

## Optical Absorption and Fluorescence of Oxygen in Alkali Halide Crystals

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Single crystals of NaCl, KCl, and KBr were grown from the melt in an oxygen atmosphere, and their optical absorption, fluorescence excitation, and fluorescence emission spectra were measured at 300°, 77°, and 4.2°K. The weak absorption band caused by oxygen was the same in all three crystals, and did not vary with temperature. The band had maximum absorption at 5.0 eV and a half-width of 1.0 eV. All fluorescence excitation spectra contained a component identical to this absorption band. The fluorescence emission spectra consisted of a series of peaks in the wavelength range 4000–10 000 Å, with an approximately equal energy separation of 1000 cm<sup>-1</sup>. At 300°K, 12 to 15 peaks were resolved, and at 4.2°K each of these peaks split into 4 to 6 components. From these optical results and from paramagnetic resonance experiments, it is concluded that O<sub>2</sub><sup>-</sup> molecule-ions located in anion sites in the crystal are responsible for the absorption and fluorescence.

### INTRODUCTION

A YELLOW fluorescence is always associated with the presence of hydroxide impurity in alkali halide crystals.<sup>1</sup> Its structure has been investigated by Honrath<sup>2</sup> and Ewles and Barmby.<sup>3</sup> However, the fact that the fluorescence is excited at wavelengths outside the hydroxide absorption band indicates that it is not due to the hydroxide ion itself. The appearance of a strong fluorescence without a corresponding increase in the hydroxide absorption band in crystals grown in oxygen supports this conclusion. In this paper the optical absorption and fluorescence excitation spectra associated with the yellow fluorescence will be described, and more accurate data for the fluorescence emission presented for the three alkali halides NaCl, KCl, and KBr. We will also discuss the nature of the fluorescent centers.

### EXPERIMENTAL

#### Crystals

All crystals used in this investigation were pulled from molten salt contained in a platinum crucible, using Harshaw seed crystals suspended from a rotating water-cooled rod. The crucible and seed holder were enclosed in a silica tube, through which oxygen gas was circulated. Thermocouples for controlling the temperature of the melt were sheathed in platinum. The heaters were mounted outside the silica tube.

Crystals were grown at a rate of approximately 2 in./hr, and cooled down to room temperature in about 2 hr after completion of growth. Specimens were then cleaved from the crystals without further treatment.

The mechanical properties of crystals grown in oxygen differ from those of pure crystals. This was indicated by the ease with which they were cleaved, and by the

fact that the cleaved faces were exceptionally free of steps.

#### Optical Absorption Measurements

In the visible and ultraviolet regions (200 mμ to 750 mμ), optical absorption was measured with a Perkin-Elmer Spectracord recording spectrophotometer, model 4000. In the infrared region (2.5 μ to 15 μ) a Perkin-Elmer Infracord recording spectrophotometer, model 137B, was used. A metal cryostat in which specimens were clamped to a copper block cooled with liquid nitrogen was used in the measurement of absorption at 77°K.

The optical absorption due to oxygen was extremely small, and special precautions were necessary when measuring it. Specimens about 1 cm thick were used, and careful corrections were made both for surface reflection losses and internal scattering, by subtracting from the results the absorption of pure crystals of the same thickness. Furthermore, at 77°K it was found that butane from the O rings used in the window mountings condensed on the crystals. Although the extra absorption caused by the condensation was small, it was enough to cause serious errors in the determination of small absorption coefficients. The effect was eliminated by removing the O rings and attaching the windows to the cryostat with Edwards' Picein black wax.

#### Fluorescence Measurements

The apparatus used for fluorescence measurements has already been described.<sup>4</sup> It has, however, been improved in the following respects: A foreprism monochromator was placed at the entrance slit of the excitation monochromator to reduce stray light in the exciting light, and a 1600-w xenon lamp (Osram XBO 2001 S) was used as the exciting light source.

Excitation spectra were obtained by measuring the fluorescent emission as a function of the exciting wavelength, with the detection monochromator set at a wavelength (about 510 mμ) for peak fluorescence

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<sup>1</sup> H. W. Etzel and D. A. Patterson, *Phys. Rev.* **112**, 1112 (1958).

<sup>2</sup> W. Honrath, *Ann. Physik* **29**, 421 (1937).

<sup>3</sup> J. Ewles and D. S. Barmby, *Proc. Phys. Soc. (London)* **B69**, 670 (1956).

<sup>4</sup> F. R. Lipsett, *J. Opt. Soc. Am.* **49**, 673 (1959).

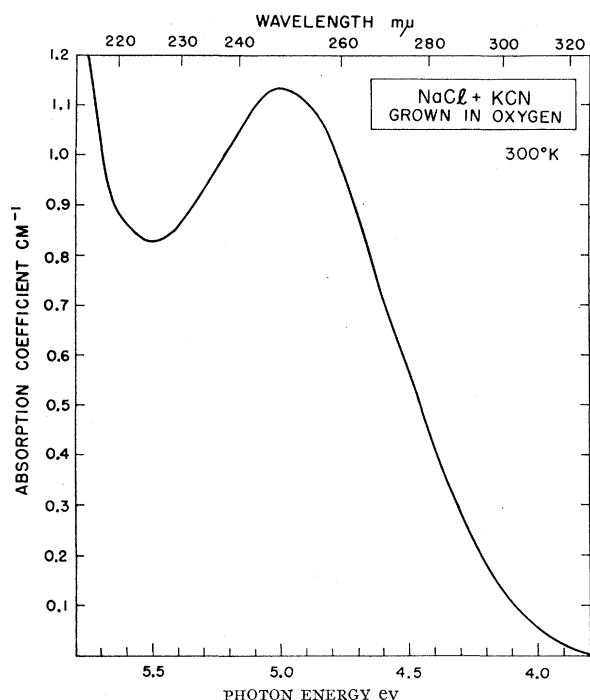


FIG. 1. Absorption spectrum of NaCl+KCN crystal grown in oxygen. 0.1M% KCN added to melt. Crystal thickness 3.20 cm. Measured at room temperature.

emission. The results were corrected for the variation with wavelength of the exciting light intensity. This calibration was made with a special thermistor bolometer (Optitherm detector made by Barnes Engineering Company) without a window, placed at the focus of the exciting beam.

Fluorescence emission spectra were measured with the exciting light set at a wavelength of 275 mμ. The wavelength of the detection monochromator was varied at constant speed, and a record obtained from the output terminals of a micro-microammeter. No corrections were made for the variation of photocell sensitivity and monochromator efficiency with wavelength. The detection photomultiplier tubes used were an EMI 6256B for the wavelength range 4000–7000 Å, and an RCA 7102, cooled with liquid nitrogen, in the wavelength range 6000–10 000 Å.

The method of mounting crystals for the measurement of emission and excitation spectra at 77°K was the same as that used in absorption measurements. A spurious blue fluorescence, consisting of three peaks, caused by condensed butane, was removed by the substitution of Picein wax for O rings.

Crystals were cooled to 4.2°K for emission measurements in a metal cryostat in which helium gas was used for heat transfer. The small enclosure containing the helium transfer gas was immersed in liquid helium, and was connected by means of a metal capillary tube to a vacuum gauge, which was used as a gas thermometer to measure the temperature of the crystal.

## OPTICAL ABSORPTION

The absorption bands produced when NaCl, KCl, and KBr are grown in oxygen are shown in Figs. 1–3. The bands are unusual in three respects: (i) They are very broad and very feeble, (ii) they do not change their shape or position in cooling from 300° to 77°K, and (iii) the shape and position of the bands are almost the same for NaCl, KCl, and KBr. They consist, in all three halides, of an absorption band whose peak is somewhere below the wavelength limit of the instrument used (200 mμ), and a smaller broad absorption band with a maximum absorption at about 248 mμ (5.0 eV) and of half-width about 1.0 eV.

The brightest fluorescence and greatest absorption occurred in crystals grown in oxygen from a melt doped with 0.1 mole% KCN. However, infrared absorption measurements on long crystal specimens indicated that only hydroxide, carbonate, nitrate, and nitrite ions were present. No cyanide or cyanate absorption bands could be detected, so that the fluorescence must have resulted from products of decomposition of the cyanide.

The very large hydroxide absorption band occurring in KBr and KCl crystals doped with KCN overlapped the oxygen absorption band to such an extent that accurate measurements of oxygen absorption were impossible. However, the hydroxide absorption band in NaCl (185 mμ)<sup>5</sup> is sufficiently removed from the oxygen absorption band that the overlap is negligible. The relatively large oxygen absorption of an NaCl+KCN crystal is shown in Fig. 1.

In Fig. 2 the absorption of a KCl crystal grown in oxygen is shown. The hydroxide band produced by hydrolysis is not large enough to overlap the oxygen absorption band. In KBr, however, the hydroxide and the oxygen bands are so close that overlap cannot be avoided. In Fig. 3, curve (a) is the absorption of an

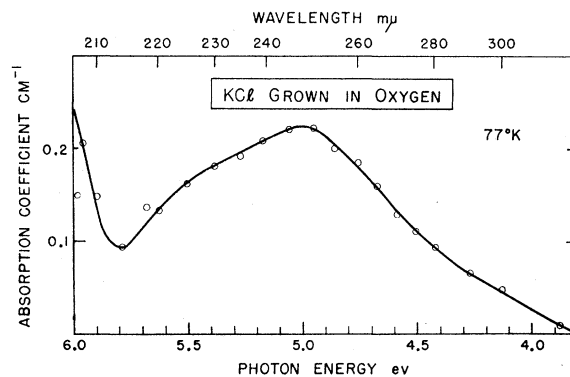


FIG. 2. Absorption spectrum of KCl crystal grown in oxygen. Crystal thickness 1.007 cm. Measured at 77°K.

<sup>5</sup> The value of 190 mμ previously quoted by one of the authors [J. Rolfe, *Phys. Rev. Letters* 1, 56 (1958)] is incorrect. The error was caused by stray light in the spectrophotometer used in the region below 200 mμ. The authors are grateful to Dr. H. W. Etzel for pointing this out.

undoped crystal grown in oxygen. Obviously, there is an hydroxide absorption band present. (This could be recognized experimentally with certainty, since the hydroxide band narrows on lowering the temperature to 77°K, whereas the oxygen band is unaffected.) Curve (b) is a computed hydroxide absorption band of reasonable absorption, which is subtracted from (a) to give the corrected curve (c). Since there was no *a priori* reason to choose a curve (b) of this particular absorption coefficient, the left-hand side of curve (c) has not been definitely established. Curve (d), referring to a crystal containing calcium, which suppresses the hydroxide absorption,<sup>1</sup> is more reliable in this region.

Infrared absorption measurements were also made on all the crystals used in these experiments. The thickness of the crystals used in these measurements ranged from 1 to 4 cm. Absorption bands of hydroxide, cyanate, cyanide, carbonate, nitrate, and nitrite ions were found in various combinations in the crystals, but no correlation between the intensity of fluorescence and the magnitude of any of these bands could be found. In particular, the infrared absorption of the crystals containing KCN, which had by far the most intense fluorescence, was examined very carefully, using crystal thicknesses between 3 and 4 cm. Hydroxide, carbonate,

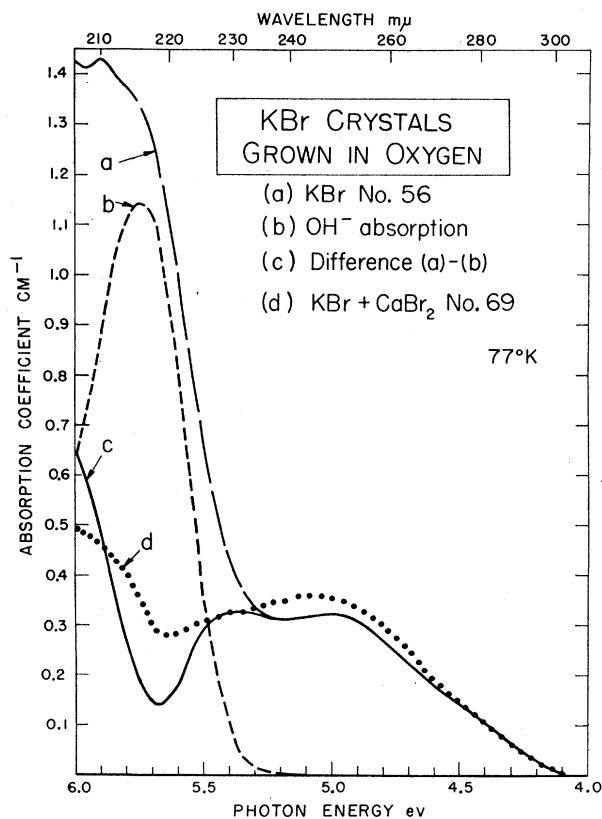


FIG. 3. Absorption spectra of KBr crystals grown in oxygen. Crystal thicknesses: No. 56: 0.733 cm; No. 69: 0.609 cm. Measured at 77°K.

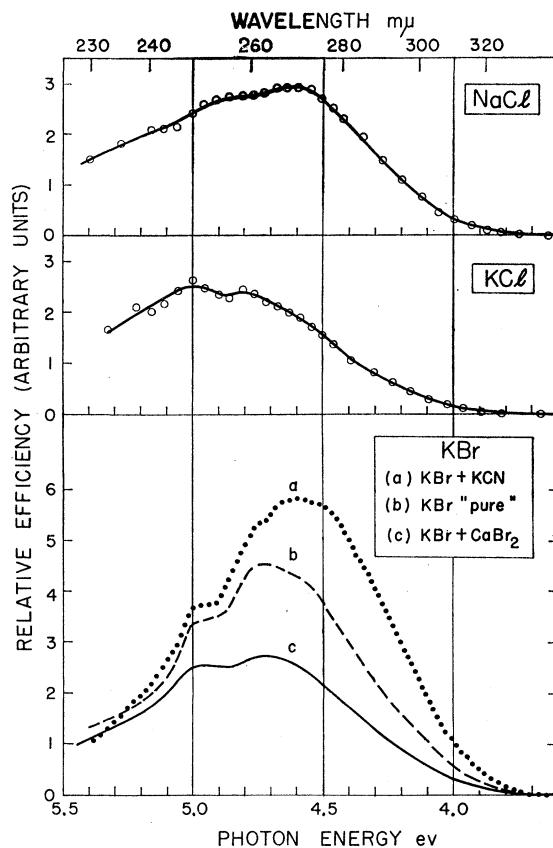


FIG. 4. Fluorescence excitation spectra of NaCl, KCl, and KBr crystals grown in oxygen. Measured at 77°K.

nitrate, and nitrite absorption bands were the only bands present, and were no more intense than those present in feebly fluorescent crystals. It is therefore concluded that there is no infrared absorption in the range 700–4000  $\text{cm}^{-1}$  associated with the presence of fluorescence in the crystals.

#### FLUORESCENCE EXCITATION

Fluorescence excitation spectra obtained at 77°K are presented in Fig. 4. Accurate results could not be obtained at wavelengths lower than 230  $\mu\text{m}$  because the energy in the exciting light at these wavelengths was too small either to stimulate appreciable fluorescence in the crystal or to be accurately measured with the bolometer. The fluorescent efficiency of the absorption peak occurring at wavelengths less than 220  $\mu\text{m}$  (Figs. 1–3) could not, therefore, be measured.

Comparison of Figs. 1–3 and Fig. 4 reveals that while there is a general agreement between fluorescence excitation and absorption spectra, there are other components present in the excitation spectra which do not appear in the absorption spectra. Though excitation could be measured with greater accuracy than absorption, the cause of the discrepancy does not lie in the experimental error of the absorption results. The explanation is that

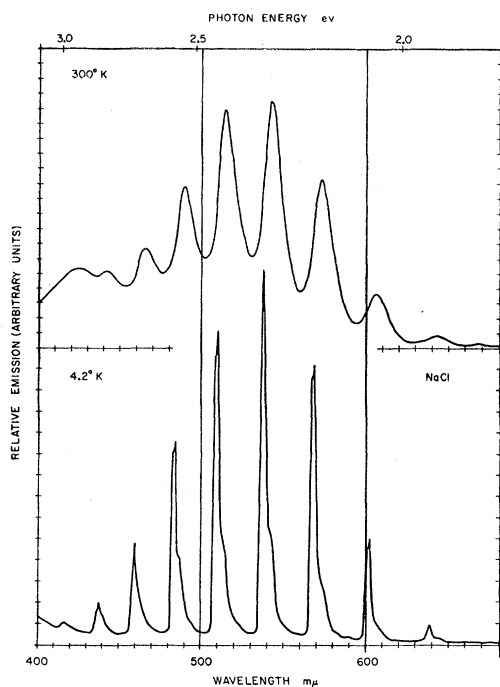


FIG. 5. Fluorescence emission spectra of NaCl crystal grown in oxygen, measured at room temperature and 4.2°K. Recorded with 6256B phototube.

excitation measurements are complicated by energy transfer between different fluorescent systems present in the crystal. The three curves for KBr crystals in Fig. 4 can be used to verify this. The excitation spectrum has at least two components, at 5.0 eV and 4.7 eV, and in curve (a) there is a third component at about 4.6 eV. The component at 5.0 eV is assigned to oxygen, in agree-

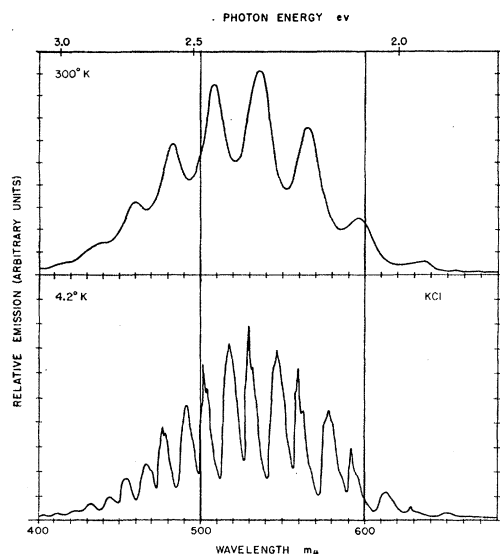


FIG. 6. Fluorescence emission spectra of KCl crystal grown in oxygen, measured at room temperature and 4.2°K. Recorded with 6256B phototube.

TABLE I. Fluorescence emission spectra at 300°K.

NaCl			KCl			KBr		
Wavelength (Å)	Wave No. (cm <sup>-1</sup> )	Diffs. (cm <sup>-1</sup> )	Wavelength (Å)	Wave No. (cm <sup>-1</sup> )	Diffs. (cm <sup>-1</sup> )	Wavelength (Å)	Wave No. (cm <sup>-1</sup> )	Diffs. (cm <sup>-1</sup> )
4213	23 736	989	4194	23 843	1137	4246	23 551	1135
4396	22 747	1093	4404	22 706	1104	4461	22 416	1044
4618	21 654	1083	4629	21 602	1101	4679	21 372	1035
4861	20 571	1063	4854	20 601	1028	4917	20 337	1029
5126	19 508	993	5109	19 573	990	5179	19 308	963
5401	18 515	990	5381	18 583	996	5451	18 345	1002
5706	17 525	1004	5686	17 587	970	5766	17 343	960
6053	16 521	962	6018	16 617	987	6104	16 383	946
6427	15 559	973	6398	15 630	950	6478	15 437	963
6856	14 586	923	6812	14 680	923	6909	14 474	909
7319	13 663	893	7269	13 757	902	7372	13 565	897
7831	12 770	885	7779	12 855	885	7894	12 668	895
8354	11 970	898	8354	11 970	898	8494	11 773	851
9032	11 072	898	9032	11 072	898	9156	10 922	842
9921	10 080	842	9921	10 080	842	9921	10 080	842

ment with the absorption, and the component at 4.7 eV is assigned to cuprous ion impurity. It can be shown by measurements on alkali halide crystals with sensitive fluorescence apparatus that cuprous copper is a common impurity in alkali halide crystals.<sup>6</sup> In well-annealed crystals the copper is mostly precipitated, but may be easily brought into metastable substitutional solution by heating to about 650°C and cooling fairly rapidly. In all alkali halide crystals we have observed, it is then possible to detect copper fluorescence. In KBr the excitation and absorption spectra of cuprous ion (in solution; the precipitated impurity is optically inactive) are identical, with a maximum at 4.69 eV at 77°K. In KCl and NaCl the respective values are 4.78 eV and 4.87 eV. The excitation spectrum of KCl shows a definite component at 4.8 eV, and the existence of a component at 4.9 eV in NaCl is not impossible. In the case of NaCl the 5.0-eV oxygen component and the

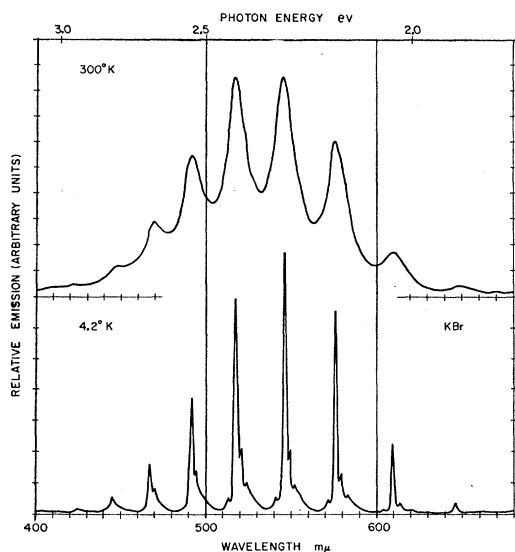


FIG. 7. Fluorescence emission spectra of KBr crystal grown in oxygen, measured at room temperature and 4.2°K. Recorded with 6256B phototube.

4.87-eV cuprous component are close enough together that neither is fully visible.

We are thus led to the conclusion that the system of alkali halide with oxygen and cuprous impurities has an impurity-sensitized luminescence, with copper as sensitizer and oxygen as activator.

The nature of the third component in the excitation curves, which appears at about 4.6 eV for both NaCl and KBr, is not known.

#### FLUORESCENCE EMISSION

Fluorescence emission spectra of NaCl, KCl, and KBr crystals grown in oxygen are shown in Figs. 5-7. Com-

<sup>6</sup> A more detailed report on this subject will be published shortly.

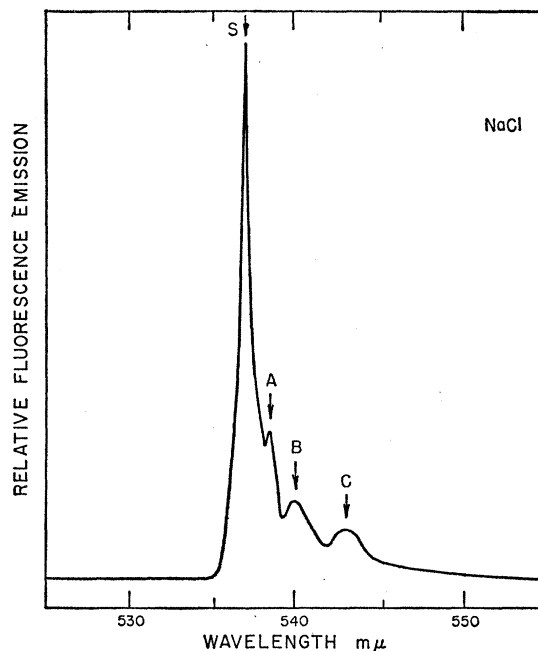


FIG. 8. Portion of the fluorescence emission spectrum of NaCl at 4.2°K, with identification of peaks shown in wavelength tables. Pass band of detection monochromator 1.16 Å.

plete wavelength measurements are presented in Tables I and II. The wavelength scale of the fluorescence apparatus was calibrated with a mercury lamp. The

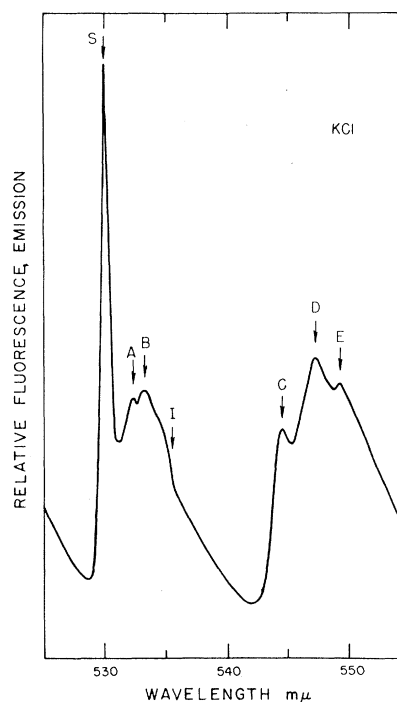


FIG. 9. Portion of the fluorescence emission spectrum of KCl at 4.2°K, with identification of peaks and inflection (I) shown in wavelength tables. Pass band of detection monochromator 0.66 Å.

TABLE II. Fluorescence emission spectra at 4.2°K.

		NaCl															
Peak S (A)	4171	4378	4599	4833	5089	5370	5674	6012	6392	6804	7265	7787	...	...	...	...	...
Peak S (cm <sup>-1</sup> )	23 975	22 841	21 743	20 691	19 650	18 621	17 624	16 633	15 644	14 697	13 765	12 842	...	...	...	...	...
Diff. (cm <sup>-1</sup> )	1134	1098	1052	1041	1029	1029	997	991	989	947	932	923	...	...	...	...	...
Peak A (A)	...	...	4608	4846	5106	5385	...	...	...	...	...	...	...	...	...	...	...
Peak B (A)	...	...	...	4855	5126	5401	...	...	...	...	...	...	...	...	...	...	...
Peak C (A)	...	...	4636	4879	5145	5430	...	6079	...	...	...	...	...	...	...	...	...
		KCl															
Peak S (A)	4154	4336	4546	4777	5026	5300	5598	5927	6294	6696	7146	7651	8222	8875	...	...	...
Peak S (cm <sup>-1</sup> )	24 073	23 062	21 997	20 933	19 896	18 867	17 863	16 871	15 888	14 934	13 994	13 070	12 162	11 268	...	...	...
Diff. (cm <sup>-1</sup> )	1011	1065	1064	1037	1029	1029	1004	992	983	954	940	924	908	812	...	...	...
Peak A (A)	...	4354	4565	4801	5045	5324	5620	5953	6321	6734	7186	7697	8278	...	...	...	...
Peak B (A)	...	...	4575	4812	5057	5334	5638	5971	...	...	...	...	...	...	...	...	...
Inf. I (A)	...	...	4596	4844	5092	5358	5671	6003	...	...	...	...	...	...	...	...	...
Peak C (A)	...	...	4657	4901	5161	5445	5758	6111	6494	6922	7400	7936	8541	9026	...	...	...
Peak D (A)	...	...	4674	4920	5187	5473	5792	6142	...	6961	7443	7986	8603	...	...	...	...
Peak E (A)	4264	4467	4691	4938	5202	5494	5803	6104	...	...	...	...	...	...	...	...	...
		KBr															
Peak S (A)	4234	4432	4651	4888	5145	5428	5735	6078	6453	6870	7328	7848	8434	9102	9861	...	...
Peak S (cm <sup>-1</sup> )	23 618	22 563	21 500	20 458	19 436	18 422	17 437	16 453	15 497	14 556	13 646	12 742	11 857	10 986	10 141	...	...
Diff. (cm <sup>-1</sup> )	1055	1063	1042	1022	1014	1014	985	984	956	941	910	885	871	845	...	...	...
Peak A (A)	...	4404	4621	4854	5115	5392	5694	6033	6403	6821	7276	7786	8364	...	...	...	...
Inf. I (A)	...	...	...	4901	5161	5448	5753	...	...	...	...	...	...	...	...	...	...
Peak B (A)	...	...	4677	4918	5181	5467	5780	6125	6501	6931	7400	7927	8528	...	...	...	...
Peak C (A)	...	...	...	4945	5214	5504	5821	6177	6558	7000	7471	8008	...	...	...	...	...

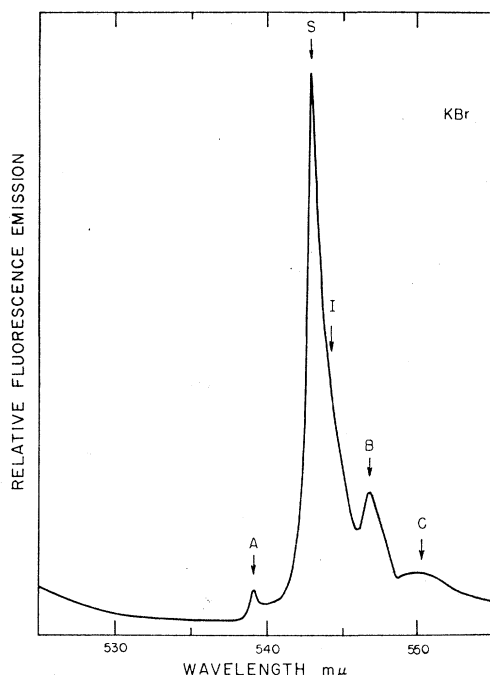


FIG. 10. Portion of the fluorescence emission spectrum of KBr at 4.2°K, with identification of peaks and inflection (I) shown in wavelength tables. Pass band of detection monochromator 0.66 Å.

estimated accuracy of the readings is  $\pm 2$  Å. The experimental traces used for measuring the wavelength of the emission peaks were recorded on a considerably extended wavelength scale compared to Figs. 5-7; examples of the detail visible on a full-scale recording are shown in Figs. 8-10, which show the most intense peaks in the emission spectra at 4.2°K.

At room temperature the emission spectra consist of 8 or 9 peaks, which are almost equally spaced in energy. The separation is about  $1000\text{ cm}^{-1}$ . The apparent decrease in intensity of the peaks towards longer wavelength is due to the falling off in sensitivity of the photocathode of the detecting photomultiplier.

At 4.2°K a great deal of fine structure becomes visible. It is immediately seen that the emission spectrum of KCl is quite different from that of NaCl and KBr. In KCl each peak at room temperature splits into two large peaks each with fine structure, whereas in NaCl and KBr one sharp peak appears, with subsidiary structure developing around it. At 4.2°K the fluorescence is more intense than it is at room temperature, but no measurements have been made on the variation of fluorescence intensity with temperature.

The emission spectra at 77°K are not recorded here, since they do not provide any further useful information. However, the appearance of the emission spectrum of KCl at 77°K provides an indication of how the double structure arises on reducing the temperature from 300° to 4.2°K. At 77°K only peaks S and D (Fig. 9) are resolved, but the intensity of peak D is only one-fifth of

that of S. Thus the double structure arises as the temperature is lowered by the appearance and gradual increase in intensity of the peak system CDE. In NaCl and KBr the change in the spectra when the temperature is lowered is simply due to a narrowing of each individual component until four peaks are visible at 4.2°K.

Attempts were made to observe polarization of fluorescence, at three temperatures, 300°, 77°, and 4.2°K. The exciting light was polarized along the [100] or [110] direction by means of a Glan-Thomson polarizing prism, and the fluorescence emission was analyzed by means of a Polaroid film. No polarization of the fluorescence was observed.

## DISCUSSION

We will discuss the nature of the impurity centers which cause the absorption and fluorescence phenomena described above. (From the general agreement between fluorescence excitation and optical absorption spectra, we assume that absorption and fluorescence are caused by the same center). Although a number of different treatments or impurity additions will cause the fluorescence to develop,<sup>1-3</sup> the common factor is the presence of oxygen. Also, from the structure of the fluorescence emission, we may assume that the oxygen is part of a molecule, with a vibrational frequency of about  $1000\text{ cm}^{-1}$ . However, the oxygen cannot be bound into a molecule with the anion of the crystal, as suggested by Honrath,<sup>2</sup> because the vibrational frequencies of molecules of oxygen with bromine or chlorine differ from each other by about  $150\text{ cm}^{-1}$ , whereas the separation of the fluorescence peaks in KCl and KBr differs only about  $10\text{ cm}^{-1}$ . The absence of any infrared absorption connected with the fluorescence suggests that the center is a symmetrical oxygen molecule, three forms of which are possible:  $\text{O}_2^+$ ,  $\text{O}_2$ , and  $\text{O}_2^-$ . The vibrational frequencies of  $\text{O}_2^+$  and  $\text{O}_2$  are accurately known, and are 1876 and  $1580\text{ cm}^{-1}$ , respectively. The vibrational frequency of  $\text{O}_2^-$  is not known, but an approximate calculation of its value may be made by using Clark's rule.<sup>7</sup> If the internuclear distance of  $\text{O}_2^-$  is taken as  $1.28 \pm 0.02\text{ Å}$ ,<sup>8</sup> the result is  $1260 \pm 70\text{ cm}^{-1}$ . Allowing for the fact that the accuracy of Clark's rule is about  $\pm 5\%$ , and also that the vibrational constants will be slightly different in a molecule in a solid, the agreement with  $1000\text{ cm}^{-1}$  from the fluorescence spectra is reasonable. Thus, from the optical measurements we can tentatively postulate that  $\text{O}_2^-$  is responsible for the absorption and fluorescence.

More direct evidence, however, is available from paramagnetic resonance experiments. Känzig and Cohen,<sup>9</sup> from resonance experiments, have recently

<sup>7</sup> G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), 2nd ed., p. 457.

<sup>8</sup> S. C. Abrahams and J. Kalnajs, *Acta Cryst.* 8, 503 (1955).

<sup>9</sup> W. Känzig and M. H. Cohen, *Phys. Rev. Letters* 3, 509 (1959).

demonstrated that the  $O_2^-$  molecule-ion is present in alkali halide crystals treated with oxygen. Measurements of the resonance signals from portions of crystals used in these experiments were kindly made for us by Känzig, and it was found that the signals increased as the intensity of fluorescence increased. In one case an accurate value for the ratio of signals from the two crystals  $KBr+KCN$  and  $KBr$  "pure," both grown in oxygen, was obtained. The ratio was 7, whereas the ratio of fluorescent intensities, which can be measured more accurately, was 6.6. Thus we assume, from the optical results and the paramagnetic resonance measurements, that the center responsible for the absorption and fluorescence is an  $O_2^-$  molecule-ion substituted for a halide ion in the crystal, aligned along the  $\langle 110 \rangle$  directions, as found by Känzig and Cohen.

Some of the results are more difficult to explain, however. One would expect that some polarization of fluorescence would be observed at 4.2°K. However, the local temperature in the vicinity of the excited  $O_2^-$  molecule-ion may be quite high, since a rather large

Stokes shift (2.5 eV) is observed. Perhaps half the energy, over 1.2 eV, may be given off as phonons before the center emits. This process may destroy any polarization.<sup>10</sup> Also, there is no other evidence to account for the fact that the fluorescence emission of  $KCl$  at 4.2°K has a quite different structure from the other two alkali halides  $NaCl$  and  $KBr$ . Finally, the very small absorption coefficients associated with oxygen might be due either to forbidden electronic transitions, or to the fact that the observed band is actually a subsidiary band, the main band lying in wavelength regions beyond our limits of measurement.

#### ACKNOWLEDGMENTS

The authors wish to thank Dr. W. Känzig for his measurements of the paramagnetic resonance signals, R. Boulet for growing all the crystals used in the experiments, and Dr. J. H. Simpson for guidance and encouragement throughout the course of the experiments.

<sup>10</sup> We are indebted to the referee for this suggestion.

## Galvanomagnetic Effects in Semiconductors at High Electric Fields

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(Received March 13, 1961)

A treatment of magnetoconductivity is developed for high electric fields and general energy-band structure using a partial solution of the Boltzmann equation in a form similar to that set up by McClure for low electric fields. The present treatment is valid when the scattering processes are such that the distribution function varies but a small amount over an entire constant-energy surface, or, in the case of the many-valley band structure, over the part of a constant-energy surface within each valley. In the latter case, different distribution functions must be used for the different valleys. The elements of the magnetoconductivity matrix that results are expressed in terms of carrier concentration, total or within each valley, and averages over the carriers of a quantity involving the momentum relaxation time and the  $S$  tensor defined by McClure. This tensor, which depends on the shape of the constant-energy surfaces and on the magnetic-field strength, is evaluated for the individual valleys in a nondegenerate many-valley semiconductor. The magnetoconductivity matrix is then in a form convenient for calculation of conductivity and galvanomagnetic effects for either low or high electric fields. It is used to obtain expressions for anisotropy voltage and Hall coefficient in high electric fields involving the number of carriers in each valley, orientation of the valleys, and valley averages over quantities involving relaxation time and energy.

### I. INTRODUCTION

IN connection with many of the investigations of conductivity in high electric fields, the Hall effect has been of interest because of the possibility of change in carrier concentration due to impact ionization or other processes. It has become apparent, however, that the Hall coefficient  $R$ , measured with due care, may change in high electric fields even though carrier concentration does not. The change in the distribution function, which is the basis of the so-called hot carrier effects, can itself

cause a change in  $R$ .<sup>1</sup> Changes in the band structure, such as change in curvature of energy vs crystal momentum, as the carriers move to higher energy states can also cause a change in  $R$ . This seems to be a sizeable effect in  $p$ -germanium<sup>2</sup> where the curvature of the light-

<sup>1</sup> For a calculation of the change in Hall coefficient with electric field, under the assumption that scattering is by acoustic modes only, see M. S. Sodha and P. C. Eastman, *Phys. Rev.* **110**, 1314 (1958).

<sup>2</sup> J. Zucker and E. M. Conwell, *Bull. Am. Phys. Soc.* **4**, 185 (1959).