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COLOR CENTERS AND RELATED PHENOMENA IN ALKALI HALIDE TYPE CRYSTALS

FINAL TECHNICAL PROGRESS REPORT

by

Theodore J. Neubert

United States Atomic Energy Commission Contract No. AT(11-1)-1044

August 1971

Freund Instrumentation Laboratory
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois
60616

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Summary of Scope and Purpose

Color centers and related phenomena were studied in a variety of alkali halide type crystals. Such crystals have a wide range of optical transparency and usually color readily upon exposure to ionizing radiation. Study of the color centers introduced provides information on the mechanism of defect formation and the subsequent reactions among defects. Those reactions occur because of the mobility of electrons, positive holes, lattice vacancies, atoms and ions either produced during the primary irradiation or produced later by thermal or photochemical means. Optical absorption measurements yield information on the electronic structure of the defect centers and on their interaction with lattice phonons, as well as on their concentration. Crystal to crystal variations yield information relative to the importance of gross crystal properties and relative to the perturbed nature of the lattice immediately adjacent to the center.

Electrical conductivity measurements were used to determine the energy of formation of lattice vacancies and the energy of motion of positive ion vacancies in KSCN, KCN and NaCN. Techniques were developed for zone refining those salts, for growing single crystals and for analysis of the crystals. Color centers in KCN were studied extensively and in NaCN, less extensively. A number of the centers, well known in KCl, were identified and characterized.

Annealing experiments on crystals heavily x irradiated at low temperatures were made to study the aggregation of F centers into M^+ , M, R^+ , R and N centers in NaF, NaCl and KI. A beginning was made by a study of aggregate centers in NaBr. Thermal, optical and x-ray induced interconversions of aggregate centers also were investigated. Some of the higher energy transitions of M^+ , R, and R^+ centers in NaF, NaCl and KI were identified by polarized absorption or, in some instances, by luminescence measurements.

The dichroism of the M center was investigated in KCN, KBr, KI, NaF and NaCl. An M center (F_2) resembles a H_2 molecule embedded in a dielectric medium. accordingly the M_1 band corresponds to a $1\Sigma_g^+ \rightarrow 1\Sigma_u^+$ transition while the M_2 and M_2' bands are associated with a degenerate $1\Sigma_g^+ \rightarrow 1\Pi_u$ transition. Particular attention was paid to the influence of the anions and cations of the lattice on the lifting of the degeneracy of the $1\Pi_u$ state.

Other experiments involved the thermal bleaching of positive hole (Cl_2^-) centers in KCl and NaCl, the temperature dependence of the shape of the F and M, bands in NaF, NaCl, NaBr and KI, the nature of the centers which are responsible for the deep red color of the mineral villiaumite (naturally occurring NaF), and the penetration of H_2O into additively colored KI at room temperature.

(quoted from pp 6,7)

COLOR CENTERS AND RELATED PHENOMENA IN ALKALI HALIDE TYPE CRYSTALS

Final Technical Progress Report

This report summarizes research carried out over a period of years with financial assistance from the U. S. Atomic Energy Commission on projects of mutual interest to the AEC and to the principal investigator, and to students working under his direction in the Freund Instrumentation Laboratory of the Department of Chemistry at Illinois Institute of Technology.

The program began in June, 1957 under Contract No. AT(11-1)-90, Project No. 8. That contract was renewed annually until June, 1961 at which point there was a change of designation to Contract No. AT(11-1)-1044. Annual renewals continued the program to the present time.

Over the fourteen years of the program more than fifty persons have become involved, in major or minor ways, with research in color centers and related phenomena or in closely associated activities such as apparatus construction, data analysis, calculations, analytical chemistry and literature searching. Of these fifteen were graduate students working on graduate degree programs. To date, eleven degrees have been awarded, 3 PhD. and 8 M.S. degrees. Two students are currently at work, one of whom will receive his PhD. in June, 1972. Three graduate students left without completing their degree research.

Five undergraduate students did their Senior Research on color center topics. Fifteen persons were associated with color center research by reason of holding Research Participant appointments in NSF supported programs in the Department: seven undergraduates, five College Teachers and three High School Teachers. Finally, twenty-seven students in the author's instrumentation

courses chose small research projects and six students in the Chemical Literature course chose literature search projects related to color centers.

Eight students were employed, at various times, as technicians to assist in some of the associated activities mentioned above, or in carrying out preliminary or confirmatory experiments. One research technician has been associated with the program, on a part-time basis, for the past seven years.

As a direct result of the financial assistance of the AEC, advances were made in our knowledge and understanding of the defects produced in crystalline solids by ionizing radiation and of the subsequent reactions among those defects. In the process, those involved were provided with a research environment within which course work and independent studies could be made particularly relevant, they got experience in the solution of practical problems and were introduced to the techniques of making contributions to knowledge and reporting those contributions to the scientific community.

All of us, especially the principal investigator and those who, in their association with the program, earned their advanced degrees are deeply grateful to the AEC for the help and encouragement which was provided.

* * * * *

Final Report Organization. This report is divided into two parts.

Part One provides lists of the documents, issued or in preparation.

Part Two, after an initial short introduction, provides a summary of research activities which covers, in some detail, the entire course of our work, up to August 31, 1971. So far as is practicable the material is presented in chronological order. References are

made to the documents in Part One using number-superscripts.

References to other literature are made by letter-superscripts to a listing at the end of Part Two.

* * * * *

PART ONE - Documents

- A. Theses. As each graduate degree was awarded the student's thesis was issued as a Special Report and six copies were submitted to the AEC with the intention that they would become appendices to this final report.

<u>S. R. No.</u>	<u>Title, Author, Degree, Date, Document Number.</u>
1.	"Electrical Conductivity of Potassium Thiocyanate", by Juan M. Lomelin, M.S. Thesis, IIT, June, 1959. Document No. COO-1044-12.
2.	"Bleaching of Cl_2^- Molecule-Ion Centers in KCl-Pb ", by John A. Reffner, M.S. Thesis, IIT, June, 1960. Document No. COO-1044-13.
3.	"Characterization of Color Centers in Sodium Fluoride", by Kwasi Amenu-Kpodo, M.S. Thesis, IIT, January, 1963. Document No. COO-1044-14.
4.	"Color Center Phenomena in Zone Refined Potassium Cyanide", by Sherman Susman, Ph.D. Thesis, IIT, June, 1963. Document No. COO-1044-15.
5.	"Electrical Conductivity of Single Crystal Potassium Cyanide", by Thomas A. Lothian, M.S. Thesis, IIT, June, 1965. Document No. COO-1044-21.
6.	"F-Aggregate Centers in Sodium Fluoride", by Karl Konrad, M.S. Thesis IIT, February, 1966. Document No. COO-1044-23.
7.	"F-Aggregate and Ionized F-Aggregate Centers in Sodium Fluoride", by Karl Konrad, Ph.D. Thesis, IIT, January, 1969. Document No. COO-1044-30.
8.	"F-Aggregate Centers in Sodium Chloride", by Moo Jin Jun, M.S. Thesis, IIT, June, 1969. Document No. COO-1044-32.
9.	"The Diffusion of Water into Additively Colored Potassium Iodide", by David L. Roskelley, M.S. Thesis, IIT, January, 1970. Document No. COO-1044-33.

10. "Color Centers in Sodium Bromide", by William C. Glennie, M.S. Thesis, IIT, January, 1970. Document No. COO-1044-34.
11. "Color Center Phenomena in Potassium Iodide", by Albert E. Gudat, Ph.D. Thesis, IIT, June, 1970. Document No. COO-1044-36.

B. Research Papers, published.

12. "Thermal Bleaching of Cl_2^- Centers", Theodore J. Neubert and John A. Reffner, J. Chem. Phys., 36, 2780 (1962). Document No. COO-1044-2.
13. "Color-Center Phenomena in Zone Refined Potassium Cyanide", S. Susman and T. J. Neubert, Bull. Am. Phys. Soc., 7, (II), 405, (1962). Document No. COO-1044-5.
14. "Electrical Conductivity of Potassium Thiocyanate", Juan M. Lomelin and Theodore J. Neubert, J. Phys. Chem., 67, 1115 (1963). Document No. COO-1044-4.
15. "Large Transparent Vacuum Melting Apparatus", Theodore J. Neubert and Sherman Susman, Rev. Sci. Inst., 34, 1436 (1963) Document No. COO-1044-8.
16. "Zone Melting Apparatus for Alkali Metal Cyanides and Alkali Metal Halides", Theodore J. Neubert and Sherman Susman, Rev. Sci. Inst., 35, 724 (1964). Document No. COO-1044-9.
17. "Purification and Single Crystal Growth of Potassium Cyanide", Theodore J. Neubert and Sherman Susman, J. Chem. Phys., 41, 722, (1964). Document No. COO-1044-10.
18. "Infrared Absorptions of Impurity Ions in Potassium Cyanide", Theodore J. Neubert and Sherman Susman, J. Chem. Phys., 42, 1848 (1965). Document No. COO-1044-17.
19. "Color Centers in Sodium Fluoride", Kwasi Amenu-Kpodo and Theodore J. Neubert, J. Phys. Chem. Solids 26, 1615 (1965). Document No. COO-1044-11.
20. "M Centers in Potassium Bromide I", Theodore J. Neubert and Sherman Susman, J. Chem. Phys., 43, 2819 (1965). Document No. COO-1044-20.
21. "Thermally Induced Aggregation of Color Centers in Sodium Fluoride", Karl Konrad and Theodore J. Neubert, Dev. Appl. Spect. 5, 217, (1966). Document No. COO-1044-22.
22. "Influence of Temperature on the F Center Absorption in Sodium Fluoride", Kwasi Amenu-Kpodo, Theodore J. Neubert, and Walter Youngblade, J. Chem. Phys., 44, 1324 (1966). Document No. COO-1044-18.

23. "Cryostat for Color Center Studies", Theodore J. Neubert and Joseph F. Sydejko, *Rev. Sci. Instr.* 38, 559 (1967). Document No. COO-1044-25.
24. "Electrical Conductivity of Single Crystalline Potassium Cyanide", Thomas A. Lothian and Theodore J. Neubert, *J. Chem. Phys.* 47, 3092 (1967). Document No. COO-1044-26.
25. "F-Aggregate Centers in Sodium Fluoride.I.", Karl Konrad and Theodore J. Neubert, *J. Chem. Phys.* 47, 4946 (1967). Document No. COO-1044-27.
26. "F-Aggregate Centers in Sodium Chloride.I.", Moo Jin Jun and Theodore J. Neubert, *J. Chem. Phys.* 55, 1583 (1971). Document No. COO-1044-37. Copies accompany this report.

C. Research Papers, written but not yet published

27. "Diffusion of water into Additively Colored Potassium Iodide", David L. Roskelley and Theodore J. Neubert. Manuscript draft of a paper to be submitted for publication in the *Journal of Chemical Physics*. Document No. COO-1044-38. Copies accompany this report.

D. Annual Technical Progress Reports.

Common Title, etc.- "Color Centers and Related Phenomena in Alkali Halide Type Crystals: Document A.," Theodore J. Neubert.

28. February, 1958. (AT(11-1)-90, Project No. 8)
29. February, 1959. (AT(11-1)-90, Project No. 8)
30. February, 1960. (AT(11-1)-90, Project No. 8)
31. February, 1961. (AT(11-1)-90, Project No. 8)
32. February, 1962. (USAEC-COO-1044-1)
33. February, 1963. (USAEC-COO-1044-3)
34. February, 1964. (USAEC-COO-1044-7)
35. February, 1965. (USAEC-COO-1044-19)
36. February, 1966. (USAEC-COO-1044-24)
37. April, 1967. (USAEC-COO-1044-28)
38. April, 1968. (USAEC-COO-1044-29)
39. April, 1969. (USAEC-COO-1044-31)
40. April, 1970. (USAEC-COO-1044-35)

E. Research Papers, in preparation

41. "Color Center Phenomena in Potassium Cyanide", by Sherman Susman and Theodore J. Neubert. A paper currently in preparation, to be submitted to the Journal of Chemical Physics.
42. "Color Centers in the Mineral Villiaumite", by Karl Konrad and Theodore J. Neubert. A paper to be submitted to a suitable geological journal.
43. "Color Centers in Sodium Bromide", by William C. Glennie and Theodore J. Neubert. A short paper or a note to be submitted to the Journal of Physics and Chemistry of Solids.
44. "M Centers in Potassium Iodide", by Albert E. Gudat and Theodore J. Neubert. A paper to be submitted to the Journal of Chemical Physics. A preliminary draft of this paper accompanies this report. The paper is to carry Document No. COO-1044-39.
45. "F-Aggregate Centers in Sodium Fluoride.II, The M Center", by Karl Konrad and Theodore J. Neubert. A paper describing M center dichroism now in the rough draft stage, to be submitted to the Journal of Chemical Physics.
46. "F-Aggregate Centers in Sodium Fluoride.III. M^+ and R^+ Centers", by Karl Konrad and Theodore J. Neubert. A paper describing the formation and absorption spectra of ionized F-aggregate centers, to be submitted to the Journal of Chemical Physics.

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PART TWO - Summary of Research Activities

Color centers and related phenomena were studied in a variety of alkali halide type crystals. Such crystals have a wide range of optical transparency and usually color readily upon exposure to ionizing radiation. Study of the color centers introduced provides information on the mechanism of defect formation and the subsequent reactions among defects. Those reactions occur because of the mobility of electrons, positive holes, lattice vacancies, atoms and ions either produced during the primary irradiation or produced later by thermal or photochemical means. Optical absorption measurements yield information on the electronic structure of the defect centers and on their interaction with lattice phonons, as well as on their concentration. Crystal to crystal variations yield information relative to the importance of gross crystal properties and relative to the perturbed nature of the lattice immediately adjacent to the center.

Electrical conductivity measurements were used to determine the energy of formation of lattice vacancies and the energy of motion of positive ion vacancies in KSCN, KCN and NaCN. Techniques were developed for zone refining those salts, for growing single crystals and for analysis of the crystals. Color centers in KCN were studied extensively and in NaCN, less extensively. A number of the centers, well known in KCl, were identified and characterized.

Annealing experiments on crystals heavily x irradiated at low temperatures were made to study the aggregation of F centers into M^+ , M, R^+ , R and N centers in NaF, NaCl and KI. A beginning was made on a study of aggregate centers in NaBr. Thermal, optical and x-ray induced interconversions of aggregate centers also were investigated. Some of the higher energy transitions of M^+ , R, and R^+ centers in NaF, NaCl and KI were identified by polarized absorption or, in some instances, by luminescence measurements.

The dichroism of the M center was investigated in KCN, KBr, KI, NaF and NaCl. An M center (F_2) resembles a H_2 molecule embedded in a dielectric medium. Accordingly the M_1 band corresponds to a $1\Sigma_g^+ \rightarrow 1\Sigma_u^+$ transition while the M_2 and M_2' bands are associated with a degenerate $1\Sigma_g^+ \rightarrow 1\pi_u$ transition. Particular attention was paid to the influence of the anions and cations of the lattice on the lifting of the degeneracy of the $1\pi_u$ state.

Other experiments involved the thermal bleaching of positive hole (Cl_2^-) centers in KCl and NaCl, the temperature dependence of the shape of the F and M, bands in NaF, NaCl, NaBr and KI, the nature of the centers which are responsible for the deep red color of the mineral villiaumite (naturally occurring NaF), and the penetration of H_2O into additively colored KI at room temperature.

The sections which follow give more complete details.

I. Electrical Conductivity Studies.

In the period during which the instrumentation for color center work was being built up, studies of electrical conductivity in alkali halide type crystals

were undertaken, because of their intrinsic interest and because of their possible use in assaying the quality of crystals important to anticipated color center studies.

The first measurements were made on NaCN crystals, residual from earlier work by Giovanni Isetti^{a,b}. In that work²⁸, Mary Feng showed that the $\log \sigma$ versus $1000/T$ curves for NaCN exhibited the expected intrinsic and impurity-dominated straight portions, with activation energies of 1.63 eV (KCl, 2.08 eV) and 0.66 eV (KCl, 0.72 eV), respectively. By making the usual assumptions, we calculated that the energy to form separated pairs of positive and negative ion vacancies was 1.93 eV and that the energy of activation for the movement of positive ion vacancies was 0.66 eV.

A second conductivity problem was one undertaken by Juan M. Lomelin^{1,14} to determine whether there were any advantages, in discussing electrical conductivity data for ionic crystals, if graphs were to be drawn of $\log \sigma$ versus (T_m/T_x) where T_m is the melting temperature and (T_x/T_m) was intended to represent a "reduced temperature". The low melting point of potassium thiocyanate (175°C) made that salt attractive as a test system.

A single-zone, manually-programmed, zone refining apparatus for producing pure KSCN and a suitable sample measuring system were designed and constructed. Measurements were made in the range 0-170°C. $\log \sigma$ versus $1000/T$ curves for carefully dehydrated samples showed the usual two straight line portions with a sharp bend near 120°C. The activation energy for the conduction process in the intrinsic region was 2.13 eV and in the impurity-dominated region, 1.30 eV. Addition of BaCl_2 enhanced the low temperature conductivity indicating that positive ion vacancies played a role in the conduction process. The crystal structure of KSCN, however, is similar to that of CsBr and since both positive and negative ion vacancies contribute to the conductivity in CsBr^c , it did not seem prudent to try to assign values for the energy of formation or the energy of motion of vacancies in KSCN¹⁴.

The data for KSCN set it apart from other ionic crystals. Its conductivity in the intrinsic range is given by $\sigma = 10^{18.6} \exp(-24700/T)$, and as a result, there was no way in which the KSCN results could be used to support the reduced temperature idea. Further, the large pre-exponential term in the $\log \sigma$ relation implies that there may perhaps be some additional mobile species, H^+ or electrons, contributing to the conductivity in the high temperature region.

When zone refined KCN crystals became available Thomas A. Lothian began a study of their conductivity^{5,24}. He encountered many difficulties so the plan to use the results to qualify different crystal specimens was not successful. For some reason KCN appeared more susceptible to corruption by a not completely pure environment than NaCN. The intrinsic conductivity of KCN single crystals is given by the equation $\sigma = 0.34 \exp(-0.93 \text{ eV}/kT)$. Addition of Ba^{++} ions does enhance the low temperature conductivity but calculation of the energy of formation (0.82 eV) and energy of motion (0.93 eV) indicate that KCN differs from both KBr (2.53 eV and 0.66 eV) and NaCN (1.93 eV and 0.66 eV) which it is expected to resemble.

II. Preparation of Alkali Cyanide Single Crystals

Prior to study of color center phenomena in NaCN and KCN, it was necessary to devise techniques for the purification of the salts and for the production of large unstrained, single crystals.

In the work with NaCN, by Isabelle J. Getz, the initial attempts at purification of reagent grade starting material involved, crystallization from CH_3OH followed by crystallization from the melt^{28,29}. The purity of the crystals obtained by this process, however, was not satisfactory. It was decided, therefore, to investigate the utility of direct synthesis of NaCN from anhydrous sodium ethylate and gaseous HCN, in ethanol solution²⁹. Although the operations are tricky, the product was much purer than that obtained earlier. Crystals grown

by the Bridgman technique were clear enough for color center studies (Sec. IV). In addition the crystals did not show the strong light scattering previously observed^{a,b}, much of which could, therefore, be assigned to impurities in the earlier samples.

The problem of preparation of good KCN single crystals was undertaken by Sherman Susman in connection with his study of color centers in that system^{4,17}. The final process involved vacuum melting¹⁵ of reagent grade KCN, and zone refining¹⁶, followed by thermal-gradient growth of monocrystals using the Bridgman technique¹⁷. Vacuum melting of KCN largely transforms oxygen-containing impurities, e.g. HCOO^- , $\text{C}_2\text{O}_4^{=}$ and $\text{CO}_3^{=}$, into OCN^- . Zone refining removes OCN^- contamination with an effective working segregation coefficient of 0.7. Iron, sodium and silicon are also readily removed. Molybdenum is a suitable container material.

Single crystals of KCN were grown under vacuum in a quartz filtering-crystallizing device¹⁷, which was automatically lowered through the natural thermal gradient of a vertically mounted tube furnace. As soon as crystallization was complete the growing ampoule was quickly lowered into a special furnace, maintained slightly below the melting point, and inverted. It was then raised into the hottest part of the growing furnace to free the crystal from the walls so that the crystal could then be brought slowly to room temperature in a strain free condition.

Samples of KCN crystals, grown as described, proved suitable for optical experiments with polarized light. They typically contained 10 ppm Na and trace quantities of OCN^- impurity^{17,18}. A pure KCN crystal shows no absorption bands in the visible or near ultraviolet regions, but does begin to absorb strongly at 190 nm. As purity decreases that absorption edge, which is related to OCN^- contamination, shifts to lower energies.

The techniques developed by Sherman Susman for KCN were applied by Alvin E. Weinstein to the purification of NaCN. The transfer, however, was unsuccessful

for at least three reasons^{27,28}. Reagent grade NaCN is less pure than KCN. The vacuum melting operation is much less effective in converting $\text{CO}_3^{=}$ to OCN^- and the zone refining process is not so efficient in removing either OCN^- or $\text{CO}_3^{=}$. As a result, the synthetic NaCN crystals mentioned earlier remain the purest so far obtained. The common anionic contaminations, however, have been identified by infrared absorption²⁹ and single crystals, albeit impure, have been grown by Joseph F. Sydejko in a controlled environment Kyropoulos apparatus which has been constructed²⁹.

III. Thermal Bleaching of Halogen Molecule Ion Centers.

The mobility of the positive hole in KCl was determined by John A. Reffner in a study of the thermal bleaching of Cl_2^- molecule ion centers in KCl-Pb^{2,12}. Although Cl_2^- centers can be introduced into pure KCl by X irradiation at 80°K, they can be generated in larger concentration in metal-doped KCl because the doping ions provide a high concentration of effective traps for electrons^{d,e}. There is a strong Cl_2^- absorption at 365 nm which can be made dichroic by irradiating into it with [011] polarized light, at 80°K. Pulse annealing experiments show that the induced dichroism begins to disappear at 190°K^d. The Cl_2^- band itself, however, does not disappear until temperatures are raised above 180°K.

The kinetics of thermal bleaching of Cl_2^- centers was studied by following the decrease of the 365 nm absorption at constant temperatures in the range 180-210°K. The bleaching reaction was shown to be second order in Cl_2^- concentration and the experimental data were analyzed to give a second order rate constant in a way which made knowledge of the absorption at infinite time unimportant¹². The activation energy determined from an Arrhenius plot was 0.53 eV.

To rationalize the kinetic observations it is only necessary to propose (a)

that Cl_2^- centers diffuse via hopping of positive holes from point to point through the lattice and (b) that the positive holes ultimately encounter an electron trapped at a $\text{Pb}^{++}\cdot\text{e}$ center and undergo recombination. The recombination of a positive hole with a $\text{Pb}^{++}\cdot\text{e}$ center is expected to possess a low activation energy. To the extent that such is the case, the observed value of 0.53 eV is a measure of the energy required to free a hole from a Cl_2^- center.

A second study of positive hole centers was undertaken by David G. Hinks who made a search for the $(\text{CN})_2^-$ center in KBr-KCN-Pb^{++} crystals³⁴. It was necessary to use a KBr-KCN mixed crystal matrix because pure KCN undergoes a transition from averaged face centered cubic to orthorhombic structure upon cooling below -106°C , becoming opaque in the process. Thus, low temperature absorption measurements would have been impossible. It was reasoned that in KBr crystals containing ca 10 percent of KCN there was a relatively high probability that a given CN^- ion would itself have a CN^- ion as one of its 12 nearest neighbors. Therefore, if the X_2^- center having the lowest electron affinity forms preferentially, $(\text{CN})_2^-$ centers were to be expected since the literature indicated a lower electron affinity for cyanogen than for bromine.

A well designed set of experiments was carried out, but no clear differences were observed in either the dichroic spectrum in samples containing preferentially aligned X_2^- centers or in the temperature at which the dichroism disappeared in pulse annealing. The whole enterprise was disheartening because later after the relevant journal came back from the bindery, we found, buried away in a paper on the crystal radius of the cyanide ion^f, a more reliable value of the electron affinity of the cyanide radical. That value was much higher than the one accepted during the time of designing and conducting the $(\text{CN})_2^-$ search and implied that the system which should have been used was KCl-KCN-Pb^{++} .

A third study of positive hole centers was undertaken by Frederick J. Sibert who investigated the kinetics of thermal disorientation of aligned Cl_2^- centers³⁶ and their disappearance by thermal bleaching^{34,35} in NaCl-Pb^{++} . All the preliminary work was completed and a respectable amount of good data obtained. The Cl_2^- disappearance was shown to be second order in Cl_2^- concentration and to occur at measurable rates between 142 and 155°K with an activation energy of 0.57 eV. The disorientation of preferentially aligned Cl_2^- was shown to be first order and to occur with measurable rates between 123 and 130°K with an activation energy of 0.5 eV.

Other studies include the work of Karl Konrad and Richard S. Lemker, who attempted to produce experimentally useful amounts of F_2^- centers, in pure NaF and in NaF-PbF_2 ⁴⁰, and the work of Rudolf J. Priepe who made a preliminary study of Cl_2^- centers in solution grown KCl-PbCl_2 crystals³³.

IV. Color Centers in the Alkali Cyanides.

Because of the great advantages of a stable color center inventory, Sherman Susman in beginning his work in the KCN system⁴ made many attempts to produce additively colored KCN. The efforts were quite unsuccessful in spite of the quality and quantity of experiments carried out. Failure to color seemed upon analysis⁴ to be in part intrinsic to KCN crystals and in part due to the fact that crystals contained OCN^- contamination. Earlier attempts to additively color NaCN had also not been successful^a.

Color centers are readily introduced into KCN crystals by ionizing radiation. An optical density of ca 1.4 at 537 nm, near the peak of the F band, can be produced in 50 min x raying at room temperature. Measured at 200°K, the principal bands observed are: F(585 nm), M_1 (857 nm), N_1 (1020 nm), N_2 (1055 nm) plus a V band at 398 nm together with some impurity related bands in the region 360-200 nm. A paper entitled "Color Center Phenomena in Potassium Cyanide" is in preparation by Dr. Susman who is a member of the research staff of the Solid State

Science Division of Argonne National Laboratory⁴¹. It will describe the general nature of color centers in KCN and the detailed nature of the M center, (see Sec. IX-A).

X-rays are less effective in introducing color centers into NaCN crystals. Irradiation for 2 hrs. at room temperature was required to produce an optical density of ca 0.25 at 500 nm, near the peak of the F band, in the synthetic NaCN prepared by Isabelle Getz³⁰. Nor was the coloration stable; about one-half of the coloration disappeared during storage in the dark for 48 hours. The instability was observed earlier in the work of Giovanni Isetti^{a,b} and later in the experiments of Alvin E. Weinstein³⁹. It appears to be strongly related to the purity of the specimen although there are suggestions^b that the instability also has an intrinsic component associated with the occasional reorientation of the librating CN^- dipoles. X irradiation of NaCN produces three principal bands: a band at 365 nm, which forms before any other band, and which may be a positive hole band; a band at 510 nm, which is assigned to the F center; and a band at 250 nm which may be related to some impurity.

Study of color centers in the alkali cyanides is limited by the fact that both NaCN and KCN undergo transitions from a high temperature averaged face centered cubic form, in which the CN^- dipoles are rotating or are librating about randomly distributed $\langle 111 \rangle$ directions, to a low temperature orthorhombic form, in which the CN^- dipoles are aligned in a $[0\bar{1}1]$ direction. The transition temperatures are +15 and -105°C for NaCN and KCN, respectively. Crystals cooled into their low temperature regions become turbid, making precise absorption spectroscopy very difficult.

V. Color Centers in Sodium Fluoride.

Investigation of color center phenomena in NaF was started because so little was known and good single crystals had become available. A general survey of the color centers produced by x irradiation was made by Kwasi Amenu-Kpodo^{3,19}.

Measured at 80°K after a 50 min. irradiation at 80°K, the F band was found at 333 nm, the K band at 282 nm, the M_1 band at 498 nm and the R_1 and R_2 bands at 395 nm and 435 nm, respectively. Four additional bands were observed at shorter wavelength, which were designated V_a (288 nm), V_b (267 nm), V_c (249 nm), and V_d (233 nm). The V_a and V_b bands formed more rapidly than the F band, in the initial stages of irradiation. Warming to room temperature caused the F-band intensity to decrease by a factor of two, removed a large part of the M, and R absorption and caused the V_a , V_b , V_c and V_d bands to disappear completely. The latter bands were attributed to positive hole centers, either intrinsic or impurity related¹⁹. Their nature has not yet been determined and is a subject of continuing concern.

The kinetics of F center formation at various temperatures were also investigated by K. Amenu-Kpodo for their own interest as well as to determine optimal conditions for production of specific centers. A useful result was the observation that F centers formed most rapidly at dry-ice temperature accompanied by relatively little F' absorption and no detectable M center production. That observation permitted a beginning to be made on a study of the dependence of the F band position and half-width upon temperature³.

The investigation of the influence of temperature on the F center absorption was continued by Walter Youngblade²². Crystals were x irradiated at 200°K and then warmed to 100°C. Such specimens, measured at 80°K, contained a stable F band at 334 nm (2.71 eV) after correction for an overlapping K band at 285 nm (4.35 eV), an unknown and as yet unassigned band at 218 nm (5.70 eV) and no other absorptions between 700 nm and 200 nm. The F band was found to have a "double-gaussian" shape, wider on the high energy side of the maximum. Areas under the band calculated as the product of peak height and width at half height, were constant to 1 percent.

Half-widths at the various temperatures were fitted to the usual hyperbolic cotangent relation with the result that the effective frequency of the phonons which interact with the F-center electron in its ground state was calculated to be $\nu_g = (7.7 \pm 0.2) \times 10^{12} \text{ sec}^{-1}$. The frequency ν_g was shown to be approximately one half the frequency of the longitudinal optical vibrational modes of the host lattice for F centers in NaF and in the five other crystals for which values of ν_g were available²².

The work of K. Amana-Kpodo³ showed that M centers form very readily in NaF during x irradiation at room temperature and that their concentration seemed to be proportional to the square of the F-center concentration. A more extensive investigation was made by James E. Brillhart^{34,35} and George H. Madany^{36,37} in which special attention was paid to the fact that there are M-center absorptions which underlie the F band. Two different kinds of experiments were done with these conclusions: (a) Although correction for M absorptions in the region of the F band is straightforward, errors enter from F' centers which could not be compensated. (b) There is a definite dependence of the so-called $2 F \rightleftharpoons M$ equilibrium on x ray intensity. (c) The $2 F \rightleftharpoons M$ "equilibrium" is quite temperature sensitive. (d) The phenomenon seems to be very dependent upon impurities. The problem proved more complex than had been anticipated.

Another problem which has been investigated involves the mineral villiaumite. Villiaumite is a natural form of sodium fluoride which occurs as small reddish crystals embedded in a rather complex fluoride bearing magma found in the Los Archipelago, French Guinea⁸. Villiaumite crystals are dichroic (carmine/yellow) and uni-axial, negative. X-ray diffraction measurements show that villiaumite has NaCl structure with the same lattice constant as synthetic NaF. Thus, both the color and the dichroism of villiaumite require explanation.

There is little doubt that the color of villiaumite is the result of natural

radioactivity in the surroundings in which it was formed. By means of a specially constructed micro-sample device for the Cary 14 PMR spectrophotometer³⁹ it was possible to show, however, that the color centers were not either F or M centers. Instead, the bands observed resembled those reported for additively colored NaF^{33,39,i}. Microscopic examination shows that the dichroism is [001]/[010] and that not all specimens are dichroic. Experiments on additively colored KCl-Na containing F_A centers indicated that specimens examined under a polarizing microscope could be made dichroic in the process of examination. It is possible that a similar effect explains the dichroism in villiaumite.

A considerable body of information is available from the work of Karl Konrad^{35,36} and of a series of undergraduate students, G. P. Behnke³³, R. A. Bauer³⁵, R. G. Karjala^{35,36}, F. J. Wodarczyk³⁷, and L. Chun³⁹. We hope by running additional absorption spectra, between pulse anneals and after x irradiation as well as after optical bleaching, to characterize the color centers and by polarized light microscopy to explain the nature of the dichroism. When such is done the results will be published⁴².

VI. Color Centers in Sodium Bromide

An investigation of color centers in NaBr was undertaken by William C. Glennie¹⁰ in order that comparison data would be available against which to judge results from the NaCN system. Color centers in KCN and KBr are quite closely related because the lattice constants are nearly equal and a similar relationship was expected for NaCN and NaBr.

A general survey of color center formation rate, peak position, and optical bleaching was made. Sodium bromide does not color as readily as other salts. Fourteen hours of x raying at 328°K are required to produce an F-band optical density of 1.75 in an "infinitely thick" Harshaw NaBr crystal. Virtually

no color centers form at 80°K. At 200°K the color center density at 14 hr. is low, but useful. The 14 hr. density increases to a maximum near 328°K and then drops precipitously at 370°K, although the initial rate at the latter temperature is very large. It is estimated that at 328°K approximately 60 hours of x-raying would be required to reach an optical density of three.

X irradiation at room temperature introduces a large F band and a very small V band at 265 nm and no other resolved absorptions between 200 and 1000 nm. An F-band bleaching produces R_1 , R_2 , M_1 , N_1 and N_2 bands. Samples x irradiated at 200°K show a large F' band. A summary of band positions, measured at 80°K, is given in the table which follows.

Table VI-1. Comparison of Band Positions in NaBr and KCl (nm, at 80°K)

Salt	F	F'	M_1	R_1	R_2	N_1	N_2
NaBr	527	500	820	650	750	930	990
KCl	539	750	802	658	731	964	1020

The F' band bleaches with a half time of ca 12 min. upon standing in the dark at room temperature. It also, as is usual, is quickly bleached optically at 80°K. Whenever F' centers are present and bleaching either optically or thermally, a luminescence due to recombination of electrons with positive hole centers is observed. This recombination luminescence is very troublesome in absorption measurements if the detector of the spectrophotometer is sensitive at the emitted wavelength, which in NaBr is estimated to be below 400 nm. Using proper technique, however, a good F' center absorption profile was developed which shows a maximum at 500 nm and an additional smaller band near

300 nm. The two absorptions correspond to processes in which the remaining F center is left in an excited 2s or 2p state, respectively^j. It is interesting to note that in both NaBr and NaCl, the peak of the principal F' band lies on the low energy side of the F band²⁶.

A careful re-examination of much of the NaBr work has recently been made with the help of Evalyn A. Chmura and after some further study, particularly of some experiments involving x-irradiation, thermal bleaching and re-irradiation^k, the NaBr work will be prepared for publication⁴³.

In association with the x irradiation experiments, attempts were made by Fr. George J. Hilsdorf, S. J. to prepare additively colored NaBr crystals. Heating crystals in saturated Na vapor for 20 hours at 600°C did not, however, yield colored crystals. The sodium which entered the crystal apparently reacted with OH⁻ and H₂O contamination already present forming H⁻ and O⁼ ions. That U centers (H⁻) were present was demonstrated by the fact that irradiating sodium vapor treated crystals with radiation from a quartz Hg resonance lamp produced F centers in good yield.

Pretreating NaBr crystals with Br₂ at elevated temperature did not appear to remove the OH⁻ and H₂O contamination so as to make the additive coloring process any more efficient. Perhaps higher temperatures and longer times of heating in a much cleaner system will be more effective. Certainly H₂O, Br₂ and HBr can diffuse through the NaBr lattice, the problem is to find the correct conditions for preparing cleaner crystals. It is an important problem. All the sodium halides with which we have had experience additively color poorly.

VII. Thermal Aggregation of F Centers

Two studies of thermal aggregation of F centers have been completed and reported. The first, by Karl Konrad^{6,21,25}, involved NaF and was patterned after

similar experiments with KCl ¹. Crystals were heavily x irradiated at low temperature (80°K , 200°K) and the absorption spectrum measured at intervals during warming to room temperature and above. In the process F' centers disappear and some F centers are destroyed by capture of thermally released positive holes. When the temperature reaches the point where the resultant α centers (negative ion vacancies) become mobile, M^+ centers (F_2^+) form by the reaction $\text{F} + \alpha \rightarrow \text{F}_2^+$. M^+ centers subsequently capture electrons yielding M centers (F_2).

The M^+ band in NaF is very efficiently produced at temperatures near 260°K , and specimens are readily prepared in which the M^+ absorption is greater than the M absorption. In the thermal aggregation process some higher F -aggregate centers form, e.g. R^+ , R , and R_2 . Subsequent bleaching with F -band light produces large increases in the M_1 , R_1 , R_2 and M_1 bands, as well as causing the appearance of a number of new bands²⁵, which remain unassigned. Both the M center and the M^+ center in NaF have been investigated in considerable detail⁶.

A second series of aggregation experiments, on NaCl , was carried out by Moo Jin Jun^{8,26}. Again, specimens were heavily x irradiated, but in this case it was necessary to study the aggregating process by a pulse annealing technique. In contrast to NaF , M^+ centers in NaCl form in low yield. Subsequent reactions producing M , R^+ , R and N centers seem to be much more efficient. Study of the M^+ center in NaCl promises to be very difficult. M^+ centers can be produced by direct ionization of M centers with 300 nm light but concentrations are low because of a counter-balancing of photoionization and electron capture processes.

VIII. Diffusion of Water into Potassium Iodide

Additively colored KI specimens fade when stored in the dark in an ordinary laboratory atmosphere. After microscopic examination Albert E. Gudat proved that the "fading" was caused by penetration of a bleached layer inwards from the surface

and that the square of the penetration depth was linear in time³⁶. Subsequently, Kathleen Coleman showed that the penetration rate depended approximately linearly upon the partial pressure of water in the sample environment³⁷. Subsequently David L. Roskelley made an extensive study of the diffusion of H₂O into additively colored KI⁹. Recently his results have been re-calculated and re-assessed and the work prepared for publication²⁷. The abstract of that paper follows.

"The diffusion of water into additively colored potassium iodide has been studied in the range 15-45°C. Penetration depths, measured by decrease in the F-band absorption, increase with $t^{1/2}$. The diffusion coefficient, $D = 0.58 \exp(-6496/T)$, agrees very well with that determined by other workers.^m The Henry's law constant $K = C_o/P_w = 1.3 \times 10^9 \exp(+4882/T)$ implies a water concentration $C_o \approx 10^{17}$ molecules per cm³ in the surface of KI crystals in equilibrium with an environment at 25°C and 35% relative humidity. The large C_o makes penetration very rapid. Diffusion occurs by interstitial migration of water molecules with an entropy of activation of 9.4 cal/mol deg and an enthalpy of activation of 12.9 kcal/mol."

The penetration of water into KI is astonishingly rapid so one should not be surprised to encounter problems of fading in KI specimens, and perhaps some other crystals, which contain kinds of color centers which can be changed by interacting with water molecules. The simple fact is that an additively colored sample of KI containing ca 6×10^{16} F centers per cm³, exposed to a laboratory atmosphere at 25°C and 35% relative humidity, will show 1/2 mm thick discolored surface layers after 6-8 weeks. The quick penetration is the result of the very large concentration of H₂O in the exposed surface implied by the Henry's law constant cited above. So far, room temperature diffusion of H₂O has been observed and studied only in additively colored KI, but the phenomenon deserves careful watching so it may be avoided or exploited. Penetration into pure KI must be expected at a somewhat

lower rate. Given time enough, however, water concentrations equal to anticipated color center concentrations can be achieved. Thus, water is an important impurity.

IX. Studies of M Center Dichroism.

The M center has been shown to consist of two F centers occupying nearest neighbor anion lattice sites. Accordingly, the M center has a figure axis which lies along a face diagonal of the cubic unit cell. Its symmetry, however, is D_{2h} rather than $D_{\infty h}$ by reason of the non-equivalence of the crystal field in the $[110]$ and $[100]$ directions of the alkali halide fcc lattice. Studies of the dichroism of samples in which the M centers have been preferentially aligned with their figure axis in the $[011]$ direction indicate an M_1 band, the classical M band, with optical dipole moment in the $[011]$ direction (z axis) an M_2 band with optical dipole moment in the $[0\bar{1}1]$ direction (y axis), an M_2' band with optical dipole moment in the $[100]$ direction (x axis), and several other bands of lesser intensity. The M_2 and M_2' bands underlie the F band and are sometimes described as M_F bands.

Since an M center is analogous to a H_2 molecule embedded in a dielectric medium, it has been suggested that the M_1 band corresponds to a $1\Sigma_g^+ \rightarrow 1\Sigma_u^+$ transition of the two electron, two center system, and that the M_2 and M_2' bands are to be associated with a degenerate $1\Sigma_g^+ \rightarrow 1\Pi_u$ transition. The degeneracy is lifted by the crystal field so that the M_2 and M_2' band correspond to $1\Sigma_g^+ \rightarrow 1\Pi_y$ and $1\Sigma_g^+ \rightarrow 1\Pi_x$ transitions, respectively. Examination of the experimental data currently available, relating to KCN, KCl, KBr, KI, NaF, and NaCl indicates that the separation between the M_2 and M_2' bands is strongly dependent upon the nature of the anion. The crystal field splittings of the $1\Sigma_g^+ \rightarrow 1\Pi_u$ transitions are in the order $KCN > NaF > KCl > KBr > KI$, an order reminiscent of the spectrochemical series of ligand ions, $CN > F > Cl > Br > I$. The dependence of splittings on the nature of the cations is not yet known. Our ultimate goal in studying the M center dichroism is to provide an experimental basis

for the understanding of the M center transitions in terms of theoretical considerations developed in our laboratory and elsewhere. A concise summary of M center theory and its present state has recently been given by W. Beale Fowlerⁿ, and a more extensive treatment has been given by Evarestov, et al^r.

A. Potassium cyanide. The first detailed study of M-center dichroism was that of F. Okamoto^o in KCl, and it was he who defined the subscript and prime terminology which is used. Shortly thereafter Sherman Susman extended investigation of M center dichroism to KCN, using x-irradiated specimens of zone-refined crystals⁴. Measurements were made at -76°C (dry ice), an experimentally practical temperature, because specimens become opaque when cooled below -100°C where KCN transforms from cubic to orthorhombic structure. Partial results of the work on KCN have already been reported in two places^{13,p} and a complete paper is in preparation⁴¹. Table IX-1 contains some KCN data. The pattern of M bands resembles that already reported for KCl^o and subsequently reported for KBr²⁰. The principal fact to emerge is the unusually large $M_2'-M_2$ splitting in KCN, indicating that the CN⁻ anions are very effective in lifting the degeneracy of the $1\Sigma_g^+ \rightarrow 1\Pi_u$ transition.

B. Potassium Bromide. As part of his investigation of color center phenomena in KCN⁴ Sherman Susman examined the optical properties of M centers in KBr for comparison purposes, since those two salts have very nearly the same lattice constants. The results of this work have been published²⁰ and their implications discussed^{20,n,p}. Perhaps the most important conclusions from the work on KBr and KCN were: (a) that the M_2' band corresponding to a $\langle 100 \rangle$ directed electric dipole transition had a higher energy than the M_2 band ($\langle 0\bar{1}1 \rangle$ directed), and (b) that the $M_2'-M_2$ splittings in potassium salts appeared to be strongly dependent upon the nature of the anions. Table IX-1 contains some KBr results.

c. Sodium Fluoride. Studies of M center dichroism in NaF were undertaken by Karl Konrad⁷ because it represented a natural extension of previous work by

him^{6,21} and by others^{3,19,22}. The investigation extended our knowledge into the sodium salt series as well as into the iso-electronic salt series: NaF, KCl, RbBr.

Bleaching x irradiated or γ irradiated NaF with (365 nm) light absorbed in the low energy side of the F band produces large M_1 and R^+ bands. M_1 -band growth is rapid at room temperature and if the bleaching is prolonged its intensity can be made greater than that of the F band, although in such a specimen the concentrations of higher aggregate bands, R_1 , R_2 , R^+ , N_1 , N_2 may be too great for some experiments²⁵. None the less, larger than usual M_1 band intensities are readily produced in NaF.

Dichroic difference spectra prepared from polarized light absorption measurements on samples containing preferentially aligned M centers were studied for many samples having differing color center densities. The dichroic results were qualitatively similar to those in other systems with two notable quantitative differences: (a) the M_2' - M_2 splitting was larger than that for KCl but smaller than that for KCN, which had been anticipated, and (b) the ratios of intensity of the M_2' (M_2') bands relative to the M_1 band were only about one half the magnitude observed in potassium salts. The latter fact suggests that there is a dependence of M center transitions on the nature of the cation, as is expected on the basis of Mollwo-Ivey correlations. Those correlations will have to be carefully re-examined, including giving some attention to a suggestion by Levy⁹ as to the importance of the high frequency dielectric constant and the cation radius in such correlations. The results of our studies of the M center in NaF are currently being prepared for publication under the title "F-Aggregate Centers in Sodium Fluoride. II" by Karl Konrad⁴⁵.

d. Potassium Iodide. An investigation of M-center dichroism in KI has recently been completed¹¹ and the results prepared for publication by Albert E. Gudat⁴⁴. The study used additively colored KI crystals in which it was possible

to produce ordered M center distributions with degrees of polarization as high as 0.7. Polarized spectra were measured at 20, 80 and 243°K. Dichroic spectra showed at least seven absorptions. Of particular interest is the observation that at 20°K the M_4 band is quite well separated from the M_2 band. The M_2' - M_2 band splitting is very small, ca 0.01 ev, showing that the efficiency with which the crystal field lifts the degeneracy of the $^1\Pi_u$ state is $Cl > Br > I$, as had been suggested. Table IX-1, at the end of this sub-section, gives a summary of the M_1 , M_2 and M_2' band peaks for KI as well as for the other salts for which data are available.

When an attempt is made to correlate the M_1 and M_2 (M_2') transition energies with those to be expected for a simple H_2 molecule like system embedded in a dielectric medium it is always found that the experimental energy differences between the M_2 (M_2') bands ($^1\Sigma_g^+ \rightarrow ^1\Pi_u$) and the M_1 band ($^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$) is larger than the calculated difference. The results of the calculations of Evarestov, et al which take explicit account of the ionic nature of the crystal are better^r. Quite good agreement for the M_1 , M_2 and M_2' transition energies are obtained and the predicted directions of the electric dipoles of the transitions are in agreement with experiment. The M_2' - M_2 splittings are, however, 2 to 10 times larger than those which are experimentally measured and do not show the $F > Cl > Br > I$ trend which has been established.

One further aspect of M center dichroism in KI deserves mention. In re-checking his data Albert Gudat paid particular attention to the M_4 band which occurs in both the primed and un-primed dichroic spectra with the same dichroic sign as the M_1 band. It is a quite weak band and its measurement is complicated by overlapping absorptions. If the M_4 band were the result of a symmetry-forbidden transition $^1\Sigma_g^+ \rightarrow ^1\Sigma_g^+$ ($1s\sigma_g 1s\sigma_g \rightarrow 1s\sigma_g 2s\sigma_g$) it would have Σ polarization but would require assistance of an appropriate odd-parity phonon. Its absorption strength accordingly should increase with increasing temperature. The idea

of vibronic assistance was examined in KI in the temperature region from 20.4°K to 243°K but, within the limits of the graphical resolution of overlapping bands, relatively little variation of the area under the M_4 band was observed. The assignment of the M_4 band to a vibronically assisted transition can thus be ruled out.

Table IX-1. Comparison of the M_1 , M_2 and M_2' absorption bands and the $M_2' - M_2$ band maxima separations in various alkali halides.

Matrix	Temp. (K)	M_1 -band maximum		M_2 -band maximum		M_2' -band maximum		$E_{\max}(M_2')$	References
		(nm)	(ev)	(nm)	(ev)	(nm)	(ev)	$-E_{\max}(M_2)$ (ev)	
KI	20.5	1006	1.231	658	1.884	654	1.895	0.011	
KI	77.4	1010	1.227	662	1.872	658	1.884	0.012	(11), (44).
KI	243	1035	1.198	680	1.823	678	1.828	0.005	
KBr	79	886	1.399	619	2.003	612	2.025	0.022	(p), (4), (20).
KBr	197	901	1.376	623	1.990	618	2.006	0.016	
KCl	79	801	1.548	546	2.270	538	2.304	0.034	(6).
KCN	197	857	1.446	551	2.250	531	2.334	0.084	(p), (4), (13), (41).
NaF	80	499	2.486	341	3.635	338	3.673	0.038	(7), (45).
<i>NaCl</i>	<i>80</i>	<i>716</i>	<i>1.731</i>	<i>450</i>	<i>2.755</i>	<i>447</i>	<i>2.773</i>	<i>0.018</i>	<i>preliminary.</i>

E. Sodium Chloride. A study of the dichroism of the M center in NaCl is currently being carried out by Alvin E. Weinstein. After a number of exploratory additive coloring experiments which are summarized in Sec. X, it was concluded that color centers were best introduced by x irradiation at 200°K. Two satisfactory procedures for preparing dichroic specimens were then developed: (a) M centers are first formed ($2F \rightarrow M$) at 0°C by irradiating with unpolarized F-band light and an aligned M center distribution produced at 0°C by irradiating into the M_1 band with polarized, broad-band, radiation, (b) M centers are both

formed and aligned by irradiating with polarized F-band light at 0°C and the degree of polarization improved by subsequent (or simultaneous) irradiation with polarized M_1 band light. It is observed that polarized bleaching into the M_1 band causes a net decrease in the number of M centers indicating that there are competing destruction and re-alignment processes in NaCl, as there are in the other systems we have studied.

Polarized spectra of samples having aligned M centers are normally taken at 66, 80, 110, 197 and 274°K. In such spectra the M_1 -band peak position varies from 715 to 727 nm and its half-width varies from 0.080 to 0.145 eV, over the temperature range 66-274°K. The temperature variation of the half-width, analyzed in the usual hyperbolic cotangent fashion, implies a value $H_0 = 0.070$ eV for the half-width at 0°K and a value of $\nu_g = 2.9 \times 10^{12} \text{ sec}^{-1}$ for the frequency of the phonons which cause the broadening of the M_1 band. Those values are significantly different from values given in the literature^x which were determined using samples containing both M and R^+ centers. The R^+ band occurs at 690 nm, but in the experiment described above, there were few R^+ centers and the data used were from a set of [010]-[001] dichroic spectra in which the R^+ center absorption at 690 nm cannot appear. Study of the M_1 -band shape shows that it is unsymmetrical: it is broader on the high energy side at 66, 80 and 110°K, symmetrical in energy at 197°K and broader on the low energy side at 274°K.

Analysis of the dichroic spectra in the M_F region is complicated by the overlapping of the M_4 , M_2 , M_3 , M_5 and M_6 bands in both the [011]-[0 $\bar{1}$ 1] and the [010]-[001] spectra. There is little improvement in resolution at 66°K relative to 80°K. In order to get estimates of peak positions and half-widths we have assumed the high energy M bands are symmetrical in energy. In this way it was determined that the M_2 peak position varies from 448 to 455 nm and its half-width varies from 0.273 to 0.285 eV, over the range 66 to 274°K. The M_3 band varies

from 409 to 412 nm over the same range. The position, intensity, and in some cases, the dichroic sign of the higher transitions are still somewhat uncertain, but the results to date do suggest that the M_5 band has the same dichroic sign as the M_1 band. We are at present using a non-linear least squares curve fitting program (developed by G. Struble) to decompose spectra in the M_F region into a series of Gaussian bands.

The crystalline field splitting of the $M_2' - M_2$ bands has been assigned a tentative value of 0.018 eV at 80°K. The comparative value for NaF is 0.038 eV⁷, so the magnitude of splittings in the sodium salts are $F > Cl$, as anticipated²⁰. In addition it appears, from the NaF and NaCl data, that there is a discernable cation effect on the M_2/M_1 band intensity ratio. That ratio is 0.4 for the potassium salts which have been studied, whereas it is 0.25 for the sodium salts. It may also be that the $M_2' - M_2$ splittings differ in magnitude in the sodium series, while preserving the $F > Cl > Br > I$ order.

As was mentioned earlier in this section, there is a definite anion-cation effect in Mollwo-Ivey plots for the position of the M_1 band. The usual relation given by Ivey⁸ is $\lambda_{\max} = 1400d^{1.56}$, where d is the anion-cation distance in Angstroms and λ is the peak wavelength in Angstroms. There are now, however, more and better M_1 -band data than were available to Ivey and plots of those data indicate that an anion family and a cation family of lines may be drawn, on $\log \lambda$ versus $\log d$ graphs, rather than a single all-inclusive line. Although there are still too many missing points, there is a definite trend suggesting that the exponent of the anion-cation distance (d) is ca 2 for the cation family of lines and 1.0 for the anion family.

X - F-Aggregate and Ionized F-Aggregate Centers.

In order to be able to prepare suitable specimens for study of M center dichroism it was necessary to develop an understanding of the means of production

and the properties of F-aggregate and ionized F-aggregate centers in the systems of interest. Aggregate centers form along with F centers and positive hole centers during x irradiation at room temperature (Sec. IV-VI). They may be produced more efficiently, in some instances, by thermal aggregation in samples which have been x irradiated at low temperature and then warmed (Sec. VII). Aggregation occurs when α centers (negative ion vacancies), generated in low temperature x irradiation or formed by thermal or optical bleaching of F centers, become mobile^{25,26}. The α centers are attracted to F centers producing M^+ centers which then become M centers upon capture of thermally released electrons²⁵. Higher aggregates, e.g. R^+ and R centers, can be formed by α center and electron capture by smaller aggregate centers, or by capture of M^+ centers by F centers. Another and particularly effective means of producing M, R, and N centers is by irradiating into the F band in either x irradiated or additively colored crystals. Subsequently, ionized aggregate centers may be produced by optical ionization of M and R centers. Brief reports on F-aggregate and ionized F-aggregate center experiments follow.

A. Potassium Iodide. In the course of his study of M center dichroism, Albert E. Gudat^{11,44} investigated the temperature dependence of half-width and intensity of M center and F center bands. In the case of the F center, experimental band shapes were corrected for the underlying K band and for a small amount of M_2 and M_2' absorption so as to provide pure F-band values for peak intensity, peak position and half-width. The corrected half-widths (H_T) were fitted to the relation

$$H_T^2 = H_0^2 \coth^{-1} (h\nu_g/2kT)$$

where H_0 is the half-width at 0°K and ν_g is the average frequency of the lattice vibrations which cause the broadening of the F band. The results obtained were: $H_0 = 0.1425 \pm 0.0005$ eV and $\nu_g = 2.00 \pm 0.03 \times 10^{12}$ sec⁻¹.

Measurements of the M_1 band absorption as a function of temperature gave values of $H_0 = 0.0447 \pm 0.0003$ eV and $\nu_g = 1.95 \pm 0.03 \times 10^{12} \text{sec}^{-1}$. The high energy half-point was almost exactly constant between 14.3°K and 141°K, and the area under the band, $H_T \times A_T$, was constant to better than 2%. The dichroic experiments described in Sec. IX-D, in addition to confirming the values for the M_1 band given above, also permitted approximation of the average frequency of the lattice vibrations which cause the broadening of the M_2 band. The value obtained is $\nu_g = 3.2 \pm 0.1 \times 10^{12} \text{sec}^{-1}$. It is unequivocally larger than obtained for the M_1 band. The data available for the M_2 band also indicate a value for ν_g which is about $3 \times 10^{12} \text{sec}^{-1}$. The experimental data have been carefully re-examined by Albert Gudat and after checking the subsequent calculations and some further study the results will be prepared for publication.

Thermal aggregation experiments were undertaken by Albert Gudat, some with help from Roy S. Teasley,⁴⁰ to establish the efficiencies of formation of M^+ , M , R^+ , and R centers. The results showed that: (a) the α band, which is readily observable in pure KI, begins to decay at 210°K and reaches its maximum rate of decay at 235°K; (b) the M^+ band appears at 225°K grows through a maximum at 240°K and is gone by 260°K; (c) the M band appears at 225°K and grows rapidly; (d) the R^+ band begins to grow at 235°K while the R_2 band appears later and is always less intense than the R^+ band. The quantities of M^+ centers formed were discouragingly small. At the temperature at which the M^+ band reached a maximum intensity of 0.008, the M band had an intensity twenty times greater. R^+ centers formed in much better yields than M^+ centers. The R^+ band lies on the low energy side of the M_1 band. At 80°K its maximum is at 1116 nm and its half-width is 0.124 eV.

It is possible to produce M^+ centers in larger concentrations by ionization of M centers using light absorbed by high energy bands of the M center. Absorbances

of 0.1 were observed after 15 minutes bleaching at 80°K with 420 nm light. Further bleaching was ineffective, however, since there are forward and backward reactions which produce a steady state concentration of M^+ centers. Subsequent irradiation with 229 nm light, which is absorbed in the tail of the fundamental absorption, releases electrons and causes decreases in the concentration of M^+ and R^+ . Irradiation with 320 nm light causes decreases in M^+ and increases in R^+ concentrations indicating that there is an R center band in the region of 320 nm. X irradiation at 80°K causes decreases in both the M^+ and R^+ bands. Difference spectra, in formation and in bleaching experiments, indicate that the M^+ band peaks at 1615 nm and has a half-width of 0.11 eV.

B. Sodium Chloride. On the basis of previous thermal aggregation studies, 8,26 Alvin E. Weinstein attempted to prepare NaCl samples with large concentrations of M^+ centers. For x irradiation at 80°K, however, entirely equivalent results were obtained, i.e. M^+ band optical densities of ca 0.08. For x irradiation at 200°K (>100 hrs.) followed by immediate warming to 255°K and subsequent measurement at 80°K a larger quantity of M^+ is produced. There are, however, very many M centers and a considerable number of R, R^+ and N centers formed and the M^+ band is overlapped by a band at 980 nm. Thus although the M^+ band optical densities can be as high as 0.25, the technique is at present not really useful.

Our studies of M-center dichroism has necessitated some attention being paid to other F-aggregate centers, in particular R and R^+ centers. Orienting M centers with [011] polarized M_1 -band light simultaneously produces aligned R_1 , R_2 and R^+ bands since some R centers are invariably present and there is an R band which lies closely on the long wavelength side of the M band. There is a strong R^+ absorption at 690 nm at 80°K. As with other ionized aggregate

center bands its peak moves to longer wavelength with decreasing temperature; it lies at 700 nm at $4^{\circ}\text{K}^{\text{V}}$. There is a second R^+ absorption at ca 400 nm. Ordered distributions of R and R^+ centers remain aligned at -35°C . R^+ centers become disaligned at $+25^{\circ}\text{C}$. R centers become disaligned at $+65^{\circ}\text{C}$.

In addition to bands assignable to R^+ centers, M_1 -light bleaching (at 0°C) produces a new band at 900 nm. This band becomes dichroic if the radiation is $\langle 010 \rangle$ polarized, but not if the radiation is $\langle 011 \rangle$ polarized. The dichroism is stable at -35°C , but unstable at $+25^{\circ}\text{C}$. The 900 nm band seems to have properties very similar to a band reported by Schneider² in KCl and designated $\text{N}_{1\text{B}}^+$. The $\text{N}_{1\text{B}}^+$ band in KCl is formed by ionization of $\text{N}_{1\text{B}}$ centers by radiation contained in the bleaching light which excites centers absorbing in the region of the classical N_1 band. Much of the absorption in that region is now considered to be due to R centers. Thus, it is suggested² that R centers, which are triples of F centers in an equilateral triangular nearest neighbor configuration, in a (111) plane, are caused to rearrange to a triple of F centers in an isosceles triangular configuration in a (100) plane. The pattern of properties; mode of formation, dichroism and thermal stability, indicate that the 900 nm band may well be the NaCl - $\text{N}_{1\text{B}}^+$ band. We have yet to check this by inducing the process $\text{N}_{1\text{B}}^+ + \text{e} \rightarrow \text{N}_{1\text{B}}$. Such should be readily done by a short irradiation with 300 nm light which is known to produce large fluxes of electrons by photoionization of F centers²⁶.

In addition to his work on x ray colored crystals Alvin Weinstein investigated additively colored NaCl for possible use in M-center dichroism studies. He found that heating Harshaw NaCl in sodium vapor at 560°C for 26 hr. produces samples which contain $<4 \times 10^{16}$ F centers per cm^3 , and that NaCl has a strong tendency to form colloids. A typical additively colored (1 mm thick) sample, which had been heated and quenched to disperse colloidal centers, showed optical

densities at 80°K of: colloid (680 nm) = 0.04; F (450 nm) = 0.83; O_{II} (290 nm) < 0.03; O_I (228 nm) < 0.2 and U (192 nm) = 3.16. The U band is due to substitutional hydride ions formed by the reaction, $NaOH + 2Na = Na_2O + NaH$. The O_I and O_{II} bands are assigned to $O^{\cdot -}$ ion absorptions. The amount of hydride formed appears to be about one third of the amount of OH^- present in the original crystal. When such specimens are irradiated at room temperature with 185 nm mercury radiation there is a 40 percent decrease in the hydride band (H_s^-) a three-fold increase in the F band and a U_2 band (H_i^0) is observed, centered at 225 nm. In addition some M, R and N bands appear because the arc emits 436 nm radiation which is absorbed by the F band. Additively colored Harshaw NaCl crystals contain so many U centers it is best to think of them as "hydride doped". As such they did not appear attractive for the M center dichroism studies. They are interesting, however, for other experiments because of the promise it offers for producing samples containing high concentrations of $O^{\cdot -}$ centers.

Finally in connection with M. J. Jun's study of thermal aggregation of F-centers in NaCl^{8,26}, it was noted that the M^+ centers had maximum concentration after the onset of α -center mobility at 240°K, a temperature corresponding to the second of the large glow peaks (170 and 235°K) observed in thermoluminescence studies. Further, it had been shown^t that those glow peaks were strongly enhanced by a thermal pre-treatment consisting of heating the NaCl crystal in air at 550°C prior to x irradiation. Accordingly Evalyn A. Chmura recently looked into the question of possible enhancement of M^+ center formation in heat treated crystals.

A double sample color center cell was designed and constructed so that a matched pair of samples, one heat-treated, could be x irradiated and pulse annealed in a comparative thermal aggregation experiment. Prior to those experiments, however, it seemed prudent to determine whether our samples of NaCl

showed the reported glow peak enhancement. Thermoluminescence studies were made using the detector system of a Farrand spectrofluorimeter. Samples were x irradiated at 80°K and warmed at ca 12°K per min. to 350°K. Glow peaks were found at the reported temperatures. They were enhanced by heat treatment, although the enhancement factors were not large. Thus, not unexpectedly, the glow enhancement appears to be an impurity controlled phenomenon. It will be necessary to seek the identity of that impurity so that larger concentrations of M^+ centers can be produced in NaCl and to explain their copious production in our NaF samples.

C. Sodium Fluoride: In the course of Karl Konrad's study of M-center dichroism some experiments were done on samples which contained rather sizeable concentrations of M^+ , R^+ , R and N centers. Whenever a sample is made dichroic by establishment of an ordered distribution of M centers a dichroic spectrum may be drawn from the set of absorption spectra measured with appropriately polarized light, eg [011] - $[0\bar{1}1]$. The dichroic difference spectrum shows only the absorptions of aligned centers. There is a tendency to overlook the fact that the total spectra at hand contain the spectrum of all centers, unaligned and/or isotropic, and that by subtracting an appropriately scaled dichroic spectrum, an undichroic spectrum can be generated.

Undichroic spectra prepared using total spectra for a sample of NaF which contained aligned M centers together with a relatively large number of unaligned R^+ centers showed clear absorptions at 737 nm (M^+), 575 nm (N), 512 nm (R^+), 435 nm (R_2), 395 nm (R_1), 370 nm (?), 333 nm (F), 303 nm (R^+) and 255 nm (?). Storing the sample at room temperature caused a small decrease in the 512 nm (R^+) band whereas three quarters of the 737 nm (M^+) band disappeared. At the same time the F and M bands increased. The two bands, at 370 and 255 nm decreased, and did so in apparent proportion to the 737 nm (M^+) band. The

sample was then irradiated for a short time with x rays and the undichroic spectrum re-computed. The 512 nm (R^+) band decreased by two thirds and there were associated increases in the R_1 , R_2 , F and N_1 bands.

The most significant changes in the spectra were those which occurred in the region of the 303 nm (R^+) band. First the experiment confirmed the fact that the R^+ center does have the absorption cited above at 303 nm. Second, when the M^+ centers were bleached at room temperature, there was a decrease in absorption at 303 nm which seemed proportionally greater than that at 512 nm indicating that there may be an M^+ transition near 300 nm. Third, the absorptions remaining after x raying which removed all of the M^+ centers and two thirds of the R^+ , and produced sizeable R_1 and R_2 bands, suggested the possibility, that there were R center transitions near 303 nm and at 270 nm.

Further support for some of the R and R^+ transition assignments result from luminescence studies by Sr. Doris Marie Roettgers who investigated the excitation spectrum of irradiated NaF crystals containing F, M and R centers. Excitation spectra obtained by monitoring the M center luminescence at 660 nm showed the M_1 , M_2 and M_3 bands as expected. Excitation spectra obtained by monitoring the R^+ center luminescence at 570 nm showed unmistakably that the R^+ center in NaF has a band at 303 nm as well as at 512 nm. Both bands are removed by a short x irradiation as is to be expected for R^+ centers and both may be restored by the bleaching with 430 nm (R_2 -band) light. The latter observation indicates that R centers are ionizable to R^+ centers. Further, the R^+ emission could also be restored by irradiating at wavelengths in the region 270-300 nm supporting the suggestion above that there are R center transitions near 270 and 303 nm.

By use of samples containing reasonable large concentrations of M^+ centers and computing undichroic spectra, as indicated above, it has been possible to associate bands in the ultraviolet with the M^+ center. The first M^+ transition

$1s\sigma_g \rightarrow 2p\sigma_u$, occurs at 737 nm; three additional transitions may be tentatively assigned: $1s\sigma_g \rightarrow 2p\pi_u$, at 370 nm; $1s\sigma_g \rightarrow 3p\sigma_u$, at ca 300 nm, and $1s\sigma_g \rightarrow 4p\sigma_u + 4f\sigma_u$, at 255 nm. These values can be placed in conformity with H_2 molecule ion calculations^u by considering that the M^+ center is a H_2^+ molecule having an internuclear separation of 2.92 Å embedded in a dielectric medium of dielectric constant 1.84 as compared with 1.74 for the NaF crystal. The anion-anion distance in NaF is 3.27 Å.

It must be emphasized that the identification of the transitions is tentative and must be confirmed by luminescence measurements. The $2p\sigma_u \rightarrow 1s\sigma_g$ luminescence of the M^+ center in NaF occurs at 943 nm⁴⁴. The $2p\pi_u \rightarrow 1s\sigma_g$ luminescence is expected to occur somewhere in the visible region of the spectrum. This problem is currently being studied by Thomas H. Jupille. The investigation will follow a pattern already established by Lüty and Aegerter who studied the M^+ center in $KCl^{V,W}$ and will be coupled with further undichroism experiments.

For reasons unknown, M and M^+ centers form abundantly in nominally pure Harshaw NaF, in contrast with other alkali halides. One possible explanation involves the presence of oxygen impurity centers in our NaF. Oxygen impurities are known to occur in crystals grown in O_2 containing atmospheres to which NaF, because of its high melting point, might be particularly susceptible. Oxygen impurities are notable in crystals by the characteristic ease of cleaving they endow. Variations in cleave-ability have been observed between NaF samples. The principal responsible center seems to be superoxide ion (O_2^-). That ion if reduced during x irradiation to $O^=$ ion would provide a supply of α -centers, since each $O^=$ is expected to be charge-compensated by a nearby negative ion vacancy.

The possibility of a relationship between efficient M^+ center formation in NaF and O_2^- contamination was investigated by Beverly A. Rubik. The O_2^- ion has

a characteristic luminescence spectrum so the first experimental work involved making our fluorimeter more sensitive by installing a tuning fork beam-chopper, a pre-amplifier plus lock-in amplifier and a set of slow-scan monochromator drive motors. The modified apparatus was capable of sensing the structured luminescence from a 1 cm thickness of a cyclohexane solution containing approximately 10^{-12} g/ml of anthracene. No characteristically structured O_2^- luminescence however, was observed in any of the crystals studied. Specimens included Harshaw and home-grown NaF, pure and OH^- doped NaCl and OH^- doped KI, both before and after x irradiation. While it had been shown that the apparatus could resolve similarly structured low-level luminescence, the O_2^- luminescence is in a relatively "dead" region of the photomultiplier which was used. (A better detector, on order with a 10 day promise of delivery, arrived 60 days late!). Further, in the course of the work a broad phosphorescence was observed in practically all of the crystals studied. This adversely affected the signal to noise ratio and necessitated designing a new mounting which will place the chopper before, rather than after, the sample. We are none-the-less fairly certain that the O_2^- concentration in our NaF samples is not large.

A review of the literature indicates that the situation with regard to oxygen impurities is more confused and complicated than we thought, at first. Beverly Rubik has recently completed such a review. She finds many contradictions between old and new papers and is presently in the process of trying to place the available information in a unified perspective so we may use it in continuing our inquiries as to why M^+ centers in NaF are so easy to generate.

D. Laser for NaF Bleaching: Over the past few months, Joseph F. Sydejko has constructed several versions of a small pulsed molecular nitrogen laser. The devices were simplified versions^B of one described by Ericsson and Lidholt^Y.

The laser operates in the superradiant mode using the 337.1 nm, $C^3\Pi_u-B^3\Pi_g$ (0,0), band system of N_2 . Since the lifetimes of the upper and lower states are 40 nano sec and 10 micro sec, respectively, the pumping process must be very fast. The high peak current and fast rise time pulses required are obtained by discharge of a low inductance co-axial 10 pf coaxial capacitor built around a glass capillary (8 cm long, 1 mm i.d.) laser tube. Nanosecond charging is achieved by first charging a larger capacitor (a 30 pf length of coaxial cable) and transferring charge to the laser capacitor across a spark gap. Thirty kilovolt 10 micro-second pulses are delivered to the 30 pf capacitor by a modified, high quality, color TV flyback transformer driven by the triggered discharge of a 10 uf storage capacitor through its primary windings at a rate of 120 pulses per second. The laser's coaxial capacitor can be charged to potentials in excess of 20 KV before the N_2 gas (5 torr) breaks down and the system lases. Lasing is readily detected in a darkened room, by observing the fluorescence of a dilute solution of rhodamine GG or 9, 10 diphenyl anthracene.

Similar lasers^Y have been shown to produce light pulses of the order of 1-2 kw having a duration of ca 0.7 n sec. For 337.1 nm radiation such pulses will contain 1.7×10^{12} photons per pulse, which in our case will amount to approximately 10^{17} photons in a 10 min. period. We propose to use the radiation for bleaching into the F band in NaF which peaks at 333 nm at 80°K. A routine-use laser system is being constructed with a mirror at the back end to double the output. It will be equipped with an appropriate filter and polarizer and used to produce aligned M centers. The 3 milliradian beam divergence will provide a very parallel beam of polarized light so that we expect to obtain larger dichroisms than were possible in our earlier experiments^{6,25}. The laser light (337 nm) will produce M^+ , R, R^+ and N as well as M centers, but specific centers can be investigated by proper choice of polarization of the bleaching light, temperature of bleaching, pulse annealing excursions, additional optical irradiations

at other wavelengths, etc. After some questions regarding M and M^+ centers have been answered, attention will be turned to R centers with particular emphasis on the N_{1A} , N_{1B} , N_{1A}^+ and N_{1B}^+ bands which are ascribed to next-nearest-neighbor R and R^+ centers^{y,z}. The laser radiation will also be useful in bleaching experiments on villiaumite.

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