0.005 eV, respectively. They are very narrow as compared with that of the F' band. In the case of KCl crystals they are also very narrow as are those in the KBr crystals. At the present stage of investigation, the reason for the narrow band width is not clear.

 R_1 and R_2 bands always behave similarly in respect to dichroism and the increase or decrease in height. On the other hand, R_1' and R_2' bands also behaved in a similar fashion with each other. Thus, R_1 and R_2 bands as well as R_1' and R_2' bands may arise from two electronic transitions in the identical Rand R' centers.

The F' type bands corresponding to N_1' and N_2' bands were not observed in the present experiment, because of the short life times of these centers.

The detail results on the F' type bands will be reported in J. Phys. Soc. Japan 17 (1962) No. 9.

PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT II, 1963

α Centers in Alkali Halide Crystals

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Optical studies are made concerning α centers in KI, KBr, KCl, NaCl and NaF. Position, half width and oscillator strength of α absorption bands, thermal stability of α centers and fluorescence by α light absorption and its quantum efficiency are investigated. The observed fluorescence suffers quite a large Stokes shift in all the crystals measured. The quantum efficiency of α fluorescence is determined on KCl by referring to that of $305 \text{ m}\mu$ emission excited by $246 \text{ m}\mu$ band in KCl:Tl phosphor. Temperature dependence of the emission spectrum of α fluorescence is found not remarkable and the quantum efficiency seems to be independent of method of coloration and concentration of α and F centers.

I. Introduction

Since the discovery of α band in additively colored KI¹, the band has been observed in RbI, RbBr, NaBr², KCl, NaCl and NaF³. When an alkali halide crystal is exposed to ionizing radiation at a low temperature or crystal that contains F centers is bleached with F light at an appropriate temperature, an absorption band due to negative ion vacancies appears in the vicinity of the fundamental absorption. From several experimental evidences it is now believed that this band, α band, is due to an absorption that forms excitons around a negative ion vacancy. The negative ion vacancy is then called α center.

In the present study, position, half width and oscillator strength of this absorption band, thermal stability of the center, and fluorescence by α light absorption and its quantum efficiency were investigated on KI, KBr, KCl, NaCl and NaF single crystals. The results together with brief account of already published work will be summarized in this report.

II. Material and Equipment

Most of crystals of KBr, KCl, NaCl and NaF used were obtained from Harshaw Chemical Company. Some NaCl samples were cleaved out from an old rock salt prism, and KI crystals were grown in our laboratory. All alkali halides investigated except NaF were able to be colored both additively and by X-irradiation. A KCl:Tl crystal grown by Dr. Aoyagi was used as a standard phosphor for determining the quantum efficiency of α fluorescence.

Vacuum spectrophotometer used has been reported separately⁴⁾. In the study of α fluorescence, emission from sample was obtained through a devised side window of the spectrometer and its spectrum was investigated photographically with a two glass prism spectrograph and photoelectrically with a quartz prism monochromator and a photomul-



Fig. 1. Optical arrangement for measurement of quantum efficiency of α fluorescence. W_1 , LiF window; W_2 , Be window; W_3 , Sapphire window; W_4 , Quartz window; W_5 , Quartz window coated with sodium salicylate; R, Reference crystal; S, Sample crystal; T, KCI: Tl as a standard phosphor; F_1 , Sapphire filter; F_2 , Sapphire filter; F_3 , Glass filter; F_4 , Resin filter. Following combinations are used in the measurement.

Measurement of	Filter	Crystal	Phototube window
Absorbance of crystals	F_2 or F_3	S or R	W_5
Emission of α -fluorescence	F_1 and F_4	S	W_4
Fluorescent emission of KCl:Tl stand- ard phosphor	F_1 and F_4	R	W_4

tiplier RCA 1P21 or 1P28. Heterochromatic sensitivity calibration for the spectrograms was made by the use of a color temperature standard lamp. Below 300 m μ in wavelength, sodium salicylate was used as a standard phosphor in the calibration because it has been known to have a fairly constant quantum efficiency of fluorescence over the wavelength range from below 1000 Å to 3500 Å^{5),6)}.

Optical arrangement for measurement of the quantum efficiency of α fluorescence is shown in Fig. 1. Two sapphire plates, one glass filter and one resin filter are set on a cylindrical holder made movable around the sample holder. They were used to eliminate higher order components in the incident light from the vacuum monochromator, or to separate the incident radiation from the fluorescent emission. The resin filter used for the latter purpose had a fairly sharp cut-off characteristics and a very weak fluorescence, if any. Three crystals-sample crystal to be measured, standard phosphor KCI:TI, and reference crystal of NaF needed in preventing the effect of formed deposit in absorbance measurement at low temperatures-were mounted on a copper holder attached to a cryostat. The housing of the photomultiplier tube 1P28 with two opposing quartz windows is made revolvable to allow any one of them to face the beam of light. One of the windows, coated with sodium salicylate, was used in measuring the incident light intensity and the other clear window in measuring the fluorescent emission.

The sample chamber is provided with a side window to admit light for bleaching or to observe the fluorescent emission.

III. Absorption

For KCl and NaCl, absorption bands were studied with additively colored crystals as well as X-irradiated ones. Coloration for NaF was

Table I. Position and half width of α band and the energy difference between the first fundamental absorption peak and α band in comparison with those calculated by several authors.

		Expe	rimental	Theoretical				
Material Position		tion	Width	Separation	Separation eV			
-	mμ	eV	eV	eV	Bassani Inchauspé	Muto et al.	Tsertz- vadze	
NaF	131.5	9.43	0.4	1.21				
NaC1	173	7.16	0.33	0.80	0.50	0.58	0.33	
KC1	178	6.96	0.32	0.80	0.53	0.54	0.41	

made successfully only by X-irradiation, and the study of α centers was made with these photochemically colored crystals. The position and half width of the bands are listed in Table I. α band in KCl was distinctly separated from β band. Since α and β bands overlapped each other in NaCl and in NaF, the position and half width of the bands were determined from a curve showing the change in absorbance by production of α centers. The position of α band predicted by theoretical calculation^{71,81,9)} for KCl and NaCl are not in good agreement with those observed as seen in Table I.

IV. Thermal Stability

The thermal stability of α centers in additively colored crystals was found to resemble that of F' centers. The experiment was carried out as follows: a colored crystal is bleached with F light at a temperature favorable to α center production until the growth of α band reaches its saturation, then cooled down to liquid nitrogen temperature and the intensity of α band is measured. The crystal is warmed up to a testing temperature and is kept there for about 15 min. The crystal is again cooled down to liquid nitrogen temperature and the intensity of α band is measured. Half decay time is determined on the assumption that the decrease of α band

-160 °C -120 -80 -40 040 104 sec KBr KC NaC 103 10^2 6 7 5 4 3 9 8 1/T × 103 °K

Fig. 2. Half decay time of α centers as a function of temperature.

intensity obeys the rule of bimolecular reaction. In Fig. 2 the half decay time is plotted as a function of temperature. This result coincides almost exactly with Pick's data on thermal stability of F' centers¹⁰, which confirms the conversion mechanism $F' + \alpha \rightarrow 2F$ proposed by Delbecq *et al.*¹⁾

V. Oscillator Strength

With additively colored crystals, oscillator strength of α bands was determined in comparison with that of F band by the use of Smakula's formula¹¹⁾ and the relation $2F \rightarrow F' + \alpha$ meaning that two F centers are converted to an F center and an α center in optical bleaching process. The values obtained are given in Table II. Theoretical value of the oscillator strength of α band in NaCl given by Dexter is 1.89^{12} which is 70% larger than the experimental value 1.13.

Table II. Oscillator strength of α band. *n* means refractive index and *f* oscillator strength corresponding to α band or *F* band according to the subscript. The value f_F is quoted from R. H. Silsbee: Phys. Rev. **103** (1956) 1675 and C. J. Rauch and C. V. Heer: Phys. Rev. **105** (1957) 914.

Material	na	n_F	$f_{\rm co}/f_F$	f_F	f_{α}
NaC1	2.10	1.56	1.30	0.87	1.13
KC1	1.92	1.49	1.39	0.85	1.18
KBr	1.99	1.56	1.31	0.71	0.93

VI. Fluorescence and its Quantum Efficiency

1. Emission by α excitation

Thomas¹³⁾ and also Martienssen²⁾ reported that α band absorption in KBr causes fluorescence. In the present study similar fluorescence was observed in KI, KCl and NaCl aswell as in KBr, and the excitation and emission spectra were measured. The excitation spectrum of α fluorescence was found to coincide well with the absorption spectrum in all alkali halide crystals measured except those samplesin which β band strongly overlapped α band and absorption in β band reduced the fluorescent emission on one side of α band.

Emission spectrum of α fluorescence was determined both photoelectrically and photographically with fairly consistent results. The spectra observed on KI, KBr, KCl and NaCl are shown in Fig. 3. Longer wavelength sides



Fig. 3. Emission spectra of α fluorescence. Since the band shape is more or less deformed by presence of F band absorption, duly correction has been made (broken line). For KI the lower energy half of the band is drawn with a broken line because steep decrease of sensitivity of the photomultiplier used in this region has made the measurement less accurate.

of these spectra seem to be more or less scraped off by F absorption as clearly seen in Fig. 3d for NaCl. These spectra being duly corrected for such F absorption, their peak positions and half widths were estimated and are listed in Table III. It is significant that all of them show a very large Stokes shift and have a fairly broad half width. Comparison between band shapes of the emission at different temperatures, -113° C, -160° C and -195° C, was carried out for KCl. As for the temperature dependence, the peak

Table III. Peak position and half width of α fluorescence.

	Excitation		Emission			
Material	mμ	eV	mμ	eV	Half width eV	
NaCl	175	7.10	420	2.96	0.9	
KC1	179	6.93	443	2.80	0.8	
KBr	202	6.14	480	2.58	0.7	
KI	240	5.16	556	2.23	0.8	

position hardly but the half width slightly showed it. The half width seems to become broader at higher temperatures.

2. Quantum efficiency of α fluorescence

Because of difficulties in measuring directly the quantum efficiency of α fluorescence in the vacuum ultraviolet region, the quantum efficiency of α fluorescence was determined relatively to that of $305 \text{ m}\mu$ emission produced by excitation at $246 \text{ m}\mu$ band in thallium activated potassium chloride crystals, quantum efficiency of which had been reported to be 0.47^{14} and is approximately constant over the temperature range of our concern according to a preliminary experiment. Quantum efficiency of α fluorescence relative to that of KCl:Tl phosphor can be determined experimentally by the following equation:

$$\frac{\eta_{\alpha}}{\eta_{Tl}} = \frac{A_{Tl}}{A_{\alpha}} \cdot \frac{E_{\alpha}}{E_{Tl}} \cdot \frac{J_{Tl}}{J_{\alpha}}$$

where η denotes the quantum efficiency, A the area of the absorption band expressed in percentage, E the area of the excitation spectrum and I the effective sensitivity of the detector including filters averaged over the emission band and the subscripts α and T1 mean the corresponding phosphors. All quantities in the righthand side are experimentally measurable. The values of η_{α}/η_{Tl} thus obtained and the absolute values η_{α} determined on the assumption that $\eta_{Tl}=0.47$ are listed in Table IV. One will find that the α fluorescence is almost as efficient as the fluorescence of thallium activated phosphor. Though accuracy of measurement is still insufficient to draw a definite conclusion, the quantum efficiency of α fluorescence seems to be almost independent of the source of material, method of coloration and concentration of α and F centers. As for the temperature dependence, however, it seems to increase slightly with increasing temperature.

VII. Discussion

Coincidence of peak positions between the excitation and absorption spectra of α fluorescence shows that the fluorescence is caused by photons absorbed by α center. As for the emitting centers, their definite assignment is still difficult, but they are most likely to be α centers by the following reasons.

1. α absorption is believed to be an absorp-

Table IV. Quantum efficiency of α fluorescence. N_F : F center concentration. N_{α} : α center concentration. T: measuring temperature. η_{α}/η_{Tl} : relative efficiency of α fluorescence. η_{α} : absolute efficiency of α fluorescence for $\eta_{Tl} = 0.47$.

	$N_F~{ m cm^{-3}}$	$N_{lpha}{ m cm^{-3}}$	T °C	η_{lpha}/η_{Tl}	7/00
KCl (add. col.)	7.9×10^{16}	9.9×10^{15}	-195	0.74	0.35
	$1.4\! imes\!10^{17}$	$4.1 imes 10^{16}$	//	0.95	0.44
	//	//	-113	1.06	0.50
	1.9×10^{17}	3.2×10^{16}	-195	0.87	0.42
	//	//	-113	0.97	0.46
	//	4.8×10^{16}	"	0.93	0.44
	//	5.1×10^{16}	-195	0.75	0.36
	"	//	-137	0.91	0.42
	//	17	- 90	1.00	0.48
KCl (X-rayed)	$\sim 10^{19}$	$\sim \! 10^{18}$	-195	0.73	0.35
	"	"	17	0.84	0.40
	//	"	-137	0.93	0.44

tion that forms a localized exciton around a negative ion vacancy, and the excitation energy of the exciton is not high enough to transfer the exciton to other centers except to those that are very close to the α center.

2. The emission spectrum of α fluorescence is quite different from any of those known emission spectra of impurity or imperfection centers.

3. The quantum efficiency is as high as 0.4; it seems to be independent of the source of the materials, method of coloration and concentration of α and F centers. If the emission takes place after the energy absorbed in α band has transferred to other centers the quantum efficiency will depend on the above factors.

The Stokes shift of α fluorescence is quite large and the band width is fairly broad. A similar phenomenon has been observed by Chiarotti¹⁵⁾ in characteristic fluorescence of plastically deformed KI crystal at low temperature when excited by light in the tail of the fundamental absorption band. Though α absorption band was not observed in this case, the emission band appears near that of α fluorescence. The similarity between these two cases of fluorescence seems to imply that the centers formed in plastically deformed crystal consist of α centers closely grouped in various degrees probably along dislocation lines.

Acknowledgements

The authors wish to express their sincere thanks to Dr. J. Aoyagi of Tokyo University for kindly giving them a thallium activated phosphor. They are also indebted to Mr. K. Inohara for his efforts in growing crystals of pure potassium iodide.

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DISCUSSION

Dexter, D. L.: In your measurement of the emission spectrum, were you able to look also in the infrared region? It would be interesting to see if there is also *F*-band emission. This might well be excited both by direct reabsorption and by resonant energy transfer from the excited α -center.

Fujita, I.: We have not measured the infrared spectrum. I think it is important.

Pick, H.: What is the influence of the β -band which surely is present on the fluorescence of the α -center?

Fujita, I.: Especially in NaCl the emission was found to be weak. It must be due to overlapping of β -band on the α -band.

PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT II, 1963

The Fine Structure of Absorption in NaCl:Ag*

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It is known that a low concentration of Ag⁺ introduces weak lines into the absorption spectrum of NaCl near the fundamental edge. The small observed oscillator strengths of these lines lend considerable plausibility to their assignment to perturbed $4d^{10} \rightarrow 4d^95s$ transitions in the silver ions as originally proposed by Seitz, but certain theoretical calculations seem to indicate, on the basis of energy level predictions, that perturbed $4d^95p$ states are directly involved as final states. In this note, the relative strengths and positions of the observed lines are shown to be consistent with the original $4d^95s$ assignment, on the basis of a semiempirical crystal-field study and an analysis of their temperature dependence.

1. Introduction

In connection with his studies of AgCl, Martienssen¹⁾ has recently made a careful study of NaCl:Ag and resolved four lines near the tail of the NaCl fundamental absorption band. As in the case of NaCl:Cu,²⁾ these lines have a fairly small oscillator strength ($\sim 10^{-4}$) and a temperature dependence of strength which seems to indicate clearly that they arise from a forbidden electronic transition. Conway, Greenwood, Krumhansl, and Martienssen³⁾ have computed the oscillator strength of a $d^{10}-d^9s$ multiplet on the basis of the interaction of Debye-model phonons with the center. These phonons mix $d^{9}b$ states into the above-mentioned even-parity configurations. These authors find good agreement with the observed oscillator strength. The purpose of the present paper is to report an attempt to explain the fine structure of the NaCl:Ag multiplet, and is thus complementary to the work of Conway *et al*.

2. Electronic and Vibrational Structure of NaCl:Ag

A. The $d^{9}s$ configuration in Ag^{+}

The energies of the $4d^{9}5s$ terms relative to the ground state are obtained from⁴⁾

$${}^{1}D_{2} = E + \frac{1}{2} \mathcal{A} + \frac{1}{4} \zeta_{4d} \\ + \left[\frac{1}{4} \left(\mathcal{A} - \frac{1}{2} \zeta_{d} \right)^{2} + \frac{3}{2} \lambda_{4d}^{2} \zeta_{4d}^{2} \right]^{1/2} \\ {}^{3}D_{1} = E + \frac{3}{2} \zeta_{4d} \\ {}^{3}D_{2} = E + \frac{1}{2} \mathcal{A} + \frac{1}{4} \zeta_{4d} \\ - \left[\frac{1}{4} \left(\mathcal{A} - \frac{1}{2} \zeta_{4d} \right)^{2} + \frac{3}{2} \lambda_{4d}^{2} \zeta_{4d}^{2} \right]^{1/2} \\ {}^{3}D_{3} = E - \zeta_{4d}$$
 (1)

^{*} Supported by a grant from the U.S. Air Force Office of Scientific Research.