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# Optical Absorption of $Cl_2^-$ Molecule-Ions in Irradiated Potassium Chloride*

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Pure KCl, KCl-Ag, KCl-Tl, and KCl-Pb, after x-ray irradiation at liquid nitrogen temperature, show identical $Cl_2^-$ paramagnetic resonance spectra. The optical absorption of the $Cl_2^-$ molecule-ion has been identified and is found to consist of two bands, one at 365 mμ and one at 750 mμ. This identification was made possible by bleaching irradiated samples with polarized light and observing the effects on the optical and also the paramagnetic resonance spectra. It was possible to reorient the $Cl_2^-$ molecule-ions such that a large fraction of them were in only one of the six possible ⟨110⟩ directions.

## INTRODUCTION

KÄNZIG[1] and Castner and Känzig[2] have reported $V$-center type paramagnetic resonance spectra in pure potassium chloride crystals which have been heavily irradiated with x-rays at liquid nitrogen temperature. They have identified the species giving rise to the resonance as $Cl_2^-$ molecule-ions.

Delbecq, Smaller, and Yuster[3,4] have observed the identical $Cl_2^-$ resonance spectra in KCl-Tl, KCl-Ag, and KCl-Pb crystals which have been weakly irradiated with x-rays at liquid nitrogen temperature.

Since the $V_1$ band[5] in the optical absorption spectrum disappears in the same temperature range as the $Cl_2^-$ resonance absorption in pure KCl, there has been some speculation[2] that the $V_1$ band is an optical absorption band of the $Cl_2^-$ molecule-ions; however, no positive correlation has been reported. This investigation was undertaken, using both optical absorption and paramagnetic resonance absorption measurements, to determine the optical absorption of $Cl_2^-$ molecule-ions in potassium chloride crystals.

## Experimental Procedures

The electron spin resonance detection system used is the same as that described previously[6] except for two modifications. The dual modulation system was modified to operate at 25 cps and 17 kc/sec. In addition, the method of holding the sample was changed to allow orientation of the crystal in the magnetic field. The crystal was mounted on the end of a Lucite rod, the axis of which could be tipped with respect to the magnetic field. The crystal could be further oriented by rotation about this axis as indicated by a pointer at the top of the rod.

Some of the pure KCl single crystals used in these experiments were obtained from the Harshaw Chemical Company. Other single crystals of pure KCl as well as the single crystals of KCl containing either $Tl^+$, $Ag^+$, or $Pb^{++}$ were grown in this laboratory using the Kyropoulos method. In general, the crystals used for optical absorption measurements were 12×7×1 mm, and those used for electron spin resonance measurements were 2.5×2.5×10 mm. The crystals were irradiated with x-rays produced in a Machlett tube operating at 50 kv and 50 ma, and filtered through 1 mm of quartz.

Polarized light was obtained by using an Ahrens or Glan-Thompson prism. The prism was mounted on the Dewar flask used to hold the crystal. The axis of the prism was oriented parallel to one of the cubic axes of the crystal; the prism could be rotated about its axis so that the electric vector of the transmitted polarized light made any desired angle with the other two cubic axes of the crystal. Absorption spectra were taken using, in general, polarized light with the electric vector oriented in either the $[0\bar{1}1]$ or the $[011]$ direction, the light from the monochromator passing through the polarizing prism and then through the crystal to the detector. In bleaching a crystal with polarized light, the light from an AH-6 mercury lamp was passed through an appropriate filter combination and then through a polarizing prism before impinging upon the crystal; in most bleaching experiments, polarized light with the electric vector oriented in the $[0\bar{1}1]$ direction was used. Bleaching of samples used in electron spin resonance measurements was done while the crystal, mounted on a Lucite holder, was immersed in a Dewar flask filled with liquid nitrogen; the polarized bleaching light entered the Dewar flask through quartz windows.

## EXPERIMENTAL RESULTS

Figure 1 shows the absorption spectrum of a crystal of pure potassium chloride which had been exposed to x-rays for four hours at liquid nitrogen temperature. The well-known $V_2$(235 mμ), $V_1$(350 mμ), and $F$(540 mμ) bands are observed. The intensity of the $F$ band was so great that the absorption could not be measured at the center of the band. The $F'$ band is also observed as a

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[1] W. Känzig, Phys. Rev. **99**, 1890 (1955).

[2] T. Castner and W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957).

[3] Delbecq, Smaller, and Yuster, Color Center Symposium at Argonne National Laboratory, 1956 (unpublished).

[4] Yuster, Delbecq, and Smaller, Bull. Am. Phys. Soc. Ser. II, **2**, 302 (1957).

[5] Casler, Pringsheim, and Yuster, J. Chem. Phys. **18**, 1564 (1950); F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

[6] Delbecq, Smaller, and Yuster, Phys. Rev. **104**, 599 (1956).

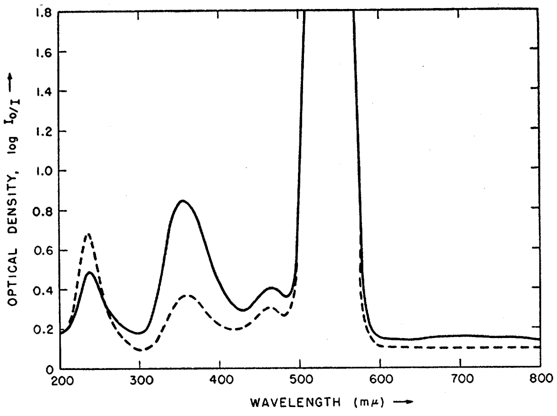

FIG. 1. Absorption spectra of Argonne grown "pure" KCl: —— after 4 hours x-ray irradiation at liquid nitrogen temperature, – – – after warming to −155°C for 2 minutes and remeasurement at liquid nitrogen temperature.

broad absorption to the long-wavelength side of the *F* band. Figure 2 shows the absorption spectra of irradiated KCl-Tl, KCl-Ag, and KCl-Pb crystals. It will be noted that in each case there is an absorption band at about 365 mμ and that the x-ray dosage needed to obtain equivalent absorption intensity in this region of the spectrum in these three crystals is a good deal less than that needed in the pure potassium chloride. All of the above-mentioned irradiated crystals (pure KCl, KCl-Tl, KCl-Ag, and KCl-Pb) show identical $Cl_2^-$ electron spin resonance spectra. In order to compare the thermal stability of the $V_1$ center and the $Cl_2^-$ molecule-ion in pure potassium chloride, pulse annealing experiments were carried out in which the optical absorption of the $V_1$ band and the resonance intensity of $Cl_2^-$ were followed as functions of annealing temperature. In both cases the crystals were held at liquid nitrogen temperature for measurement, warmed rapidly to the desired annealing temperature, held at this temperature for two minutes, and then cooled to liquid nitrogen temperature for remeasurement. It is quite clear from Fig. 3 that the optical absorption of the $V_1$ band and the spin resonance of $Cl_2^-$ have their maximum decay rates at appreciably different temperatures. The thermal stabilities are sufficiently different that holding the crystal at −155°C for a period of time causes the $V_1$ band to disappear while leaving the intensity of the $Cl_2^-$ resonance essentially unchanged. Warming the crystal again to −155°C causes little change in the intensity of the $Cl_2^-$ resonance; this result indicates that the decay of $V_1$ centers does not result in the formation of $Cl_2^-$ centers.

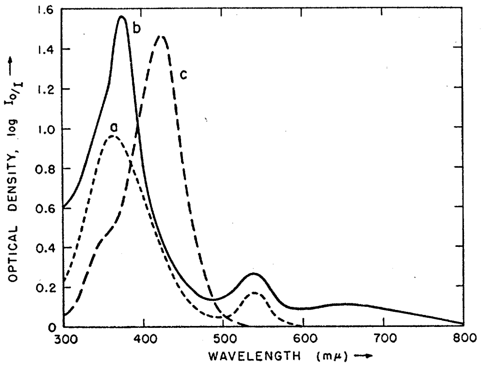

FIG. 2. Absorption spectra after x-ray irradiation at liquid nitrogen temperature. (a) KCl-Pb, 10-min x-ray, (b) KCl-Tl, 10-min x-ray, (c) KCl-Ag, ½-min x-ray.

Another method used to check the correlation between the $V_1$ center and the $Cl_2^-$ molecule-ion was the comparison of the intensity of the $Cl_2^-$ resonance for equal optical absorption in the region of the $V_1$ band for pure KCl and for KCl containing either $Tl^+$, $Ag^+$, or $Pb^{++}$. Since in the case of irradiated KCl-Pb crystals the absorption band at 365 mμ is relatively free from overlapping neighboring absorption bands, KCl-Pb was chosen to be used as comparison with pure KCl. These two crystals were irradiated such that the intensity of the absorption in the region of the $V_1$ band was the same in both crystals, and then the intensity of the $Cl_2^-$ resonance was measured in each. The intensity of the $Cl_2^-$ resonance was ten times greater in the KCl-Pb crystal. This result, as well as the results of the thermal annealing experiment, shows that the $V_1$ band is not an absorption band of the $Cl_2^-$ molecule ion.

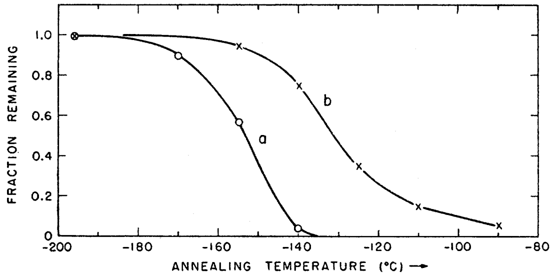

FIG. 3. Fraction of (a) $V_1$ absorption, and (b) $Cl_2^-$ electron spin resonance absorption remaining after pulse anneal, plotted as a function of annealing temperature.

Castner and Känzig[2] have shown that the $Cl_2^-$ molecule-ions are oriented in the six ⟨110⟩ directions of the KCl crystal. It therefore might be possible with the use of polarized light to bleach preferentially those $Cl_2^-$ molecule-ions having certain orientations. Ueta[7] has already shown that it is possible to obtain such anisotropic bleaching in the case of *M* centers in KCl.

If we let the faces of a cube be parallel to the (001), (010), and (100) planes of a KCl lattice, then the face diagonals indicate the six possible orientations of the $Cl_2^-$ center in the lattice. It is possible that bleaching a crystal containing $Cl_2^-$ centers with $[0\bar{1}1]$ polarized light[8] of the appropriate wavelength will excite all $Cl_2^-$

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[7] M. Ueta, J. Phys. Soc. Japan 7, 107 (1952).

[8] $[0\bar{1}1]$ polarized light indicates polarized light with the electric vector oriented parallel to $[0\bar{1}1]$ in an alkali halide lattice.

centers except those oriented in [011]. The result of such an excitation might be that the number of $\mathrm{Cl}_2^-$ centers oriented in [011] remains constant and that the number of $\mathrm{Cl}_2^-$ centers in the other five orientations will decrease; or, if the excited $\mathrm{Cl}_2^-$ center is not very mobile and loses its excitation energy before annihilation, there will be a reorientation of the $\mathrm{Cl}_2^-$ centers into [011] from the other five directions. Since the intensity of the $\mathrm{Cl}_2^-$ resonance obtained upon irradiation is greatest in the case of the crystals with added impurities, it was convenient to do most of the polarized light experiments with these crystals rather than with pure KCl. After x-ray irradiation, the optical absorption of these crystals was measured with [011] and also $[0\bar{1}1]$ polarized light. No absorption measurements were made at wavelengths lower than 290 mμ because of the high absorption of the polarizing prism at lower wavelengths. Bleaching with light was usually done with $[0\bar{1}1]$ polarized light. After bleaching, the absorption of the crystals was again measured with [011] as well as $[0\bar{1}1]$ polarized light. Figure 4 shows the results of such a bleaching experiment carried out at liquid nitrogen temperature on a KCl-Pb crystal. The curve labeled [011], $[0\bar{1}1]$ shows the absorption spectrum taken immediately after x-ray irradiation; the absorption spectrum is the same whether taken with [011] or $[0\bar{1}1]$ polarized light. The effect of bleaching with $[0\bar{1}1]$ polarized light (436 mμ) is shown by the upper and lower curves. The absorption spectrum taken with [011] polarized light shows the 365-mμ band to be increased by over a factor of 2 while the spectrum taken with $[0\bar{1}1]$ polarized light shows the 365-mμ band to be decreased by more than a factor of 5. These results show that, although there may have been some "real bleaching" due to recombination of electrons and holes, the principal effect of this bleach with $[0\bar{1}1]$ polarized light is to cause a reorientation of a very large fraction of the centers such that the dipole moment associated with the transition giving rise to the 365-mμ band is parallel to either [011] or [111]. That the dipole moment is oriented in the [011] direction is shown by the fact that bleaching with [001] polarized light in the 365-mμ band produces a dichroism in this band, as observed in the absorption spectrum taken with [001] and [010] polarized light.

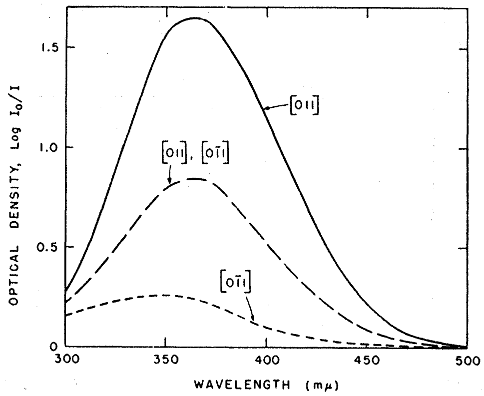

FIG. 4. Absorption spectra of KCl-Pb (a) after 10-min x-ray irradiation at liquid nitrogen temperature as measured with either [011] or $[0\bar{1}1]$ polarized light; and then after bleaching with $[0\bar{1}1]$ polarized light (436 mμ) as measured with (b) [011] polarized light, and (c) $[0\bar{1}1]$ polarized light.

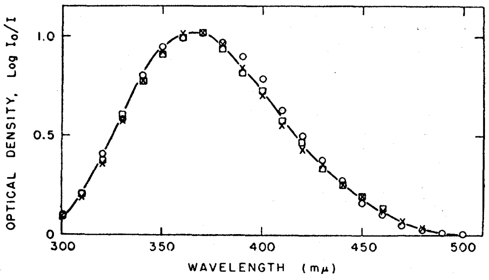

FIG. 5. Subtraction curves, after normalization to give the same peak optical density, for ○ KCl-Pb, × KCl-Ag, and □ KCl-Tl, showing dichroism introduced by bleaching with $[0\bar{1}1]$ polarized light absorbed by the 365-mμ band.

If the $[0\bar{1}1]$ absorption is subtracted from the [011] absorption, the absorption spectrum obtained is due to those centers which bleach in an anisotropic manner. Any center which shows no anisotropy contributes the same absorption to both the [011] and the $[0\bar{1}1]$ absorptions and therefore is eliminated in a subtraction. Figure 5 shows the subtraction curve not only for irradiated KCl-Pb but also for KCl-Ag and KCl-Tl obtained in the same manner; the data were normalized to give the same optical density at the peak in each case. These subtraction curves, after normalization, are identical within experimental error, indicating that a common species gives rise to the absorption band in each of these crystals.

The final proof that the $\mathrm{Cl}_2^-$ centers give rise to the 365-mμ band rests on a correlation of the optical bleaching experiments with changes in the resonance spectra. A crystal of KCl-Pb was irradiated with x-rays at liquid nitrogen temperature so that the $\mathrm{Cl}_2^-$ resonance was readily observed. With $\mathrm{Cl}_2^-$ centers distributed at random among the six $\langle 110\rangle$ directions and with the magnetic field parallel to [011], a resonance spectrum similar to that shown in Fig. 6(A) is observed. As pointed out by Castner and Känzig,[2] this spectrum consists of three basic patterns—0°, 60°, and 90° (the angle indicated is that between the magnetic field and the molecular axis). Figure 6(B) shows the resonance spectrum after the crystal had been exposed to $[0\bar{1}1]$ polarized light absorbed in the 365-mμ band. The 0° pattern has been enhanced considerably after such a bleach (the ratio of the intensity of the 0° pattern to that of the 60° pattern has changed by a factor of 16), and therefore a large fraction of the $\mathrm{Cl}_2^-$ centers have been reoriented such that the molecular axis is parallel to [011]. The correlation between the behaviors of the

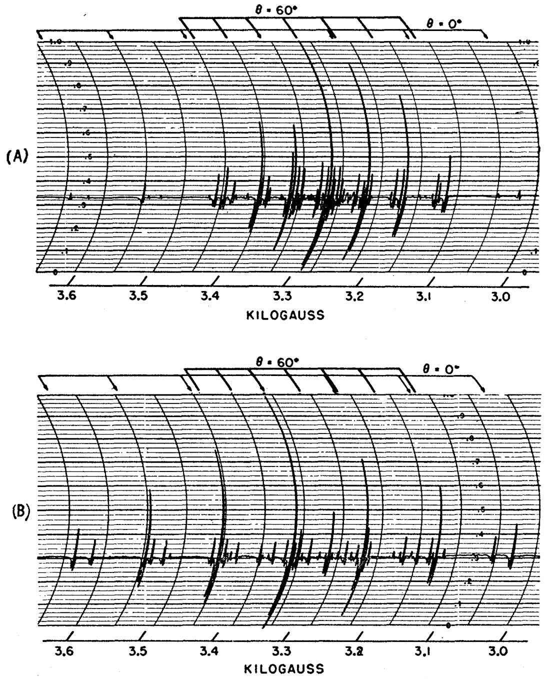

FIG. 6. Electron spin resonance spectrum ($H\|[011]$) of a KCl-Pb (A) immediately after x-raying at liquid nitrogen temperature, and (B) after bleaching with $[0\bar{1}1]$ polarized light absorbed by the 365-mμ band.

365-mμ band and the $Cl_2^-$ resonance spectrum shows that the $Cl_2^-$ centers give rise to the 365-mμ absorption band. It can be further concluded that the dipole moment associated with the transition giving rise to the 365-mμ band is oriented parallel to the molecular axis of the $Cl_2^-$ center.

Theory[9,2] predicts that the $Cl_2^-$ molecule-ion has, in addition to the absorption in the ultraviolet, two absorptions at longer wavelengths. A weak absorption band associated with $Cl_2^-$ centers and having about 1/60 of the intensity of the band in the ultraviolet was found with peak at 750 mμ (Fig. 7). Both KCl-Ag and KCl-Pb after x-irradiation at liquid nitrogen temperature show this peak in the red; however, in the case of KCl-Tl the absorption due to the trapped electron is sufficiently intense in this region that it masks the long wavelength absorption of the $Cl_2^-$ center. Upon bleaching a KCl-Pb or a KCl-Ag crystal which contains $Cl_2^-$ centers with $[0\bar{1}1]$ polarized light in the 750-mμ band, no dichroism is produced in the crystal. However, that this long-wavelength absorption band is associated with $Cl_2^-$ centers is shown by the following experiment. After a KCl-Pb or a KCl-Ag crystal which contains $Cl_2^-$ centers is bleached with polarized light absorbed in the 365-mμ band so as to produce a dichroism in that band, it is found that subsequent bleaching with light absorbed in the 750-mμ band causes the dichroism to disappear. It should be pointed out at this time that the stimulation peaks[3] in the infrared, observed in KCl-Tl crystals after x-ray irradiation at liquid nitrogen temperature, cannot be associated with $Cl_2^-$ centers as suggested by Castner and Känzig,[2] since these stimulation peaks are still present after all the $Cl_2^-$ centers have been destroyed.

The $V_1$ band in pure KCl was also bleached with polarized light in experiments similar to those performed on the 365-mμ band. Only a very slight anisotropy occurred in bleaching with either [001] or $[0\bar{1}1]$ polarized light. It is quite clear that the behavior of the $V_1$ band is not the same as that of the 365-mμ band. However, the slight anisotropy which developed on bleaching showed optical properties in the ultraviolet and infrared characteristic of $Cl_2^-$. The intensity of this anisotropic absorption was about that expected from the intensity of $Cl_2^-$ as measured in paramagnetic resonance on a similar sample. It appears that the absorption in this region of the spectrum consists of two bands, the major absorption being due to $V_1$ centers and another smaller absorption being due to $Cl_2^-$ centers. In irradiated pure KCl, the $Cl_2^-$ centers represent only a small fraction of the hole centers formed, while in the case of the irradiated doped crystals it is believed that the $Cl_2^-$ centers account for essentially all of the hole centers.

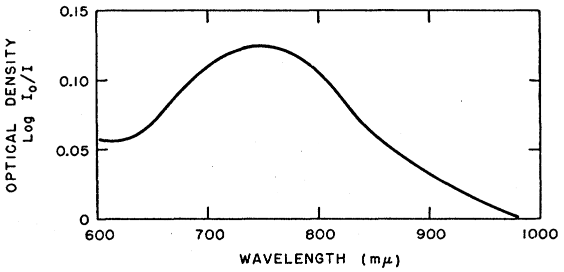

FIG. 7. 750-mμ band absorption introduced into KCl-Ag by 2 hours x-ray irradiation at liquid nitrogen temperature.

Upon x-raying a KCl-Tl, KCl-Pb, or KCl-Ag crystal at liquid helium temperature, it is found that $Cl_2^-$ centers are formed just as rapidly as at liquid nitrogen temperature. In addition, the 365- and 750-mμ $Cl_2^-$ bands, when exposed to polarized light, behave the same at liquid helium temperature as at liquid nitrogen temperature.

Additional information was obtained through a study of the thermal stability of the $Cl_2^-$ center. Upon pulse annealing a crystal of KCl-Ag, KCl-Pb, or KCl-Tl which contains preferentially oriented $Cl_2^-$ centers, it is observed that the dichroism begins to disappear at about −100°C; at this temperature the $Cl_2^-$ centers are just beginning to move through the lattice at an appreciable rate and as a result of the jumping lose their preferred orientation. However, it is believed that at −100°C the $Cl_2^-$ center does not move very rapidly

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[9] M. H. Cohen, Phys. Rev. **101**, 1432 (1956); Inui, Harasawa, and Obata, J. Phys. Soc. Japan **11**, 612 (1956).

through the crystal, since no appreciable decrease in the concentration of $Cl_2^-$ centers is observed until about $-70$°C. It is observed that the maxima in the rates of decay of both the $Cl_2^-$ resonance and the 365-m$\mu$ band occur at about $-65$°C in KCl-Ag or KCl-Tl, and at $-55$°C in KCl-Pb. At the same temperature at which the $Cl_2^-$ centers disappear, a glow peak[10] is observed; the spectral distribution of the luminescence depends on the impurity present in the crystal ($Tl^+$, $Ag^+$, $Pb^{++}$). It is believed that these impurity ions emit as a result of the recombination of trapped electrons with wandering $Cl_2^-$ centers.

## DISCUSSION

Three different types of experiments reported above show that the $V_1$ band is not the optical absorption of $Cl_2^-$ molecule-ions. (1) The $V_1$ band and $Cl_2^-$ resonance in pure KCl do not decay at the same temperature. (2) The intensity of the $Cl_2^-$ resonance absorption is not proportional to the intensity of the $V_1$ band. (3) The $V_1$ band does not bleach in an anisotropic manner with $[0\bar{1}1]$ or [001] polarized light. This last result is in agreement with those obtained by Lambe and West.[11]

Castner and Känzig[2] have pointed out that two models which would be consistent with the $Cl_2^-$ resonance absorption observed in pure KCl are (1) $Cl_2^-$ with no vacancies, (2) $Cl_2^-$ with two positive-ion vacancies. Their conclusion, as well as ours, is that in the case of KCl crystals with added impurities it is highly unlikely that the rate of production of positive-ion vacancies could be as great as the observed rate of production of $Cl_2^-$ centers, and therefore the two-vacancy model is improbable. Also we have found that the rate of production of $Cl_2^-$ is essentially the same at liquid helium temperature as it is at liquid nitrogen temperature, which fact also refutes the two-positive-ion vacancy model. The bleaching experiments with polarized light show perhaps as well as any of the other experiments that vacancies are not involved. In order for a reorientation to take place, if two positive-ion vacancies are associated with the $Cl_2^-$, it is necessary (a) that there be many other pairs of positive-ion vacancies that have no $Cl_2^-$ attached or (b) that the pair of positive-ion vacancies reorient as well as the $Cl_2^-$. The first alternative would require an exceedingly large concentration of pairs of positive-ion vacancies, while the second would require the movement of positive-ion vacancies at liquid helium temperature due to excitation with 750-m$\mu$ light; both of these possibilities seem unlikely. In the case of $Cl_2^-$ molecule-ions formed in the potassium chloride crystals containing added impurities, there is another possible model—a $Cl_2^-$ with an impurity associated with it. Since the resonance spectra are all identical, it means that the electric fields closely surrounding the $Cl_2^-$ are very similar. It is possible that $Ag^+$ and $Tl^+$ have electric fields which are so similar to $K^+$ that their presence cannot be detected in the resonance spectra. However, in the case of KCl-Pb this possibility does not seem likely, since lead is believed to be present as a divalent ion. Whether or not the vacancy which enters the crystal along with the lead is directly associated with the $Pb^{++}$, the neighborhood of the $Cl_2^-$ should probably be sufficiently distorted to affect the electron spin resonance spectrum. Since no difference is observed, it is concluded that the $Cl_2^-$ has no impurities as nearest neighbors.[12]

Two other sets of experimental data, (1) that the optical absorption of $Cl_2^-$ is the same in KCl-Ag, KCl-Tl, and KCl-Pb, and (2) that $Cl_2^-$ molecule ions begin to move through the lattice at the same temperature in the doped crystals, indicate further that the $Cl_2^-$ molecule ions are located in regions in the lattice characteristic of pure KCl and not influenced by the added impurities.

The experimental facts that the maximum rate of disappearance of the $Cl_2^-$ molecule-ion occurs at $-140$°C in pure KCl, at $-65$°C in KCl-Tl and KCl-Ag, and at $-55$°C in KCl-Pb appear to be inconsistent with the conclusion that the $Cl_2^-$ molecule-ion has no impurities as nearest neighbors. The following is offered tentatively as an explanation for these differences. Since the reorientation experiments show that $Cl_2^-$ begins to move through the lattice at the same temperature in KCl-Pb, KCl-Tl, and KCl-Ag, it is suggested that the difference in decay temperature in KCl-Pb is not because of a difference in the $Cl_2^-$ but rather a difference in the retrapping and recombination processes involving the mobile $Cl_2^-$. No successful reorientation experiments have been performed on pure potassium chloride because of the low concentration of $Cl_2^-$ centers; consequently no reorientation temperature has been measured. Nevertheless, it is believed that in pure KCl, the $Cl_2^-$ molecule-ion does not have mobility at $-140$°C but is destroyed by some electron which is released at this temperature.

The changes in the $Cl_2^-$ resonance absorption spectrum along with the changes in the optical absorption spectrum, which are produced by irradiation with polarized light, show that the $Cl_2^-$ molecule-ion has two optical absorption bands with peaks at 365 m$\mu$ and 750 m$\mu$. Absorption of light in either of these two bands leads to an excited state from which a $Cl_2^-$ molecule-ion reforms, oriented at random in one of the six $\langle 110 \rangle$ directions in the crystal. The result that very little real bleaching occurs after excitation suggests

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[10] These glow peaks and the processes which take place at higher temperatures will be the subject of a later paper.

[11] J. Lambe and E. J. West, Phys. Rev. **108**, 634 (1957).

[12] In irradiated KCl-Ag, electron spin resonance spectra have been observed which arise from the presence of a hole trapped at $Ag^+$ and also from an electron trapped at $Ag^+(Ag^0)$. These results will be included in a later paper.

that the $Cl_2^-$ molecule-ion reforms very close to its original neighborhood. Therefore, when a potassium chloride crystal is irradiated with x-rays at liquid nitrogen temperature, it seems likely that a positive hole which has been created moves only a very short distance before forming a $Cl_2^-$ molecule-ion. Since the rate of formation of positive holes by x-ray irradiation should be the same in pure potassium chloride as in doped potassium chloride, $Cl_2^-$ molecule-ions should be formed at the same rate in each of these crystals; yet it is observed that the net rate of formation of $Cl_2^-$ centers is from 100 to 1000 times greater in the case of the doped crystals. It is believed that the added impurities act as very efficient electron traps,[12] decreasing the rate of recombination of electrons and positive holes, while in the pure crystals electron traps must be created slowly by the irradiation and consequently the recombination rate is much greater.

### ACKNOWLEDGMENTS

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# Control of Luminescence by Charge Extraction*

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(Received May 14, 1958)

It has been discovered that the application of a potential of a few volts to phosphors of the ZnS group can quench the fluorescence. The effect has been observed in single-crystal and recrystallized wafers of the phosphors by illuminating one side with nonpenetrating light and applying a field, through suitable contacts, normal to the illuminated surface. With the illuminated surface negative, the fluorescence is reduced by an amount dependent on the voltage for as long as the voltage is maintained, and total extinction can often be obtained. The luminescent output follows variations in the applied voltage up to a maximum frequency which depends on the fluorescence time constant.

The effect is shown to be a fundamental property of phosphor materials possessing large differences in hole and electron mobilities or capture cross section. It is explained in terms of a decrease in the excess electron density due to the extraction of holes from the illuminated surface by the field. A simple mathematical theory is proposed which accounts in detail for the observed effects and which predicts current-voltage relationships which have been confirmed experimentally.

## I. INTRODUCTION

IN the literature on phosphors there are many reports on effects of applying an electric field to photoluminescent materials. These include the Gudden-Pohl effect[1] (the transient stimulation of luminescence), Dechene's[2] experiment on the quenching of luminescence with a high field, and the Destriau[3] effect of stimulation of luminescence by an alternating field. Halsted[4] has observed modulation of fluorescence by an alternating field and explained the effect by assuming that the optically created hole-electron pairs are first separated and then brought back together under the influence of the field. These, and a number of less clearly defined effects have been reviewed recently in an article by Ivey.[5]

The purpose of this paper is to describe a new electrophotoluminescent effect and to propose an explanation for it. The effect is unusual in that dc as well as ac fields can be used, that these fields are very low, and that the effect produced can be very large, almost complete extinction or significant stimulation of fluorescence being obtained depending on the direction of the field.

In Sec. II the experimental arrangements are described. In Sec. III experiments are described which essentially repeat those of Halsted except that single-crystal phosphor material was used instead of a phosphor powder in a dielectric matrix. This allowed the field modulation effect to be studied in a more controlled manner. The results observed when a transparent conducting coating is placed in direct contact with the single crystals (and also with sintered layers of phosphor material) are described in Sec. IV and the interpretation of these results is discussed. A mathematical description of the observed effects is presented in an Appendix.

## II. EXPERIMENTAL METHOD

In the majority of experiments, wafers of single-crystal cadmium sulfide were used. These were activated by heating in the presence of cupric chloride and

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* The work described here was supported in part by the BuShips.

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[5] H. F. Ivey, J. Electrochem. Soc. **104**, 740 (1957).