The above discussions regarding band shapes and positions could be greatly enhanced with a theoretical study of the band structure of Na+C222Na<sup>-</sup>. The crystal structure and many other physical properties of this sodide have been studied in detail. The new capabilities of computers could use the available information to calculate the three-dimensional, anisotropic band structure. These calculations would assist in the correct interpretations of the physical properties of Na+C222Na<sup>-</sup>.

## III.C. Photobleaching Study

DeBacker saw intriguing results upon photobleaching solvent evaporated thin films of Na+C222Na<sup>-</sup> (Figure 44).<sup>66</sup> His experimental set-up allowed for microsecond optical spectroscopy. The new absorbing species observed in the near infrared, though, was fairly long-lived (seconds to minutes at room temperature, longer at colder temperatures). The amount of bleaching in this partially reversible process depended in a non-linear way on the laser power. The present research attempts to look at the same process by using vapor deposited films and a wide variety of illumination intensities and wavelengths.

Each of the experiments starts by creating a thin film of



Figure 44. Absorbance (top) and normalized absorbance (bottom) spectra of a solvent-evaporated Na+C222Na<sup>-</sup> film taken during a bleaching experiment of DeBacker, *et. al.*: a). initial spectra; b). spectra immediately after a 15 ns pulse from a 605 nm dye laser; c). spectra one second after the pulse.

Na+C222Na<sup>-</sup> in the typical manner. Film thicknesses were usually around 1500 Å. The films were made at fairly warm temperatures (-10 °C to room temperature) and then cooled to very low temperatures (-60 to -100 °C). The films were cooled for photobleaching in an attempt to slow the partially reversible process enough so that the slow spectroscopy methods (many seconds to minutes) employed in the present system would have a chance to observe the new absorbing species.

A small He-Ne laser was the first light source used to investigate photobleaching. The initial optical absorbance spectrum showed the typical Na+C222Na<sup>-</sup> shape. The -40 °C film was moved to a position above the mirror in an empty oven chamber. The 632 nm laser beam was manually rastered over the entire film as uniformly as possible. The absorbance spectrum showed no change. Next, the film temperature was cooled to -60 °C and then the laser was slowly rastered over the film for a total of five minutes. Again, the absorbance spectrum showed no change.

Two other attempts to bleach a Na+C222Na<sup>-</sup> film with the He-Ne laser were made. One attempt used a much colder substrate temperature (-100 °C) and the other used a warmer temperature (-20 °C and 0 °C). The beam was rastered over the film slowly for very long times (up to 10 minutes between each of several scans). Neither of these attempts produced a bleaching effect of the absorbance spectra. These null results agree with DeBacker's observation that the bleaching is a nonlinear effect. A simple calculation shows that the total number of photons from the He-Ne laser in the present experiments is much larger than the total number of photons from each of DeBacker's dye laser pulses. If it were a linear effect, the same number of photons would produce the same effect, which is not the case with this photobleaching experiment.

A xenon flash lamp increased the intensity of the photon beam by four orders of magnitude over the He-Ne laser. The flash lamp does have one drawback, though, it emits a pulse of white light, not a pulse of photons of only a single wavelength. Thus, the intensity of the spectral portion of the beam with enough energy to bleach the film is probably not quite four orders of magnitude greater than the He-Ne laser.

A 1020 Å film of Na+C222Na<sup>-</sup> was sequentially deposited at -40 °C. The xenon flash lamp gave the film 10 flashes each at -40 °C, -60 °C, -20 °C, 0 °C and 20 °C with no effect on the optical absorbance spectra. It appears that the flash lamp still did not have enough intensity to reproduce the photobleaching effect that DeBacker saw. Again, the total number of photons incident on the film from the flash lamp was greater than the total number of photons from the dye laser pulses, but a similar effect was not observed, indicating again that the process is nonlinear.

The Nd:YAG laser beam increased the intensity of the illuminating source four more orders of magnitude over the xenon flash lamp. Each 532 nm pulse was on the order of ten times more intense than each of DeBacker's pulses. Each 355 nm pulse had approximately the same intensity as DeBacker's pulses. Thus, this Nd:YAG pulsed laser experiment should definitely be able to recreate the previous photobleaching conditions.

Fourteen different vapor deposited Na+C222Na<sup>-</sup> films were studied with the Nd:YAG pulsed laser. Ten films used the 532 nm beam and the other four used the 355 nm beam (the experimental results were the same with either of the beams). The results of a typical run will be discussed first. After codepositing a Na+C222Na<sup>-</sup> film, its optical absorbance spectrum was taken. The usual substrate temperature during deposition was -20 °C. A series of single laser pulses and absorbance scans followed. The laser pulses were varied in intensity and the film temperatures were varied between -100 °C and 20 °C. Figure 45 shows several representative absorbance spectra plotted versus wavenumbers. Figure 46 shows the same absorbance spectra plotted as ABS/ABS<sub>max</sub> versus wavenumbers. The peak has been irreversibly partially bleached and new absorbing species are present on both the low and high energy sides of the peak. At a constant temperature below -20 °C, the bleached spectra remain unchanged for extended periods of time after the laser pulse. When the films are warmed above -20 °C, the new absorbances quickly decay and the remaining Na<sup>-</sup> absorbance peak sometimes increases slightly (but never back to its original absorbance maximum).

Some specifics of several of the experiments will now be discussed. Successive laser pulses did not continue to bleach away the peak until it was gone. The bleaching process eventually saturates, as shown in Figure 47. Thus, the bleaching appears to be ineffective after a large number of pulses. As DeBacker showed,<sup>66</sup> each pulse almost completely bleaches the peak to a flat line absorbance immediately after the pulse. Thus, the fact that the final



Figure 45. Absorbance spectra of a 1300 Å codeposited Na+C222Na<sup>-</sup> film before (diamonds) and after (circles) a 7 ns pulse from a 532 nm Nd:YAG laser. Film temperature = -60 °C.
Normalized Absorbase

Figur



Figure 46. Normalized absorbance spectra of a 1300 Å codeposited Na+C222Na<sup>-</sup> film before (diamonds) and after (circles) a 7 ns pulse from a 532 nm Nd:YAG laser. Film temperature = -60 °C.

Peak Absorbance

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Figure 47. Peak absorbance value of a 1000 Å Na+C222Na<sup>-</sup> film versus 532 nm Nd:YAG pulse number. Shows the bleaching process becomes saturated after repeated pulses. Film temperature = -10 °C. The solid curve represents a double exponential fit to the data.

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absorbance spectra after many pulses do not show a decay after each pulse means that the process has become totally reversible. The total oscillator strength of the films may continue to decrease slightly with each pulse even after saturation. An explanation of this decrease is that the excited electrons, which are chemically and energetically very hot, react with the cryptands and decompose small portions of the film. This reaction would make the electrons "invisible" to the optical absorbance scans.

Also, there was a threshold intensity that needed to be attained before any bleaching was observed. The long-pulse mode of the laser (with an intensity similar to that of the He-Ne laser), which was used to align the beam, did not bleach the sample even when it illuminated the sample at 10 Hz for many minutes prior to the 7 ns pulses. The lowest intensities of the 7 ns pulses also did not bleach the peak. Approximately 100 times the intensity of the laser's threshold intensity was needed to begin bleaching the samples. A detailed study of the amount of bleaching as a function of the laser intensity would have divulged information regarding the nonlinear behavior of this process. Such a study, though, was not undertaken due to the saturation behavior described above and the irreversibility of the bleaching process.

What does the nonlinearity of the bleaching proccess indicate? One possibility is that the bleaching requires a two-photon process. This proccess will now be discussed, but it will also be shown that the experimental results are not consistent with all of its predictions. If a low intensity laser beam illuminated the film, the electrons with accessible states of that energy would be promoted up into the

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excited p-band (see Figure 24 again). Within 5 ns these electrons would quickly fall down to the bottom of the p-band and then decay down to the ground state s-band via one of the schemes described above (radiationless decay to the s-band, fluorescence from state A to the s-band or a relaxation from state A to state B followed by fluorescence to the s-band). If the intensity of light is high enough, though, the electrons excited into the p-band would be promoted even higher by other photons before they have a chance to decay back down to the ground state. These highly excited electrons would have a large amount of energy and may be quite mobile in the pband and conduction band. As these mobile electrons lose their energy, they may find traps in the energy gap between the excited bands and the ground state. The traps would keep the electrons from falling all the way down to the ground state. The optical absorbance spectra demonstrate that after intense laser pulses there are not as many electrons in the ground state and that some of these electrons are trapped at different energies. The problem with this two-photon picture of bleaching is that the higher energy laser pulses (355 nm) show a threshold behavior similar to the 532 nm pulses. If the mechanism to produce the new absorbing species is that the second 532 nm photon promotes the electron out of the p band and into a highly excited state, the low intensity 355 nm pulses would also promote the electrons into energy states above the p band and should produce the same bleaching result. This phenomenon is not observed with low intensity 355 nm pulses. Only intense pulses from both the 532 nm and 355 nm laser beams cause bleaching.

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A nonlinear process that does describe the experimental bleaching results is a mechanism that requires a crossing of a threshold population of exciton-polariton pairs in the excited state. The threshold appears to be at the point where the intensity of the laser light is high enough so that there are more photons incident on the film than there are Na<sup>-</sup> ions in the illuminated sample. The photoluminescence studies demonstrated that laser excitations of the ground state electrons of the sodide into the excited states produced mobile exciton-polariton pairs.<sup>61,63</sup> These pairs can fluoresce back down to the ground state via the two different decay channels or they can become trapped at defect sites in the polycrystalline film. At low Nd:YAG laser pulse intensities (fewer photons than sodides, approximately  $1 \ge 10^{15}$  photons and  $2 \ge 10^{16}$  sodides), the p band is not densely populated with exciton-polariton pairs. The pairs do not strongly interact with each other due to the low concentration. They fluoresce quickly or are trapped for short times at defects. This low intensity process leads to no change in the absorbance spectrum at long times (many seconds). At high Nd:YAG laser pulse intensities (more photons than sodides, approximately  $1 \ge 10^{18}$  photons and  $2 \ge 10^{18}$  $10^{16}$  sodides), the p band is densely populated. Essentially, half of the ground state electrons have been promoted into the p band. This dense population leads to strong interactions between the exciton-polariton pairs. When two excitons collide, they can form another exciton with a much higher energy and several phonons.<sup>54</sup> The strong interactions which lead to high energy excitons allow the pairs to access new areas of the electronic structure as they move through the sample. The pairs are trapped by long-lived defect

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states in these new areas that were not energetically accessible during the low intensity pulses. These long-lived trapping states have also been seen in the photoelectron emission spectra during recent bleaching experiments performed on solvent-evaporated Na+C222Na<sup>-</sup> films.<sup>69</sup> The defect states may trap the electrons at large enough distances away from the neutral sodiums that they are left behind upon excitation to greatly slow down the recombination process. The separation of the electrons from the neutral sodium atoms leaves two new species in the polycrystalline sample, which will alter the electronic structure. Obviously, there are new trapped electron states that would appear as new absorbing species in the optical absorbance spectrum. Also, the neutral sodium atoms would appear to the surrounding material as vacancies with positive charges. These vacancies will perturb the ground state and excited state electronic structure of the sodide, which will also alter the optical absorbance spectrum.

How does the saturation phenomenon of the bleaching process fit into this model? It appears that when the concentration of defect states reaches some maximum value, then the bleaching becomes reversible. A similar result is seen in the photoemission studies of solvent-evaporated Na+C222Na<sup>-</sup> films.<sup>69</sup> When a pure, defect-free film is prepared, no bleaching effect is observed. When a film is prepared which has a small number of defects present, laser pulses increase the emission from trapped defect electrons considerably. After repeated laser pulses, the emission saturates. Thus, as seen in the present absorbance study, eventually no new trapped electrons are created. Of course, the photoluminescence studies showed that



defect electrons quench the fluorescence and limit the mobility of the exciton-polariton pairs.<sup>64,65</sup> Thus, once the maximum concenration of defect trapping states are formed by successive laser pulses, the exciton-polariton pairs are only allowed to travel a very short distance before they encounter defect electrons and are quenched. The short lifetime of the electrons in the excited state leads the bleaching process to become totally reversible. The electrons are still being promoted, the exciton-polariton pairs are still interacting in the p band, the pairs are still very mobile, but with the high concentration of long-lived trapped electron states around, the electrons quickly decay back down to the ground state and produce a reversible absorbance spectrum. The long-lived trapping states eventually decay after long times and at higher temperatures.

What is the absorbance shape of the new absorbing species of Na+C222Na<sup>-</sup>? Subtracting fractions of the Na+C222Na<sup>-</sup> spectral absorbance shape (found in Section III.B.) from a bleached spectrum demonstrates the approximate spectrum of the trapped states (Figure 48). Qualitatively, the spectral shapes represent the joint density of states between the ground state and the newly accessible energy states. A quantitative description of the spectral shape and origin of these new absorbers is not known.

#### III.D. <u>Stoichiometry Study</u>

Solvent evaporated and vapor deposited films with sodium-to-C222 ratios of approximately unity demonstrate that it is possible to

1.6 1.4 1.2 B) 1.0 0.8 0.6 0.4 0.2 0.0 0.7 0.6 0.5 Absorbance 0.; 0. 0. Figu



Figure 48. Absorbance spectra of a 1000 Å Na+C222Na<sup>-</sup> film: Top, spectra taken before (solid line) and after (dashed line) a 7 ns pulse from a 532 nm Nd:YAG laser; Bottom, spectra of fraction of "true" sodide absorbance subtracted from the dashed line above (dot-dashed line) and remaining absorbing species (large dashed line).

produce the electride Na<sup>+</sup>C222e<sup>-</sup>, even though powders and crystals of this electride cannot be synthesized.<sup>4,40</sup> These studies showed the electride peak to be localized at  $\approx$  1300 nm (0.94 eV, 7.6 x 10<sup>3</sup> cm<sup>-1</sup>). The electride peak was well separated from the residual Na<sup>-</sup> peak in the spectra. Faber sequentially deposited stoichiometric Na+C222e<sup>-</sup> films and found a metastable electride shoulder on the low energy side of the Na<sup>-</sup> peak instead of a separate electride peak (Figure 49).<sup>6</sup> This electride shoulder was positioned at approximately 800 nm (1.55 eV, 1.25 x  $10^4$  cm<sup>-1</sup>) and it decayed rather quickly with time. As the shoulder decayed, the Na<sup>-</sup> peak grew as if the process were a conversion of electride to sodide. A rough isosbestic point (Figure 49) also indicated a conversion from electride to sodide instead of a decomposition of the electride. This conversion agrees with the fact that in sequential deposition the Na has to diffuse through the C222 to find an empty C222 and be encapsulated. The diffusion process may be rather slow at colder temperatures and intermediate phases may be present. The interfaces between the Na and C222 layers would have enough Na to form mostly Na+C222Na-, whereas deep inside the C222 layer there may only be enough Na present to form Na<sup>+</sup>C222e<sup>-</sup>. Faber noted that it does appear that  $Na^+C222Na^-$  is more stable than  $Na^+C222e^-$  so that even the process  $2(Na+C222e^{-}) -> Na+C222Na^{-} + C222$  is favorable.

Shoulders such as the ones seen by Faber were observed under two different circumstances during the present research. The low energy shoulders were first seen during sequential deposition of Na+C222Na<sup>-</sup> films at cold temperatures. Figure 50 shows that the shoulder is similar to that seen by Faber and that it disappears with



Figure 49. Absorbance spectra of a sequentially deposited 2100 Å Na+C222e<sup>-</sup> film deposited by Faber. Film temperature = -100 °C. Spectrum 1 = Initial, 2 = 2 hours after deposition, 3 = 3.5 hours and 4 = 4.5 hours.



Figure 50. Absorbance spectra of a sequentially deposited 1020 Å Na+C222Na<sup>-</sup> film at -40 °C: Diamonds = initial spectrum; circles = 30 minutes after deposition.

time upon warming. However, the shoulder did not appear every time a sequentially deposited film was synthesized at low temperatures.

The low energy shoulder was also observed during a stoichiometry study of the Na+C222Na<sup>-</sup> spectra. The proper stoichiometric ratio for the Na<sup>-</sup> is, of course, Na:C222 = 2:1. Films were made with excess Na (Na:C222 ratios of 2.2:1 and 2.4:1) and with excess C222 (Na:C222 ratios of 2:1.1 and 2:1.2). Each of these films displayed a small shoulder on the low energy side of the Na<sup>-</sup> absorbance peak. Figure 51 shows the spectra of a film with a Na:C222 ratio of 2:1.1 as a representative of these off-stoichiometry experiments. Again, the shoulders decayed with the passage of time coupled with warmer temperatures.

What do these studies say about the electronic structure of Na+C222Na<sup>-</sup>? Why is the extra optical absorbance a shoulder to the main Na<sup>-</sup> absorption peak instead of a separate localized peak? In the case of the films of Le, *et. al.*, the majority of the anions are trapped electrons.<sup>40</sup> These trapped electrons are far enough apart to optically behave similar to other localized electrides, such as  $Cs^+(18C6)_2e^{-.24,70}$  The sequentially deposited and off-stoichiometry films have a small number of trapped electrons, many of which may be trapped in close proximity to the Na<sup>-</sup> anions. The interaction between the trapped electrons and the sodides changes the local electronic structure. The optical absorbance spectra demonstrate this structural change.

The position of the trapped electron peak occurs at the same energy as the new, low energy absorbers observed during the



Figure 51. Absorbance (top) and normalized absorbance (bottom) spectra of a codeposited 1200 Å Na+C222Na<sup>-</sup> film with Na:C222 = 2:1.1: Crosses and diamonds = initial spectrum at -20 °C; circles = spectrum after 20 hours at room temperature.

photobleaching studies. This correlation lends credence to the model that trapped electrons lead to a perturbed electronic band structure. The electrons are trapped due to exciton-exciton interactions in the densely populated p bands in the photobleaching experiments and they are trapped due to spatial variations of the stoichiometry during deposition in the present experiments. These trapped electrons imply the presence of neutral Na atoms in the anionic sites which act as vacancies with positive charges. The combination of trapped electrons and neutral Na atoms leads to a perturbation of the electronic structure of Na+C222Na<sup>-</sup>. This perturbation is apparent in the optical absorbance spectrum in the form of extra absorbances in addition to the typical sodide absorbance.

There is still an unanswered question regarding this study. If there are excess trapped electrons near the sodides, where do they go upon warming? In the present study, the decay of the trapped electron peak is not accompanied by an increase in the sodide peak. There are two possibilities: (1) the trapped electrons do find neutral sodium atoms and form sodides but the increase in the sodide peak is so small that the normal overall decay from reaction with impurities and normal decomposition makes it impossible to detect, or (2) each of the trapped electrons attacks a C222 molecule to cause its decomposition. These two possibilities cannot be distinguished from the present experimental data.

# III.E. <u>Conductivity Study</u>

Many conductivity studies have been performed on Na+C222Na<sup>-</sup>. The results from solvent evaporated thin films, polycrystalline pressed pellets and single crystals demonstrate a band gap between the ground state and conduction band of 2.4 eV.<sup>2</sup> Faber's conductivity study on vapor deposited films was inconclusive due to technical difficulties with the electrical contacts.<sup>6</sup> The present research was able to overcome these problems for longitudinal conductivity measurements. Transverse measurements were not attempted.

The photoelectron emission from Na+C222Na<sup>-</sup> and other sodides has been studied previously.<sup>67</sup> The photoionization action spectrum over the energy range 1.5 to 3.5 eV (350 to 800 nm) showed two peaks. The peak at 3.4 eV is relatively independent of temperature and is attributed to emission from the sodide ion. The shape and amplitude of the peak at 2.0 eV depend on the temperature, cation and complexing agent used and the age of the film. This low energy emission peak is attributed to electrons trapped at defect sites. A more detailed photoemission study which uses a new experimental set-up is currently underway.<sup>69</sup> Preliminary results indicate that an emission peak at about 3.1 eV is the result of emission from a pure, defect-free Na+C222Na<sup>-</sup> film and that the emission peak at about 2.1 eV is the result of emission from trapped electron defect states.

Two attempts to measure the thin film conductivity showed that the dark current was too small to be measured (< picoamps).

The Na<sup>+</sup>C222Na<sup>-</sup> films were both approximately 1200 Å thick and had typical optical absorbance spectra. The inability to measure the current indicated that the sample resistances were more than  $10^{12}$ When the samples were illuminated by the Guided Wave Ω. tungsten lamp, though, the current jumped up by a factor of more than 100 and was measurable. The white light passes through the sapphire and then enters the back of the film. The photo-current of the first film decayed away within an hour. The direction of the light beam was then reversed, so that the light illuminated the front of the film. The current again jumped up by a factor of more than 100 and started to decay. Switching the light to the backside of the film showed that there was still no measurable current with that configuration. For the second film, the direction of the light was switched back and forth several times before the back-illuminated current had decayed away. This switching revealed that the photoinduced conductivity for the front illumination was more than 10 times greater than for the back illumination. Both photo-induced conductivities steadily decayed.

The above results indicate that the measured photo-induced conductivity is due to photoemission. The photons actually knock some of the electrons out of the film and into the vacuum where they are attracted to the cathode and measured as a current. It is true that the amount of film illuminated by the light source through the back of the film is smaller than the amount illuminated in the front (the electrodes block approximately 50% of the light beam coming from behind the film). This difference, though, is not enough to make such a large difference in currents. Also, the backilluminated photoemission current should be reduced by more than just the geometrical factor of the electrodes. The absorbance of the film will keep many back-illuminating photons from reaching the states near the surface of the film and ejecting electrons, whereas many more of the front illuminating photons will reach the ejectable electrons.

What does the conductivity study reveal? It is apparent that the sample is so resistive that the probability of an electron to travel from the anode to the cathode via ejection into the vacuum (where the electron would then travel through the vacuum to the cathode) is much better than via excitation into the conduction band (where the electron would then have to travel 0.4 mm through the sample to the cathode). Using the measured resistivity of one of the illuminated samples ( $10^6 \Omega$  cm), an unrealistic value of the scattering relaxation time ( $\tau = 10^{-24}$  seconds) in the conduction band is obtained from  $\sigma = Ne^2\tau/Vm$ . After calculating the Fermi velocity for the sodide from  $(h/2\pi m)(3\pi^2 N/V)^{1/3}$ , an equally unrealistic value for the mean free path  $(10^{-18} \text{ m})$  can be found. Even if the Drude model which was used to calculate these numbers is not considered valid for a semiconducting material, the estimated value of the mean free path is fifteen orders of magnitude shorter than the experimental conducting path length. This implies that the measured current is not a result of photoconductivity. Another way to approach this question quantitatively is to use the Fermi velocity and the known path length (0.4 mm) to estimate a relaxation time necessary for an electron to traverse the anode/cathode gap ballistically. This estimation shows that the electron would have to remain in the conduction band for 0.9 nanoseconds in order to cross the gap. There are two experimental reasons which show that this process is not likely. One, in a material such a polycrystalline sodide film, it is highly unrealistic to expect an electron to travel 0.4 mm ballistically. The collisions would slow down the electron and, thus, the time the electron would need to spend in the conduction band would be increased. Two, the photoluminescence studies show that the *total* time an electron spends in the excited state is 5 nanoseconds.<sup>61,63</sup> The actual time spent only in the conduction band is not known, but even if it is as long as a few nanoseconds, the collisions described above would probably increase the time required to traverse the gap to a value greater than this.

Photoemission into the vacuum is a known process for Na+C222Na<sup>-</sup>. The probability of this photoemission leading to the measured conductivity is far greater than the probability for photoconduction. A photon energy dependence study of the photoemission current is presently being pursued with a newly constructed apparatus.<sup>69</sup> The white light study done here shows that photoemission is occurring, but no specifics on the structure of the energies involved in this process were studied. Since the dark current was not measurable, a temperature dependence study of the resistivity was not possible and a band gap was not calculated.

## III.F. Conclusions

We now have a better understanding of the vapor deposited thin film properties of the alkalide Na+C222Na<sup>-</sup>. The temperature dependence study of the main absorption peak has divulged information regarding the position and shape of the ground state and excited state bands. The breadth of the absorbance peaks is attributed to anisotropic excited p band states and thermal broadening. As the film temperature is increased, the absorbance peak position shifts to lower energies and the low energy side of the absorbance peak broadens. Thermal expansion of the lattice and phonon-assisted indirect optical transitions both contribute to the temperature dependent absorbance peak parameters. The photobleaching study described the new absorbances that are created when the films are illuminated by intense laser blasts. The intense laser pulses produce a high concentration of mobile excitons in the p band. When these excitons interact with each other, newly accessible defect states are found which trap the electrons. The trapped electrons, and resulting neutral sodium atoms, perturb the electronic structure of the sodide. This perturbation is apparent in the modified optical absorbance spectrum. The stoichiometry study also described new absorbances. These absorbances were created during the deposition of films that were prepared with excess sodium or cryptand. The non-stoichiometric films had trapped electrons and neutral sodium atoms physically included in the structure of the film. These "impurities" perturbed the ground state and excited state bands in the same way as the "impurities" of the photobleaching experiment. Finally, even though a band gap was not determined with the conductivity study, evidence for photoemission was observed. Adding these experimental pieces to the total picture of the Na+C222Na<sup>-</sup> puzzle assists in the understanding of how and why this unusual compound behaves as it does.

IV. K+C222e<sup>-</sup>

#### IV.A. Introduction

K+C222e<sup>-</sup> is the most conducting alkalide or electride. The vapor deposition apparatus allows a unique opportunity to simultaneously study both the optical and electrical properties of this intriguing compound. Previous studies, as described below, examined these two properties (and many others) on samples prepared in a variety of ways. The present research is designed to look for correlations between the optical and electrical properties of K+C222e<sup>-</sup>.

Several previous discussions relate the structural, optical, electrical and magnetic properties of K+C222e<sup>-,45,71</sup> The open, twodimensional channels which interconnect pairs of trapped electrons (as described in Chapter I) allow strong electron-electron interactions. The strong interactions lead to interesting physical properties. This section will elaborate on these properties.

A study of K+C222e<sup>-</sup> would not be complete without a parallel study of K+C222K<sup>-</sup>. The crystal structures are similar and sometimes the synthesis of either of these compounds is complicated by "impurities" of the other. Most characterizations of these compounds use material that is crystallized from solution. Special care is taken during these syntheses to assure that the pure compound is prepared. For example, to make a pure electride, excess C222 is used in the solution synthesis. This procedure assures that every

135

potassium atom is encapsulated by a C222 molecule as a K<sup>+</sup> ion. The solution then contains mainly electrons (few potasside ions) as the anionic species. The solvent is removed from the crystals, which leaves only the electride material (any excess C222 is washed away with another solvent). The vapor deposition process does not have the luxury of removing excess complexant or metal by such a procedure. The consequences of this limitation will be demonstrated.

The optical absorbance spectra of K<sup>-</sup> in solution showed a single, solvent-dependent peak between 850 and 950 nm (1.3 and 1.5 eV, 10500 and 11800 cm<sup>-1</sup>).<sup>14,72</sup> This peak was assigned to the  $4s^2$  to 4s4p transition. This assignment is analogous to the Na<sup>-</sup> peak assignment in Na<sup>+</sup>C222Na<sup>-</sup>.

Optical absorbance spectra of thin films of K+C222K<sup>-</sup> from rapid solvent evaporation showed a major peak at approximately 880 nm (1.4 eV, 11400 cm<sup>-1</sup>).<sup>4,5,37</sup> The spectra of films prepared from ammonia solutions also showed a low energy shoulder at 1300 nm (0.95 eV, 7700 cm<sup>-1</sup>) accompanying the K<sup>-</sup> peak, whereas the films prepared from ethylamine and methylamine did not demonstrate a shoulder. The shoulder, when present, was attributed to trapped electrons in the films.

The optical absorbance spectra of solvent-evaporated K+C222e<sup>-</sup> films showed three different types of behavior. A dry film prepared from an ammonia solution demonstrated a plasma edge spectrum that increased in absorbance from 400 to 2000 nm (3.1 to 0.62 eV, 25000 to 5000 cm<sup>-1</sup>.<sup>4</sup> Faber saw a plasma edge using a dry film from a solution of single crystals dissolved in dimethylether.<sup>6</sup>

Another dry film prepared from an ammonia solution initially showed both a K<sup>-</sup> peak and an e<sup>-</sup> peak (900 nm, 1.4 eV, 11000 cm<sup>-1</sup> and 1800 nm, 0.69 eV, 5600 cm<sup>-1</sup>, respectively).<sup>5</sup> This spectrum evolved (or annealed) over several hours into a plasma edge with a small K<sup>-</sup> bump remaining at 900 nm. The third type of optical absorbance spectra found for a dry electride film was a well-defined peak at 1350 nm (0.92 eV, 7400 cm<sup>-1</sup>).<sup>37</sup> This film was prepared from a methylamine solution. The question that needed to be answered was: Would the real K+C222K<sup>-</sup> and K+C222e<sup>-</sup> absorbance spectra please stand out and be recognized?

The first vapor deposited films did not have well-defined stoichiometry or thickness, but they did demonstrate that potasside and electride films could be synthesized without the use of a solvent.<sup>40</sup> The potasside films showed a K<sup>-</sup> peak and a trapped electron shoulder similar to the solvent-evaporated films. The electride films showed a very broad peak centered at approximately 1350 nm (0.92 eV, 7400 cm<sup>-1</sup>) with a bump at about the K<sup>-</sup> position (800 - 900 nm).

The vapor deposited films prepared by Faber in the evaporation apparatus had better stoichiometry and thickness control.<sup>6</sup> The spectra for the K+C222K<sup>-</sup> films contained two peaks: a potasside peak at 870 nm (1.4 eV, 11600 cm<sup>-1</sup>) and an electride peak at 1250 nm (0.99 eV, 8000 cm<sup>-1</sup>). These peaks decayed upon warming. The initial K+C222e<sup>-</sup> spectra appeared to contain the same two absorbance peaks. At a constant temperature of -60 °C, though, the peaks "annealed" to a plasma edge within an hour or two. The plasma edge decomposed upon warming.

The electronic conductivity of polycrystalline samples of the apparently delocalized K+C222e<sup>-</sup> was found to be 10 orders of magnitude larger than that of other electrides with localized electron traps (such as  $Cs+(15C5)_2e^{-}$ ).<sup>46</sup> Four-probe measurements on pressed pellets found a resistivity at 130 K of not greater than 0.2  $\Omega$  cm and a band gap of 86 meV. The leads for the measurements were coated with potassium metal to minimize electrode effects (such as a Schottky barrier). Impedance spectroscopy (ac conductivity as a function of frequency) indicated that even the few ohms of residual resistance may be dominated by grain-boundary or other electrode effects. K+C222e<sup>-</sup> appeared to be a highly conducting semiconductor, but extrinsic electronic conductivity from defects could not be eliminated as a possibility.<sup>46</sup>

Electron paramagnetic resonance (EPR) studies on K+C222e<sup>-</sup> also indicated that this compound is a good conductor (possibly a metal or near-metal).<sup>6</sup> The samples absorbed the microwave radiation so efficiently that it was impossible to tune the cavity even with an extremely small amount of material. This behavior is indicative of a metallic sample.

The magnetic susceptibility results for K+C222e<sup>-</sup> were interpreted with the crystal structure in mind.<sup>7</sup> The simplest interpretation of the behavior was that the two electrons in the large double-trap cavities interact strongly and lead to singlet ground states with excited triplet states lying about 50 meV above the ground state. The interactions between adjacent electron pairs through the two-dimensional network of channels were assumed to be much weaker.

How are the above physical properties related to the open. two-dimensional channel structure of K+C222e<sup>-</sup>? The optical spectra appear to anneal to a plasma edge, which would indicate that after they anneal the electrons are communicating with each other via the channels. The conductivity demonstrates that the electrons not only communicate via the channels, but are also very mobile through the channels (although, defects and an activated hopping mechanism may be the true reasons that the conductivity is so high). Fourprobe single crystal conductivity measurements along the three different axes would provide definitive evidence regarding the conducting properties of this electride, but such measurements have extreme experimental problems to overcome. EPR studies indicate that the electride is a very good microwave conductor, similar to metals. The magnetic susceptibility behavior was interpreted by using the known crystal structure as a guide, but it does raise another interesting question: Is K+C222e<sup>-</sup> a triplet state conductor?

The results presented in the rest of this chapter will look at K+C222e<sup>-</sup> from a different point of view. First, the thin film optical absorbance properties of both the alkalide and electride will be presented. A resolution to the question of the true absorbance spectra for the compounds is discussed. Then, combined conductivity and optical properties of the thin films will be presented and discussed.

Most of the films synthesized with the vapor deposition apparatus for the present research and described in this chapter were deposited at -60 °C. Any time-dependent changes in the absorbance spectra at temperatures below -30 °C are annealing processes since the films are stable at low temperatures. Most of this annealing is assumed to be due to the migration of potassium atoms in an attempt to make the film more homogeneous. Some of the annealing may be due to a surface reorganization similar to that seen in thin alkali metal films by Rasigni and Rasigni.<sup>73,74</sup> Time dependent changes in the optical spectra at temperatures above -30 °C are accompanied by decomposition of the films and therefore cannot be assigned only to annealing processes.

## IV.B. Absorbance Spectra

The description of the search for the true optical absorbance spectra of vapor deposited thin films of K+C222K<sup>-</sup> and K+C222e<sup>-</sup> begins with the potasside. Two different types of spectra were seen for K+C222K<sup>-</sup>. The first type, shown in Figure 52, is a single peak centered at 860 nm (1.44 eV, 11600 cm<sup>-1</sup>). The noise in the data is due to the limited spectral range of the grating used in the spectrophotometer The effect of this grating was to lower the intensity of light being sent to the detector enough to make the data appear noisy. This type of absorbance spectra was seen only once. The synthesis of this film was not special in any noticeable way. The peak quickly decayed, even though the film was kept at -60 °C. It was later found that the cause was the white light from the optical analysis system that was trained on the film at all times for conductivity purposes. The light may have heated the film which lead to the decomposition or the light may have bleached the



Figure 52. Absorbance spectrum of a codeposited 1200 Å K+C222Kfilm at -60 °C. This type of spectrum was only seen once.

film, but a photolytic decomposition mechanism (as discussed in Chapter III) probably caused the decay of the absorbance.

The other, more common type of K+C222K<sup>-</sup> film spectrum is shown in Figure 53. Variations of this double peak were seen for every potasside film synthesized during the course of this research. except for the film described above. The main absorbance peak is largely due to K<sup>-</sup> although peaks and shoulders caused by potassium metal globules may also contribute.<sup>75</sup> The usual position of the K<sup>-</sup> peak is 870 nm (1.43 eV, 11500  $\text{cm}^{-1}$ ). The lower energy peak is attributed to trapped electrons. Its usual position is at 1300 nm  $(0.94 \text{ eV}, 7600 \text{ cm}^{-1})$ . The initial spectra always show that the potasside peak is larger than the trapped electron peak. Sometimes the trapped electron peak appears as only a broad shoulder on the low energy side of the K<sup>-</sup> peak. These two peaks are fairly stable at low temperatures. Upon warming, though, both peaks begin to decay. The K<sup>-</sup> peak decays more quickly than the trapped electron peak. This usually leaves the absorption spectra at later times and warmer temperatures in the shape of a plasma edge with small K<sup>-</sup> and trapped electron peaks.

The optical absorption spectra of vapor deposited thin films of stoichiometry K+C222e<sup>-</sup> also demonstrate two different initial shapes. Several of the electride films initially had plasma edge spectra, as shown in Figure 54. A small trapped electron peak appears on the plasma edge at the same position as in the potasside spectra (1300 nm, 0.96 eV, 7700 cm<sup>-1</sup>). At cold temperatures, these spectra are stable for at least several hours. When the films are warmed above -30 °C, though, the entire spectrum slowly decays.


Figure 53. Absorbance spectrum of a codeposited 1400 Å K+C222Kfilm at -60 °C. Notice the extra absorbance "bumps" at 14000 and 18000 cm<sup>-1</sup>.



Figure 54. Absorbance spectrum of a codeposited 1400 Å K+C222e<sup>-</sup> film at -40 °C. Notice the trapped electron peak at 8000 cm<sup>-1</sup> on the plasma edge-shaped spectrum.

The small trapped electron peak does not change in shape with respect to the plasma edge. The absorbance spectra are completely flat before the film temperature reaches 0 °C.

Most of the films with the stoichiometry K+C222e<sup>-</sup> have initial optical spectra that contain a large K<sup>-</sup> peak (870 nm, 1.43 eV, 11500 cm<sup>-1</sup>) and a small trapped electron peak or shoulder (1280 nm, 0.97) eV, 7800 cm<sup>-1</sup>). Figure 55 and 56 show spectra of such films. The spectra in Figure 55 are from a film that did not have accurate substrate temperature control (it is now assumed that the temperature for this film was approximately -40 to -50 °C). The temperatures quoted on the spectra in Figure 56 are accurate. The peak positions correspond well with the positions of the peaks found in the initial spectra of the potasside films. The electride spectra, though, anneal at low temperatures. If two separate peaks are initially present, the trapped electron peak will evolve first into a trapped electron shoulder and then disappear into the plasma edge. During the electron peak annealing process, the K<sup>-</sup> peak is also continually decaying, which usually leaves only the plasma edge. The trapped electron peak (or shoulder) always anneals faster than the K<sup>-</sup> peak. If an electron shoulder is initially present on the low energy side of the  $K^-$  peak, a similar annealing process occurs. The amount of residual potasside in the film spectra is sample dependent. Several runs showed that most of the potasside is converted to the plasma edge during the annealing process. Usually, though, a small K<sup>-</sup> peak remained atop the plasma edge. After the annealing process, the spectra (with either a plasma edge shape or a plasma edge shape with a small K<sup>-</sup> peak) were stable for at least



Figure 55. Evolution of the absorbance spectra of a codeposited 1350 Å K+C222e<sup>-</sup> film at approximately -60 °C: plus signs = initial spectrum; crosses = one hour after deposition; squares = two hours after deposition; circles = three hours after deposition. Notice the isosbestic point at 7000 cm<sup>-1</sup>.



Figure 56. Evolution of the absorbance spectra of a codeposited 1800 Å K+C222e<sup>-</sup> film at -60 °C: solid line = initial spectrum; dotted line = one hour after deposition; dashed line = 1.5 hours after deposition; dot-dashed line = two hours after deposition. Notice the rough isosbestic point at 7000 cm<sup>-1</sup>. several hours. These absorption spectra decayed when warmed above -30 °C. Some of the spectra showed the K<sup>-</sup> peak to decay faster than the plasma edge during decomposition, while other spectra showed that the two features decay uniformly.

A qualitative analysis of the spectral shapes of K+C222K<sup>-</sup> and  $K+C222e^{-}$  indicates a new type of electron trapping site in the polycrystalline films. The physical interpretation of the trapped electron peak or shoulder when a K<sup>-</sup> peak is present is the same as for the Na+C222Na<sup>-</sup> case described in Chapter III. That is, the energy levels of the electrons which are trapped in a region containing mostly potasside ions are perturbed, resulting in the trapped electron peak or shoulder. Some of the spectra show that the separate peak evolves first into a shoulder of the K<sup>-</sup> peak and then into the plasma edge. Thus, a possible description of the environment of the absorbing electrons can be hypothesized. The trapped electron absorbance appears more localized (a separate peak) when the electrons are surrounded by many K<sup>-</sup> ions and appears less localized (a shoulder) when the electrons are surrounded by fewer K<sup>-</sup> ions. The evolution of the absorbance is describing the annealing of the film. The electrons that are trapped in regions containing mostly electride have a plasma edge spectral shape. This physical interpretation needs a slightly modified description to explain the trapped electron peak observed in spectra of electride films which contain a plasma edge, but no K<sup>-</sup> peak. The implication of this peak is that it is not necessary for the trapped electron to be in the vicinity of K<sup>-</sup> ions to produce such an absorbance peak. The question becomes: Why don't these trapped

electrons act like the other plasma-type electrons? One possible explanation for this lone trapped electron peak is that it represents the electrons that are somehow isolated from the rest of the plasmatype electrons. In this case, the isolation implies localization. This isolation may be due to grain boundaries present in the polycrystalline samples or imperfections in individual crystallites. Both of these irregularities would interrupt the channel structure of the electride. The interruptions would lead to isolated cavities of trapped electrons which would be seen as localized absorbance peaks in the optical spectra. These localized electrons probably contribute to the trapped electron peaks or shoulders in the film spectra that also contain alkalide ion peaks.

A quantitative study on the electride absorbance spectra looks at the conservation of oscillator strength. Simple conversion from a spectrum that contains a large K<sup>-</sup> peak with a small trapped electron peak or shoulder to a spectrum that contains a plasma edge should conserve the total oscillator strength. The occurrence of a rough isosbestic point during the evolution indicates a conversion of potasside to electride and not a decomposition. It is obvious from Figure 56 above that the oscillator strength, which is proportional to the area under the absorbance versus wavenumbers curve, is not conserved during the conversion from potasside to electride in the spectral range attainable with the present equipment (400 nm to 2200 nm, 4500 cm<sup>-1</sup> to 25000 cm<sup>-1</sup>). Thus, there must be an increase in the absorbance spectra outside this range. Clearly, the absorbance continues to increase at wavenumbers below 4500 cm<sup>-1</sup>. To conserve the oscillator strength, though, the absorbance curve of the plasma edge in Figure 56 would need to continue to increase steeply and intersect the zero energy axis at an absorbance value of about 2.0. Of course, there may be other transitions in this infrared region. It is known that there are many vibrational modes from the cryptand molecule in the infrared region. It is possible that the loss of some of the oscillator strength in the optical region accessible in this study is a result of coupling of the vibronic modes of the cryptand to the electrons in the infrared region. A sample holder is presently being constructed to allow thermally unstable and air sensitive samples, such as electrides, to be analyzed with an existing infrared absorbance instrument. It is hoped that this analytical technique will assist in laying to rest the mystery of the disappearing oscillator strength.

Payan originally studied thin film absorbance spectra of the alkali metals.<sup>75</sup> Potassium films demonstrated two absorbances in the 250 to 1100 nm range: one peak at 13000 cm<sup>-1</sup> and another, small peak at 19000 cm<sup>-1</sup>. Occasionally, several extra, small absorbance bumps were observed in the initial optical spectra (for example, the small bumps at about 14000 and 18000 cm<sup>-1</sup> that can be seen in the spectra of the potasside in Figure 53) which usually disappeared rather quickly. The peak positions observed in Payan's work on potassium metal compare well with these peak positions. The extra absorbance bumps were always more prominent when a potasside or a potassium "doped" electride (Figure 57) were synthesized. An attempt to reproduce Payan's results was made. A thin film of potassium metal (150 Å, a thickness similar to the total amount of K metal used for a thick K+C222e<sup>-</sup> film) was deposited,



Figure 57. Absorbance spectrum of a 2750 Å off-stoichiometry K/C222 film at -60 °C. K:C222 = 1.5:1. Notice the extra absorbance "bumps" at 14000 and 18000 cm<sup>-1</sup>.

but the optical absorbance spectrum was flat. A thick film of potassium metal (500 Å) was deposited. The optical spectrum of this film had three large absorbance peaks (Figure 58). Only one of these peaks (the large one at  $18000 \text{ cm}^{-1}$ ) corresponds well to any of the peaks observed by Payan. The highest energy peak (23000 cm<sup>-1</sup>) was not observed by Payan and the lowest energy peak (10000 cm<sup>-1</sup>) appears shifted to a much lower energy than Payan's second peak. The spectrum is time and temperature dependent. This dependence did not allow the spectra to be used in a systematic way in assisting the fits performed on the entire K+C222e<sup>-</sup> spectra. Also, the 10000 cm<sup>-1</sup> absorbance peak from the K metal (Figure 58) is not at the same energy as the  $K^-$  peak (Figure 57, for example). This result reconfirms that we are not just looking at metallic film absorbance spectra, but actually potasside and electride spectra. The K metal is probably mobile on the sapphire substrate and it may form islands. The one unusual deposition parameter for this thick film of potassium is that a bias voltage was applied across the substrate during the deposition. No conductivity was observed, even at 500 Å. Thus, a continuous film was never formed on the substrate. There will be more discussion of this topic in the next section of this chapter.

The Drude model of metals is an oversimplified model of how free electrons behave in a metal. K+C222e<sup>-</sup> is not a metal, but it appears to be nearly metallic and the optical absorbance spectra resemble broad plasma edges. An approximation of the mean free path of the electrons in the electride can be made by using the Drude model. This model<sup>54</sup> treats the electrons as free particles in a



Figure 58. Absorbance spectrum of a 500 Å K metal film at -60 °C. These peaks were time and temperature dependent.

gas. The electrons are moving rapidly in all directions if no external field is applied. An external electric field E applies a force -eE to each electron. This force superimposes a drift velocity  $v_d$  onto each electron. If it is assumed that the electrons have a mean scattering time  $\tau$ , which causes  $v_d$  to relax to zero if E is suddenly turned off, the equation of motion becomes:

$$m^*(dv_d/dt) + m^*v_d/\tau = -eE.$$

The crystal plays no direct part in this model, but it does cause the electron mass m to be replaced with an effective mass m<sup>\*</sup> and it does provide a mechanism for scattering. Replacing  $v_d$  with  $dr_d/dt$  (where  $r_d$  is the mean electron displacement resulting from the applied field) yields:

$$m^{*}(d^{2}r_{d}/dt^{2}) + (m^{*}/\tau)(dr_{d}/dt) = -eE.$$

This equation is identical to the equation used in Chapter I for deriving the oscillator strength, except this model has  $\omega_0 = 0$  (the electrons are not bound by harmonic forces to the cores) and the damping constant  $\gamma$  is replaced by  $1/\tau$  (from the comparison of the two equations of motion). The solutions to the more complex equation of motion were derived at that time. Using the new set of constants leads to:

$$\varepsilon = 1 - \omega_p^2/(\omega^2 + i\omega/\tau)$$

where  $\omega_p^2 = 4\pi e^{2N/m*V}$  defines the plasma frequency. If the overall density of the electride is used, a plasma frequency of 2 x  $10^{15}$  sec<sup>-1</sup> is found. This corresponds to a plasma energy of 1.4 eV or a plasma wavelength of 940 nm (11000 cm<sup>-1</sup>). The Drude model says that all wavelengths of light that are longer than the plasma wavelength are reflected and all shorter wavelengths are transmitted. This is the origin of the phrase "UV transparent" metals. The slope of the curve dividing the transparent and reflective portions of the optical spectrum is infinite for an ideal Drude metal. As the mean free path (or the relaxation time t) of the electrons in the metal becomes shorter, though, the slope of this curve becomes smaller. This qualitative description compares well with the optical absorbance spectra of the electride that are observed. The small slope seen in the spectrum implies that the electride has a short mean free path.

The relationships between the dielectric function and the optical constants of a material (also derived in Chapter I) reveal:

 $\alpha = (\omega_{\rm p}^2 \tau / n_1 c) (1 + \omega^2 \tau^2)^{-1}.$ 

Thus, fitting the absorbance spectra with a curve of the form ABS =  $A/(1 + B\omega^2) + C$  will yield a value of  $\tau = 4.5 \times 10^{-15}$  sec from the constant B = 1.494 ± 0.027 (Figure 59). A small gaussian peak was added to this particular fitting routine to accommodate the small K<sup>-</sup> peak that remains atop the plasma edge. This fit also yields an estimate of  $n_1 = 7.5$  from the constant A = 0.7062 ± 0.0032 (using the  $\tau$  found from B). The value of C for this fit is 0.0438 ± 0.0015.



Figure 59. Absorbance spectrum of a codeposited 1800 Å K+C222e<sup>-</sup> film at -60 °C (dots). The solid line represents the fit to a plasma edge absorbance plus a potasside peak.

To calculate a mean free path length, an estimate needs to be made for the mean electron velocity. Continuing the assumption that K+C222e<sup>-</sup> is nearly metallic, the Fermi velocity is calculated from  $v_F = (h/2\pi m)(3\pi^2 N/V)^{1/3}$  and used to determine a mean free path of approximately 17 Å. This implies that the electrons may be able to move ballistically for a distance equivalent to the distance between 2 or 3 electron-pair cavities.

There are many problems with the assumptions made to calculate this mean free path of 17 Å for K+C222e<sup>-</sup>. The most obvious is that the electride is not a free-electron metal. Another serious problem is that the Drude model assumes an isotropic material. The channel structure of K+C222e<sup>-</sup> is highly anisotropic. One basic question that does arise from the comparison of the Drude model for metals and the semiconducting electride is: Can a semiconductor be considered a metal with a very short mean free path? The answer to this question is: probably not (although it may be used as a crude approximation). One of the major defining characteristics of the difference between a metal and a semiconductor is the value of the conductivity extrapolated to 0 K. No electrons in a semiconductor can thermally populate the conduction band even with a very small band gap, whereas metals have no such restriction for conductivity.

Is there a physical model that parallels the annealed behavior that is seen for K+C222e<sup>-</sup>? The keys to formulating such a model are the different energy scales used to probe the physical characteristics of the electride. The optical absorbance spectra demonstrate that the electrons that are participating in the absorption process are

populating a continuum of states above an energy of approximately 0.5 eV (lowest energy photons used). One possible interpretation of this observation is that the electrons occupy a partially filled conduction band (Figure 60a). This interpretation is not the only possibility. Another possible interpretation of the experimental data is that the electrons participating in the absorption process are in a band or in trapped states below the continuum band. As was shown in earlier studies<sup>46</sup> (and will be shown in the next section of the present work), the conductivity measurements demonstrate an activated conductivity process that only requires energy on the order of 0.05 to 0.10 eV. The use of this piece of experimental data leads to three other diagrams. Figure 60b represents a model where the singlet ground state is the valence band and the triplet excited state is the conduction band (an intrinsic semiconductor). Figure 60c represents a model where there is a large energy gap between the valence band and the conduction band, but a donor band of electrons lies just below the conduction band (an extrinsic semiconductor). Finally, Figure 60d represents a model where there is a large energy gap between the ground state valence band and the conduction band again, but in this case there are trapped electron states below the conduction band. The conduction band is thermally inaccessible to these trapped electrons, but a thermally activated hopping mechanism still allows conductivity. The measurement of absorbance and conductivity probe two different energy scales which can be used together to form these elementary pictures.

A Beer's Law plot is shown for K+C222e<sup>-</sup> in Figure 61. It is quite scattered, but shows the proper trend of increasing absorbance



Figure 60. Schematic representation of several simple band-like models as described in the text.



Figure 61. Beer's Law plot for the absorbance value at 8000 cm<sup>-1</sup> of many K+C222e<sup>-</sup> spectra.

maxima for increasing thickness. The slope shown in the figure is  $3.24 \pm 0.44 \times 10^{-4}$  Å<sup>-1</sup>. The y-intercept (-0.098 ± 0.069) also does not go directly through the origin (probably due to light scattering if not to the scatter of the data), but it is within about 2 standard deviations. The major reason for the scatter of the data is the variety of types of spectral shapes obtained for the optical absorbance of the electride. Where is the true absorbance maximum for a specific spectrum? An attempt was made to choose an absorbance value at 8000 cm<sup>-1</sup> from a spectrum of each film that was similar in shape (a plasma edge with small K<sup>-</sup> and/or trapped electron peaks). The choice of this specific shape and the specific position in wavenumbers was arbitrary, but it decreased considerably the amount of scatter in the data to that shown in Figure 61.

The picture of the true vapor deposited thin film optical absorbance spectra of K+C222K<sup>-</sup> and K+C222e<sup>-</sup> is now clearer than before. It is very difficult to form a pure potasside film via vapor deposition techniques, although a film with a single K<sup>-</sup> absorbance peak was observed once. All attempts to synthesize a film that repeats this spectrum resulted in absorbance spectra with both a potasside peak and a trapped electron peak or shoulder. The implication of this observation is that the K<sup>-</sup> ions block the open channels and make it very difficult for the excess trapped electrons and potassium ions to migrate through the potasside film in an attempt to form a nearly homogeneous film.

The results for the K+C222e<sup>-</sup> spectra were much more successful. It appears that the absorbance spectrum for the films of

the electride that are thermodynamically stable is a plasma edge. No matter what the initial optical absorbance spectral shape was, an annealing process converted the spectrum into a plasma edge. The diffusional mobility of the excess trapped electrons and K<sup>-</sup> ions appears to be much higher in the electride films than in the potasside films. This is presumably due to the relatively small concentration of K<sup>-</sup> ions blocking the open channels in the electride. The high mobility allows the annealing process to homogenize the small regions of the films that have a slight excess of trapped electrons or potassium.

What is the chemistry behind the annealing process? When a film is codeposited with a stoichiometry of K:C222 = 1:1, the majority of the material on the substrate has reacted to form K+C222e<sup>-</sup>. There will be, however, slight inhomogeneities in the film composition which lead to the conclusion that K<sup>-</sup> ions, potassium atoms, trapped electrons and excess C222 are present. The K<sup>-</sup> ions, K atoms and trapped electrons will diffuse through the channels of the material quite easily in the regions where the concentration of K<sup>-</sup> ions is small. Regions of large concentrations of K<sup>-</sup> ions, such as in pure potasside films and potassium "doped" electride films, block the open channels and limit the diffusive migration. When a K<sup>-</sup> ion happens upon an empty C222 molecule, two electrons are released into the channel structure as the potassium cation is encapsulated by the cryptand. Likewise, when a K atom finds an empty C222 molecule, one electron is released into the channels as the potassium cation is complexed. It is also possible for the K<sup>-</sup> ion to lose its electron. This process leaves the neutral K atom and the electron to diffuse separately through the material. What is the result of all of these chemical processes? The optical absorption spectra show that the initial K<sup>-</sup> peak and trapped electron peak or shoulder evolve into a plasma edge with time at a constant temperature. This evolution is due to the diffusive migration (and then chemical reaction) of the initial "impurities" in the film to the more thermodynamically stable pure electride.

## IV.C. Conductivity Study

This section will detail the combined optical and conductivity studies of vapor deposited thin films of K+C222K<sup>-</sup> and K+C222e<sup>-</sup>. The correlation between these two types of measurements will be discussed. The results for the potasside will be presented first and then the electride results will be presented. The ensuing discussion will explain how these results expand the overall picture of the nature of this electride.

Two-probe conductivity measurements were performed on  $K+C222K^{-}$  films which had both of the types of optical absorbance spectra described above. The conductivity of the 1200 Å potasside film with a single K<sup>-</sup> absorbance peak (Figure 52) was too small to be measured. With a bias voltage of 5 Volts, the dark current through the sample was less than picoamps. Shining the white light from the Guided Wave source on the film induced a measurable current. A plot of  $ln(\rho)$  versus time for this experiment is shown in Figure 62. The units of  $\rho$  used throughout this work are  $\Omega$  cm. The current eventually drops below the measurement capabilities of the



Figure 62. Two-probe  $ln(\rho)$  versus time for the codeposited K+C222K<sup>-</sup> film shown in Figure 52.

amplification circuit after 25 minutes of illumination. This corresponds with the time when the K<sup>-</sup> peak has decayed to a flat line absorbance spectrum.

One possible interpretation of the observed behavior is that the conductivity is a result of photoemission. This phenomenon occurred with the Na+C222Na<sup>-</sup> films, as described in Chapter III. The emission continued until the illuminating light warmed and decomposed the entire sample. It would be desirable to repeat this experiment and then treat the sample with more care for better analysis. However, no other potasside film had a spectrum with a single K<sup>-</sup> absorption peak.

The rest of the conductivity studies on K+C222K<sup>-</sup> were performed on films which had optical spectra containing both K<sup>-</sup> and trapped electron absorbance peaks. The thickness of these films ranged from 1000 to 1500 Å. These films were better than three orders of magnitude more conducting in the dark than the illuminated films which had a single absorbance peak. The resistivity of the films with a mixed potasside/electride absorbance spectrum was typically  $\ln(\rho) = 8$ , compared to  $\ln(\rho) = 16$  for the potasside alone. In fact, the resistivity continually decreased as the two absorbance peaks decreased in intensity. Eventually, the conductivity became so large that the amplifier (with the  $10^9 \Omega$ resistor) could no longer handle the current and the conductivity portion of the experiment was halted. At warmer temperatures, the spectra evolved into a plasma edge with two small absorbance peaks at the typical K<sup>-</sup> and trapped electron positions.

It appears that portions of the potasside film were annealing to an electride. This process increased the conductivity steadily. The electride "impurities" in the potasside film increase the conductivity of the potasside significantly. Since all of the potasside films undergo a transformation to an electride-like film and the conductivity continually increased during this transformation, the study turned to take a closer look at the electride conductivity. The first set of K+C222e<sup>-</sup> conductivity results used the two-probe set-up and the amplification circuit. To avoid the problem of the amplified current going off-scale, a  $10^6 \Omega$  resistor was used in the amplification circuit for these two-probe measurements.

A typical K+C222e<sup>-</sup> conductivity experiment proceeded as follows after a codeposited film was formed. A bias voltage was applied to the sample and the output voltage from the amplification circuit was recorded on an XY plotter. The film temperature was held constant at -60 °C until the absorbance spectrum was time independent. The temperature was then varied (usually between -30 and -100 °C) in an attempt to measure the apparent band gap of the electride material. Then the temperature was allowed to warm above -30 °C to observe the optical and electrical effects of decomposition.

A typical two-probe  $ln(\rho)$  versus inverse temperature plot is shown in Figure 63 for K+C222e<sup>-</sup>. The initial conductivity of the K+C222e<sup>-</sup> films at -60 °C ranged from 0.1 to 1 ( $\Omega$  cm)<sup>-1</sup>. These values were only 10 to 100 times larger than previous four-probe pressed pellet resistivity values for this electride.<sup>46</sup> As described above, the absorbance spectra anneal at -60 °C from two peaks (or a



Figure 63. Two-probe  $ln(\rho)$  versus inverse temperature for a codeposited 1400 Å K+C222e<sup>-</sup> film after the film has been annealed.

peak and a shoulder) to a plasma edge. The change in conductivity during this conversion was sample dependent. As the optical spectra evolved, the conductivity increased, decreased or remained the same, but no correlation could be found between these changes and the spectral shapes of the absorptions or the film deposition parameters. Figure 64 just happens to show an example where the resistivity during the annealing process increased.

The data for the apparent band gap measurements were taken at cold temperatures (-100 °C < -30 °C) in a time-temperature region where the absorbance spectra were stable. The value found for the apparent band gap with the two-probe set-up was 57 ± 17 meV. This is slightly smaller than the value found by Moeggenborg, *et. al.*, of 86 meV in the same temperature range.<sup>46</sup>

The sharp rise in resistivity between -5 and 5 °C coincides with decomposition, as indicated by the optical absorbance spectra. Usually, after the resistivity has increased to a value too large to be measured, the optical spectrum is nearly a flat line. The decomposed electride sample is an insulator.

One puzzling feature, which is apparent on the plots shown in Figure 63 and 64, is the large increase and then decrease in resistivity observed as the film is warmed between -30 and -5 °C. The optical spectra taken during this warming period show the plasma edge decaying normally. The film is in the early stages of decomposition. However, if the temperature is warmed slowly through this temperature range (stopping at 5 °C intervals for five minutes each), the "bump" in the plot is not seen. These results began to raise questions regarding resistive electrode effects.



Figure 64. Two-probe  $ln(\rho)$  versus inverse temperature for a codeposited 1800 Å K+C222e<sup>-</sup> film which shows an increase in the resistivity upon annealing.

A typical I-V plot for the conductivity measurements is shown in Figure 65. The plot is linear (slope = 706.9 ± 2.9), which implies an ohmic situation. Moeggenborg, *et. al.*, found non-ohmic behavior during the previous experiments.<sup>46</sup> The main difference is that the present amplification circuit allowed maximum bias voltages of only 0.1 Volt, compared to the tens of Volts used by Moeggenborg, *et. al.* It is possible that upon application of such large voltages the electride films would display similar electrode effects.

As can be seen in Figure 65, the I-V plots made during the experiments did not quite go through the origin. The y-intercept is  $0.273 \pm 0.022$  V. This says that even when no bias voltage is applied to the circuit, there is still a small offset voltage between the input and ground terminals of the operational amplifier. This offset is due to the fact that the operational amplifier used in the circuit is not ideal. Small deviations such as this are expected. The amount of residual current falls within the published specifications for this operational amplifier. Thus, the bias voltage was kept large compared to this offset, except during I-V measurements.

The substrate with the two-probe electrodes which has two different conducting widths was designed to test whether or not resistive electrode effects play an important role in the resistivity measurements. The  $\ln(\rho)$  versus inverse temperature data for one of these conductivity experiments is shown in Figure 66. Since the length of the conducting path is taken into account in the calculation of the resistivity of a sample, the  $\ln(\rho)$  values for both the wide and narrow paths should be equal. It is obvious that the values are quite different. The fact that the apparent resistivity of the narrow



Figure 65. A typical two-probe I-V plot for a K+C222e<sup>-</sup> conductivity experiment. The output voltage of the amplification circuit is proportional to the current.



Figure 66. Two-probe  $ln(\rho)$  versus inverse temperature for a codeposited 1650 Å K+C222e<sup>-</sup> film. The substrate with electrodes having two different path lengths was used in this experiment. The two lines represent the data from the wide (solid) and narrow (dashed) path lengths.

path is approximately twice that of the wide path implies that the electrode/sample interface resistance is much larger than the resistance of the sample itself.

A simple model illustrates this implication (Figure 67). Let the sample resistance be  $R_S$  and the resistance of each electrode/sample interface be R<sub>I</sub>. The measured resistivity of the sample would be  $(2R_I + R_S)A/I$ . Take another resistivity measurement of the same sample, but with the conducting path length twice as long. The resistance of the sample scales linearly with the path length. The measured resistivity of this portion of the film would be  $2(R_{I} +$  $R_S$ )A/21 = ( $R_I + R_S$ )A/1. In the limit that  $R_S >> R_I$ , the measured resistivities would be equal. This situation was not found in the experiment described above. In the opposite limit that  $R_I >> R_S$ , the measured resistances of the two paths would be nearly equal so that the resistivity of the narrow path would be twice the resistivity of the wide path. The experimental values of  $\rho_{narrow}/\rho_{wide}$  are approximately 2 at all temperatures below -20 °C. Thus, the conclusion is that the electrode/sample interfaces are major contributors to the measured resistivities of the electride films. A four-probe measurement procedure was designed and used in an attempt to overcome these effects.

The four-probe experiments were performed in a manner similar to the two-probe experiments. The output from the conductance bridge was recorded on an XY plotter. The conductance bridge also allowed two-probe measurements between several combinations of the electrodes. The results from these two-probe measurements were similar to the results discussed above. The



Figure 67. Schematic diagram of the resistances of a sample and two resistive sample/electrode interfaces.

four-probe results, in general, have three major differences from the two-probe results: the resistivity values are lower, there is no "bump" in the  $ln(\rho)$  versus inverse temperature plots and the initial resistivity values do not change significantly as the K<sup>-</sup> and trapped electrons absorbance peaks anneal into a plasma edge.

A typical  $ln(\rho)$  versus inverse temperature plot for the electride when the four-probe set-up was used is shown in Figure 68. The resistivity values of the four-probe thin film experiments on K+C222e<sup>-</sup> correspond well with the four-probe pressed pellet resistivity values of Moeggenborg, *et. al*, which are also shown on Figure 68.<sup>46</sup> The apparent band gap measured for the electride films was 62 ± 20 meV. This value is in good agreement with the value obtained with the two-probe measurements described above.

One way to quantitatively compare these conductivity results with the optical results is to calculate the relaxation time  $\tau$  from a point on the linear portion of the ln( $\rho$ ) versus inverse temperature curve. A model which presumes that the electride is an intrinsic semiconductor is one where the singlet ground state is the valence band and the excited triplet state is the conduction band (Figure 60b). The conductivity equation to use is  $\sigma = ne^2\tau_e/m_e + pe^2\tau_h/m_h$ where:

$$n = p = 2(2\pi k_B T/h)^{3/2}(m_e m_h)^{3/4}exp(-E_g/2k_B T)$$

is the density of carriers.<sup>68</sup> The calculation is made assuming  $m_e = m_h = \text{rest}$  mass of an electron and  $\tau_e = \tau_h = \tau$ . The point used was  $\ln(\rho) = -3.0$  at 249 K. The value found for  $\tau = 7.8 \times 10^{-15}$  seconds.



Figure 68. Four-probe  $ln(\rho)$  versus inverse temperature for a codeposited 2400 Å K+C222e<sup>-</sup> film after annealing. The solid line represents a linear fit to the diamond-shaped data points. The typical apparent band gap is 62 meV. The circles show the decrease and then increase in resistivity as described in the text. The dashed line represents the data of Moeggenborg, *et. al.* (gap = 86 meV).

This is in fairly good agreement with the value of  $\tau = 4.1 \times 10^{-15}$  seconds found using the optical absorbance spectrum and the Drude model.

Another way to quantitatively approach these conductivity results is with an extrinsic semiconductor model. In this model, there is a large energy gap between the ground state valence band and the excited state conduction band, but a donor band lies just below the conduction band (Figure 60c). If the conducting electrons originate from a donor level, the density of carriers can be approximated by:

$$n = (n_0 N_d)^{1/2} exp(-E_d/2k_BT)$$

where  $N_d$  is the donor concentration,  $E_d$  is the energy gap between the donor level and the conduction band and  $n_o = 2(2\pi mk_BT/h)^{3/2}.68$ The  $\tau$  from this calculation (which assumes  $N_d$  is equal to the density of electrons in the electride) is 8.3 x 10<sup>-15</sup> seconds. This value is also in good agreement with the value calculated using the Drude model with the optical absorbance data.

Another possible model which fits both the optical and electrical data is an activated hopping mechanism. In this model, there are trapped electron states below the conduction band (Figure 60d). These states are not close enough to the conduction band, though, to thermally populate it. Thus, the conduction is from a thermally activated hopping mechanism. The temperature dependence of the conductivity data of Moeggenborg, *et. al.*,<sup>46</sup> is presently being analyzed to determine if it can be described by a variable-range hopping conductivity model.<sup>76</sup>

A discussion of the connection between the resistivity measurements and the optical absorbance spectra of the K+C222e<sup>-</sup> films will now be presented. Just as in the case of the two-probe measurements where there appeared to be no explanation for the variety of changes in resistivity as the films annealed, there also appears to be no explanation to why the resistivity doesn't change during the annealing of the films in the four-probe measurements. As portions of the films anneal from what appears optically to be a more localized material to a more delocalized material, the expectation is that the film should become more conducting. This is not observed. A possible explanation is that the resistive grain boundaries between the crystallites are dominating the measurements. Thus, the annealing process may decrease the resistivity in each grain as more of the grain converts into the electride, but it may not effect the grain boundaries at such cold temperatures.

The connection between the optical and electrical properties appears to be a little clearer once the annealing process is over. At this point, the plasma edge of the electride is stable at temperatures below -30 °C. This is also the region where the  $ln(\rho)$  versus inverse temperature plots are linear and where the apparent band gap measurements are made. As was concluded in the previous section, this appears to be where the "true" absorbance spectra of the K+C222e<sup>-</sup> films are found.
When the film is warmed above -30 °C, the optical absorption spectra begin to decay and the resistivity begins to decrease (Figure 68). This combination seems contradictory. The decay in the absorbance spectra indicates that there is less electride material remaining in the thin film. Previous measurements demonstrated that the final product after decomposition is insulating. Intuitively, one would think that a film with less electride and more decomposed, insulating material would be more resistive. A closer look at the method of decomposition assists in the explanation of this apparent contradiction. Several recent publications show that alkalides and electrides made with crown ether complexants decompose by a reductive elimination process which leads to the formation of an ethylene molecule and an open ring complexant.<sup>77,78</sup> An analogous process for a cryptand complexant is shown in Figure 69. Notice that this process would remove two electrons from the channels. As the temperature increases, the trapped electrons become more reactive. These chemically hot electrons could attack the complexant molecule in this manner and ethylene gas molecules would be released. The removal of electrons from the channels would decrease the magnitude of the plasma edge optical absorbance. At the same time, the removal of electrons from the channels would also "dope" the channels with vacancies. The increase in the number of these vacancies could increase the conductivity of the electride by providing the remaining electrons access to a hopping conductivity mechanism.

This model of a hopping mechanism implies that defects are the main reason for the increase in conductivity. It seems to say



Figure 69. Schematic representation of a possible decomposition mechanism in K+C222e<sup>-</sup>. Two electrons attack the cryptand molecule and an ethylene molecule is ejected into the vacuum.

that if there were exactly one electron in each cavity, this pure electride would be an insulator because the electrons have no unoccupied cavities into which they could hop. Having two electrons at the same trapping site would be energetically unfavorable due to the repulsive Coulomb force. This argument is similar to the Hubbard picture used by Singh, *et. al.*, to assist in the explanation of why Cs+(15C5)<sub>2</sub>e<sup>-</sup> is an insulator.<sup>53</sup>

As the temperature increases, the electrons from the channels would continue to attack the complexing molecules. Eventually, the number of electrons remaining in the channels would become small enough that the resistivity would begin to increase. The optical absorbance spectra would become a flat line and the sample would become an insulator. This is the behavior that is seen experimentally.

A four-probe resistivity versus thickness study was also conducted on K+C222e<sup>-</sup>. The results are plotted in Figure 70. The resistivity was already measurable at a thickness of 100 Å. The resistivity of the electride settled down to nearly a constant value once approximately 300 Å was deposited. This is in comparison to a similar study performed on potassium metal where 500 Å was deposited and no conductivity was detected at any thickness. Thus, vapor deposition allows very thin films of the electride to be deposited which have conductivity properties similar to the thicker films.

The conductivity studies presented in this section assist in the overall description of K+C222e<sup>-</sup>. The resistivity values obtained for the thin films were similar to the values obtained with earlier



Figure 70. Four-probe  $ln(\rho)$  versus thickness of a K+C222e<sup>-</sup> film during deposition at -60 °C. Notice the resistivity settles down at a relatively small thickness.

pressed pellet experiments. An apparent band gap for the films was obtained (57  $\pm$  17 meV and 62  $\pm$  20 meV with two- and four-probe measurements, respectively). These are slightly lower than the pressed pellet values. A decomposition mechanism where the electrons leave the trapping channels and attack the cryptand molecules assists in the explanation of the optical and electrical behavior when the samples are warmed above -30 °C. Upon total decomposition, the films are insulating.

There are still several significant questions that remain, though. Is K+C222e<sup>-</sup> an intrinsic or extrinsic semiconductor? Would another conductivity mechanism, such as a two-dimensional hopping model, a terminated chain conductor model or a granular metal model, describe the results better? Measurement of resistivity over the limited temperature range studied in this research cannot really distinguish between these models, but suggests that defect conductivity is important. What is the density of the charge carriers? The numerical calculations in this study used the overall electride density as an approximation. Are the charge carriers electron-like or hole-like? The simplest intrinsic semiconductor model, where n = p, was used in the present calculations. Thermopower and Hall effect studies are now underway in an attempt to answer some of these questions.

IV.D. Conclusions

The stable thin film absorbance spectral shape of K+C222e<sup>-</sup> resembles a plasma edge. This implies that the trapped electrons in

the open, two-dimensional channels have a continuum of states accessible to them upon excitation by photons with energies greater than 0.5 eV. The apparent band gap of the electride has been determined with a temperature dependent resistivity study. The value (62 meV) is only slightly smaller than the previously determined pressed pellet value (86 meV). The small value of this apparent gap suggests that the conductivity is from an activation process and that the electrons are in a band or in traps slightly below the continuum band. The usefulness of combining the optical absorbance results with conductivity measurements has been clearly demonstrated. This combination leads to a portrait of how a decomposition mechanism assists in the explanation of the optical and electrical behavior at temperatures above -30 °C.

## V. CONCLUSIONS AND FUTURE WORK

## V.A. <u>Conclusions</u>

The vapor deposition apparatus was used to study the optical and electrical properties of thin films of an alkalide (Na+C222Na<sup>-</sup>) and an electride (K+C222e<sup>-</sup>). The optical studies included absorbance and photobleaching measurements. The electrical studies included conductivity and photoemission measurements. The versatility of the vapor deposition apparatus is not only apparent by the wide range of measurement capabilities listed here, but also by the wide range of compounds described in the appendix which were synthesized during this research.

Several improvements were made to the vapor deposition apparatus. The measurement and control of the temperature of the substrate is now more accurate. Changing the size and the material of the substrate helped improve the accuracy. Heat is now removed more quickly from the center of the substrate and poor thermal contact effects of the grease have been eliminated. The copper chimney used during codeposition of the films was realigned. The stoichiometric films are now deposited directly on the center of the substrate. A new spectrophotometer was integrated into the vapor deposition system. Fiber optic cables now take the light for the optical absorbance analysis into and out of the system through a home-made vacuum feedthrough. The new spectrophotometer can scan a wider spectral range with smaller wavelength step sizes than

185

the old monochromator system and do it twenty times faster. This new capability assists in analyzing absorbance spectra that are changing rapidly with time or wavelength.

The Na+C222Na<sup>-</sup> films were investigated using a temperature dependence study of the absorbance spectra parameters, a photobleaching study, a stoichiometry study and a conductivity study. The temperature dependence study of the peak parameters of the sodide absorbance spectra assists in describing how the energy band picture of Na+C222Na<sup>-</sup> changes with temperature. The ground state s band, the excited state p band and the conduction band are all thermally broadened. This broadening is attributed to thermal expansion of the lattice and phonon-assisted indirect transitions. The photobleaching study demonstrated that new absorbances appear in the optical spectra after intense laser pulses interact with the sodide films. The irreversible bleaching process depends on the intensity of the laser pulses in a nonlinear way. This dependence implies that there is a threshold concentration of excited electrons (excitons) in the p band and when this concentration is surpassed the mobile excitons interact strongly. When two of these excitons collide, a higher energy exciton is created and phonons are released. These high energy excitons are now able to sample areas of the electronic structure that were not otherwise accessible. Also, due to the highly mobile nature of the exciton-polariton pairs, when these excitons lose their energy they may become trapped far away from the neutral Na atom they left behind. The neutral Na atom looks like a defect with a positive charge to the rest of the material. These trapped electrons and neutral Na atoms will perturb the electronic band structure of the sodide film. This perturbation appears in the form of new absorbers in the optical absorbance spectrum. The stoichiometry study also demonstrates new absorbers in the optical spectrum. These films are purposefully synthesized with excess trapped electrons and/or excess neutral Na atoms. The fact that the new absorbances are at the same energies as in the bleaching experiment imply that these new absorbers lead to the same perturbation of the electronic band structure of the sodide. The conductivity study showed that Na+C222Na<sup>-</sup> is an insulating material. A current could only be measured when the sample was illuminated. This current was identified as a photoemission current and not a photoconductivity current.

The K+C222e<sup>-</sup> films were investigated by an optical absorbance method and by two-probe and four probe conductivities. The stable thin film absorbance spectrum of the electride was determined and it resembles a broad plasma edge in the spectral region from 0.5 eV to 3.0 eV. The conductivity study determined that the apparent band gap of the stable electride film is 62 meV below -30 °C. The combination of these two observations implies that the electrons in the open, two-dimensional channels of the electride are in energy traps that are less than 0.5 eV below a continuum of excited states, but they can conduct via a thermally activated process with an apparent band gap of only 62 meV. The combination of the changing optical absorbance spectra and the temperature dependence of the resistivity above -30 °C implies that a particular decomposition mechanism is occurring that maintains the conducting The conductivity studies also suggest that defect behavior.

conductivity is important in the electride. Another correlation between the optical and electrical studies was made. A relaxation time of  $\tau = 4.1 \times 10^{-15}$  seconds was calculated from the optical absorbance spectrum using the Drude model approximation. Using the electrical resistivity data and assuming the density of electrons and holes to be equal, a relaxation time of  $\tau = 7.5 \times 10^{-15}$  seconds was found. These two crude approximations are in fairly good agreement.

The results of this research show that the vapor deposition apparatus is a powerful tool in the study of alkalides and electrides. The combination of optical and electrical measurements on the same sample allows the correlation between these two probes to be studied without the fear of sample-dependent irregularities that may occur when two separate syntheses and instruments are used.

## V.B. Future Work

Several design improvements to the vapor deposition apparatus are already underway. To allow the evaporation of complexing materials with large molecular weights and high vaporization temperatures, the TEC is being replaced with a ceramic heater. The ceramic heater will continue to sit on the copper cooling block which, it is hoped, will allow volatile complexants to still be cooled during the evacuation of the bell jar. The method or the equipment to allow the optical absorbance spectrum to be extended into the UV (200 - 350 nm) needs to be perfected. Presently, not enough light gets through the system in this region to be able to

I ŀ l С ť n b h b СС ca is di сŋ be inc ele hav pre pre stuc pho pho com inter resolve the absorption peaks. A method is currently being studied which employs a quartz collimating cylinder between the fiber optic lens and the substrate. It is hoped that this collimating cylinder will collect the UV photons that are being lost and direct them through the sample and into the pick-up fiber optic cable. The search for a method to allow the analysis of the films *ex situ* should continue to be pursued. Once a video microscope camera is installed in the helium-filled glove box, the morphology of the deposited films could be studied.

The band structure of Na+C222Na<sup>-</sup> needs to be calculated. The computing capabilities are now accessible to allow such a large calculation to be carried out. The electronic structure of this sodide is expected to be much more complicated than the general, onedimensional description used in this dissertation. The anisotropic crystal structure is one of the reasons for this expectation. It would be interesting to compare the calculated band gaps, both direct and indirect, and the calculated band shapes with the optical and electrical properties that studies such as the work presented here have demonstrated.

Photoemission and reflectivity studies of Na+C222Na<sup>-</sup> are presently being pursued in this laboratory. The combination of the previous photoluminescence, conductivity and photobleaching studies with the present absorbance, reflectivity, photobleaching and photoemission studies should allow a complete picture of how photons interact with this sodide. Again, comparison of this complete picture with the calculated band structure would be interesting. Thermopower measurements are presently underway on solvent-prepared samples of K+C222e<sup>-</sup>. An attempt to measure the Hall voltage in the vapor deposition apparatus should also be made. A set of electrodes in a Hall effect measurement arrangement could be deposited and wired onto a substrate. A permanent magnet could be mounted in one of the oven chambers, which is directly below the substrate and film. Moving the substrate back and forth across the magnetic field lines would allow a crude measurement of the induced Hall voltage. The thermopower and Hall effect measurements will allow the calculation of the density and the sign of the charge carriers in this highly conducting material. Such measurements would greatly assist in the determination of a model that best describes the electride. Will the model be that of an intrinsic or extrinsic semiconductor, a granular metal, a twodimensional metal, or something else?

Theoretical calculations and models have been recently developed for the  $Cs+(15C5)_2e^-$  system. It is hoped that similar studies will be instigated with the K+C222e<sup>-</sup> system. A band structure calculation on this electride would also assist in the determination of a model that best describes it.

Occasionally during this research, compounds other than Na+C222Na<sup>-</sup> and K-C222e<sup>-</sup> were synthesized and studied. A list of these compounds and some of their properties are given in the Appendix. One of the most interesting and promising categories of the extra compounds that were studied is the large organic globular electron acceptor (LOGEA) precursor compounds. The goal of this line of research is to attempt to prepare buckyball-like compounds

by using large complexing agents that fall into this LOGEA category. Thin films of these LOGEAs can be codeposited with alkali metals in the vapor deposition apparatus. The optical properties of these new compounds provide information about the location of the electron. A localized peak may imply that the alkali cation is complexed and that the electron is located on an alkalide ion. A delocalized spectrum may indicate that the electron has been donated to a system of  $\pi$ -bonds. The electrical properties will divulge whether or not the compound is a good conductor. This research is presently being carried out with the vapor deposition system.

APPENDIX

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## APPENDIX

The optical and electrical properties of miscellaneous azaanalog and precursors to large organic globular electron acceptors (LOGEAs) were studied. The overall goal of the LOGEA research is to synthesize adducts of alkali metals and large electron-accepting molecules in the hope of mimicking the behavior of the superconducting alkali metal-fullerene compounds,  $M_3C_{60}$ . Thin film absorbance spectra and conductivities are important indicators of the extent of delocalization of the added electrons and the presence or absence of intermolecular electron transfer. In this study, smaller subunits of LOGEAs were codeposited with sodium to form films of the radical ion salts. For non-volatile organic compounds, sodium was added to pre-existing films formed by solvent evaporation. As described below, the surprise was the apparent presence of Na<sup>-</sup> in non-complexant films. If verified, these would be the first examples of alkalides formed from aromatic compounds and alkali metals.

Sodium metal was used with all of the compounds listed below. In many cases, the optical absorbance spectra were found to be similar to a typical sodide spectrum. A "typical" thin film sodide spectrum has a broad, sample-dependent absorbance peak centered between 13800 and 15400 cm<sup>-1</sup>.<sup>83</sup> One question (which cannot be answered here) that arises is: Where are the Na<sup>+</sup> and Na<sup>-</sup> ions in the film? With cryptands and crown ethers it has been shown that usually the cations are inside the complexing molecules and the anions or trapped electrons find vacancies in the packing of these large molecules.<sup>1</sup> This scenario is probably the case with the first three compounds listed below (TETMCY, PMPCY and TMTACM). The above scenario does not work well with the rest of the molecules discussed below. They will, however, be termed loosely as "complexants" during the discussions. Hopefully, this preliminary work will lead other researchers to study and characterize these compounds and many others like them.

Figure 71 shows the absorbance spectrum of a 2000 Å codeposited film which has the stoichiometry Na+TETMCYNa<sup>-</sup>, where TETMCY is tetramethyl tetracyclen (the aza-analog of 12-crown-4). The film temperature during deposition was -50 °C. The spectrum was stable at -50 °C for several hours, but decayed very quickly when warmed to 0 °C.

Figure 72 shows the absorbance spectrum of a 2500 Å codeposited film which has the stoichiometry Na+PMPCYNa<sup>-</sup>, where PMPCY is pentamethyl pentacyclen (the aza-analog of 15-crown-5). The film temperature during deposition was -60 °C. The spectrum was stable at -60 °C for several hours, but decayed slowly and shifted slightly when warmed to 0 °C.

Figure 73 shows the absorbance spectrum of a 1800 Å codeposited film which has the stoichiometry Na<sup>+</sup>TMTACMNa<sup>-</sup>, where TMTACM is tetramethyl tetra-aza cyclam. The film temperature during deposition was -60 °C. The spectrum was stable at -60 °C for several hours, but decayed slowly when warmed to 5 °C. Three days later, 100 Å of Na was deposited on the remaining film material and a broad absorbance appeared at 17000 cm<sup>-1</sup>

Fig



Figure 71. Absorbance spectrum of a 2000 Å codeposited film of Na:TETMCY = 2:1 at -50 °C.



Figure 72. Absorbance spectrum of a 2500 Å codeposited film of Na:PMPCY = 2:1 at -60 °C.



Figure 73. Absorbance spectrum of a 2550 Å codeposited film of Na:TMTACM = 2:1 at -60 °C.

indicating that not all of the TMTACM had been destroyed by the decomposition process.

As a basic test of the following "complexing" systems, 50 Å of Na was deposited onto 150 Å of adamantane. The optical absorbance spectrum was flat. This null experiment demonstrated that not just any organic molecule will complex Na and give a sodide absorbance spectrum.

Figure 74 shows the absorbance spectrum of 50 Å of Na deposited at room temperature onto a thin film of supertriptycene.<sup>79</sup> The maximum temperature of the thermoelectric cooler (TEC) was not high enough to vaporize supertriptycene in the vacuum chamber. Thus, tetrachloroethylene was used as a solvent to put a thin film of the supertriptycene onto the substrate before loading it into the deposition system. The absorbance decayed slowly at room temperature. It is now thought that there was residual solvent in the films and that the reaction of Na with tetrachloroethylene is probably the reason for the decay of the sodide-like peak. If it is verified that this is a genuine Na<sup>-</sup> absorbance peak, it represents the first sodide found with an aromatic molecule that does not contain any O or N heteroatoms.

Figure 75 shows the absorbance spectrum of a 500 Å codeposited film of Na and tris(2,6-dimethoxyphenyl)methyl radical<sup>80,81,82</sup> at -60 °C. The metal:complexant ratio was 2:1. The sodide-like peak was stable at -60 °C, but slowly decayed when warmed to 0°C. Figure 76 shows another absorbance spectrum of a codeposited film of Na and this carbon radical compound with a wider spectral range. This 200 Å film was deposited at -60 °C and



Figure 74. Absorbance spectrum of 50 Å of Na deposited onto a film of supertriptycene at 25 °C.



Figure 75. Absorbance spectrum of a 500 Å codeposited film of Na:tris(2,6-dimethoxyphenyl)methyl radical = 2:1 at -60 °C.



Figure 76. Absorbance spectrum of a 200 Å codeposited film of Na:tris(2,6-dimethoxyphenyl)methyl radical = 2.5:1 at -60 °C.

had a metal:complexant ratio of 2.5:1. The two peaks have been tentatively assigned to a sodide (15000 cm<sup>-1</sup>) and to an electron donated to the central carbon atom of the complexant to form a carbanion (20000 cm<sup>-1</sup>).

Figure 77 shows the absorbance spectrum of 50 Å of sodium deposited on a film of tris(2,6-dimethoxyphenyl)borane<sup>80,81,82</sup> at -60 °C. The maximum temperature of the TEC was not high enough to vaporize the borane compound in the vacuum chamber. Thus, pentane was used as a solvent to put a thin film of the borane compound onto the substrate before loading it into the deposition system. The spectrum was stable for more than an hour at -60 °C. Mechanical problems ended the experiment before any other spectra were taken.

Figure 78 shows the absorbance spectrum of a 2250 Å codeposited film of Na and tris(2,6-dimethoxyphenyl)amine<sup>80</sup> at -60 °C. The metal:complexant ratio was 1:1. The absorbance peak was stable at -60 °C and fairly stable when warmed to 0°C, but slowly decayed when warmed above 0 °C. The resistivity of the sample at -60 °C was 3 x 10<sup>9</sup>  $\Omega$  cm in the dark and 2 x 10<sup>7</sup>  $\Omega$  cm when illuminated by the Guided Wave light source. Both of these values slowly increased steadily with time, even though the absorbance spectrum did not change significantly, until the resistance became too large for the amplification circuit.

The optical absorbance spectrum of a 1000 Å codeposited film of Na and tris(2,6-dimethoxyphenyl)methane<sup>80</sup> was similar to Figure 75. The sodium probably attacked the methane and released



Figure 77. Absorbance spectrum of 50 Å of Na deposited onto a film of tris(2,6-dimethoxyphenyl)borane at -60 °C.



Figure 78. Absorbance spectrum of a 2250 Å codeposited film of Na:tris(2,6-dimethoxyphenyl)amine = 1:1 at -60 °C.

hydrogen into the vacuum. This reaction would yield the methyl radical compound and the same absorbance spectrum.

Figure 79 shows the absorbance spectrum of a 1450 Å codeposited film of Na and phenanthrene at -25 °C. The metal:complexant ratio was 1.2:1. The spectrum increases steadily from 10000 to 25000 cm<sup>-1</sup>. The absorbance was not stable at -25 °C and quickly decayed.

Figure 80 shows the absorbance spectrum of a 1200 Å codeposited film of Na and triphenylene at -30 °C. The metal:complexant ratio was 1:1. The spectrum contains a peak at 25000 cm<sup>-1</sup> and a broad absorbance feature centered at 20000 cm<sup>-1</sup>. The absorbance spectrum was stable up to room temperature, where it slowly decayed.

Figure 81 shows the absorbance spectrum of a 1250 Å codeposited film of Na and triptycene at -40 °C. The metal:complexant ratio was 2:1. Triptycene contains three isolated benzene rings, each connected at the meta positions to two bridgehead carbons. The spectrum contains a peak at 20000 cm<sup>-1</sup>, probably due to the triptycene radical anion. The absorbance spectrum was stable up to about 0 °C, where it quickly decayed.

Figure 82 shows the absorbance spectrum of a 1000 Å codeposited film of Na and anthracene at -35 °C. The metal:complexant ratio was 1:1. The spectrum contains three absorbances: a peak at 25000 cm<sup>-1</sup>, a small broad feature centered at 22000 cm<sup>-1</sup> and an even smaller broad feature centered at 17000 cm<sup>-1</sup>. The absorbance spectrum was stable up to about 0 °C, where it quickly decayed.



Figure 79. Absorbance spectrum of a 1450 Å codeposited film of Na:phenanthrene = 1.2:1 at -25 °C.



Figure 80. Absorbance spectrum of a 1200 Å codeposited film of Na:triphenylene = 1:1 at -30 °C.



Figure 81. Absorbance spectrum of a 1300 Å codeposited film of Na:triptycene = 2:1 at -40 °C.



Figure 82. Absorbance spectrum of a 1000 Å codeposited film of Na:anthracene = 1:1 at -35 °C.

The surprising results of this study on LOGEA precursors indicate the need for further research. Absorbance spectra similar to those of sodides were observed in non-complexant thin films. If the presence of Na<sup>-</sup> ions is confirmed, these materials would be the first examples of alkalides formed from aromatic compounds and alkali metals. The results presented here also indicate that the vapor deposition system will be a powerful tool in the study of other LOGEA precursors and, eventually, actual LOGEA compounds.

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