

Paramagnetic Resonance and Optical Absorption of a V Center*

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The paramagnetic resonance and optical absorption spectra of KCl and KBr crystals containing divalent calcium, strontium or barium ions have been investigated. After x-irradiation at 195°K a resonance spectrum is observed with three distinguishable centers; the centers are similar and each has approximate axial symmetry about a different cube edge. The optical spectra show bands near 325 $m\mu$ in KCl and near 345 $m\mu$ in KBr which arise from the same centers. The centers are assigned to Cl_2^- and Br_2^- molecule ions and are closely related to the Cl_2^- and Br_2^- centers of Castner and Känzig.

INTRODUCTION

THE application of electron spin resonance techniques to the study of V centers in alkali halides has resulted in accurate descriptions of the structure of these centers.¹⁻³ V centers may be defined as trapped positive holes. It has been shown that when crystals of KCl, NaCl, KBr, or LiF which are pure or doped with Ag, Tl, or Pb ions, are x-irradiated at 77°K, complex electron spin resonance spectra are observed which may be assigned to the molecule ions Cl_2^- , Br_2^- , and F_2^- (henceforth referred to in general as X_2^-). The optical absorption spectra of these defects have been investigated and correlated with their resonance spectra.^{3,4}

In the resonance spectrum of X_2^- the hole is localized on two halogen nuclei and an extensive anisotropic hfs is observed due to the interaction of the unpaired electron with these nuclei. An investigation of this structure¹ showed that the molecule ion is accurately aligned along a $[110]$ axis of the crystal [Fig. 1(a)]. The symmetry of the center is orthorhombic with two face diagonals and a cube edge as principal axes; six such combinations of axes are possible and there are six distinguishable centers in the magnetic unit cell. In the case of Cl_2^- a seven line hfs is observed when the magnetic field is parallel to the axis of the molecule ion, with intensities in the ratios 1:2:3:4:3:2:1. This structure arises because the chlorine nuclei are equivalent and each has a spin of $\frac{3}{2}$ so that the magnetic spin quantum number $m(I) = m(I_1) + m(I_2)$ can take the values $-3, -2, -1, 0, 1, 2, 3$ weighted according to the above intensity ratios. The isotopes ^{35}Cl and ^{37}Cl occur in the ratio 3:1 and have slightly different nuclear moments so that three sets of spectra are resolved with intensities in the ratios 9:6:1 corresponding to the isotopic species 35-35, 35-37, 37-37. When the mag-

netic field is perpendicular to the axis of the ion, the hfs is considerably collapsed and the degeneracy of the hyperfine lines is raised by second-order hyperfine and quadrupole effects. In the case of Br_2^- a spectrum with similar properties is found. Bromine has two equally abundant isotopes, ^{79}Br and ^{81}Br , each with a nuclear spin of $\frac{3}{2}$; three sets of spectra are resolved with intensities in the ratios 1:2:1 arising from the isotopic species 79-79, 79-81, and 81-81.

The correlation of the optical and resonance spectra may be achieved³ by

- (a) Comparing the variation of intensities of the spectra with irradiation time.
- (b) Observing the effect of bleaching in the optical absorption band with polarized light.

In the case of Cl_2^- , for example, an optical absorption band occurs at 365 $m\mu$. After irradiation into this band with light polarized in the $[011]$ directed at 77°K, a diachroism is subsequently observed in the absorption spectrum measured with $[011]$ and $[0\bar{1}1]$ polarized light; the optical and resonance measurements show that a realignment of a large fraction of the centers

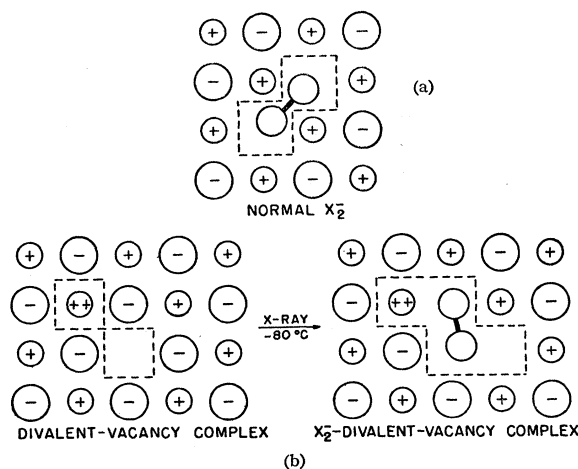


FIG. 1. Models for X_2^- centers (X is a halogen). The upper model (a), has been suggested by Castner and Känzig, reference 1, for the $\langle 110 \rangle$ oriented centers. It is proposed that irradiation of crystals containing divalent-vacancy complexes, (b), produces $\langle 100 \rangle$ oriented centers.

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¹ T. Castner and W. Känzig, J. Phys. Chem. Solids 3, 178 (1957).

² T. O. Woodruff and W. Känzig, J. Phys. Chem. Solids 5, 268 (1958).

³ C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. 111, 1235 (1958).

⁴ C. J. Delbecq, W. Hayes, and P. H. Yuster (to be published).

has occurred into the [011] direction from the other five possible orientations. This effect is expected to arise if the optical transition is only allowed for radiation polarized parallel to the axis of the molecule ion and if the probability of reorientation in the excited state is large.

(c) Measuring reorientation and decay curves for the two types of spectra. We define the reorientation temperature as the temperature at which the dichroism disappears in a crystal containing preferentially oriented centers, due to the movement of the holes through the lattice. The reorientation temperature is generally lower and more sharply defined than the decay temperature since the activation energy for reorientation is less than for decay and a variety of electron trapping sites may be involved in the destruction of the hole center.

A pulse annealing technique is used for measuring reorientation and decay temperatures. The starting temperature is normally that of liquid nitrogen. The sample is warmed to the required temperature in a suitable refrigerant, e.g., Freon 12, for two minutes, then cooled quickly to liquid nitrogen temperature and the spectrum remeasured. The cycle is subsequently repeated at the next higher temperature. Steps of about 15°C are used.

Delbecq and Yuster⁵ found that low-temperature x-irradiation of KCl and KBr containing Ca, Sr, or Ba ions produced a new optical absorption band in the near ultraviolet. We have examined the optical and resonance spectra of these samples and have assigned the new band to Cl_2^- and Br_2^- molecule ions; the properties of these centers are different, however, from the properties of the Cl_2^- and Br_2^- ions described by Castner and Känzig.¹

The crystals containing divalent additions were grown from reagent grade chemicals in this laboratory using the Kyropoulos method and were irradiated at 195°K with 50 kv, 50-ma x rays from a tungsten target filtered by a quartz window 1 mm thick. The paramagnetic resonance detection system and the low-temperature irradiation techniques which were used have already been described.³ A Rochon prism was used in the polarized light bleaching experiments and was arranged so that the electric vector of the polarized light could be rotated in the (001) crystal plane. Bleaching was done with an AH-6 high intensity mercury arc lamp with an appropriate combination of filters.

Paramagnetic Resonance Spectra

After irradiation at 195°K, single crystals of KCl containing alkaline earth ions exhibit a resonance spectrum with a complex hfs (Fig. 2). There are three distinguishable centers in the magnetic unit cell, each with a similar spectrum and with approximate axial

symmetry about a different cube edge. When the external magnetic field is parallel to the axis of one of these centers, the corresponding spectrum consists of seven groups of lines in the region 3046 to 3617 gauss; in this orientation the external field is perpendicular to the axes of the other two centers and their spectra are superimposed in the region 3200 to 3350 gauss. The centers are assigned to Cl_2^- molecule ions aligned approximately along a cube edge in contrast with the centers of Castner and Känzig where the alignment is accurately along a face diagonal.

It will be suggested later that the two chlorine nuclei do not have identical environments and hence are not equivalent; this results in the raising of the degeneracy which might otherwise be present in the hfs. The seven line hfs with intensities 1:2:3:4:3:2:1 observed for $\langle 110 \rangle$ oriented Cl_2^- when the external magnetic field is parallel to the axis now becomes seven groups of lines. The characteristic three line isotopic structure with intensities 9:6:1 is observed in the extreme groups which are nondegenerate and therefore clearly defined.

If we neglect the departure from axial symmetry and the inequivalence of the chlorine nuclei we may describe the resonance spectrum by the spin Hamiltonian

$$H = g_1 \beta H_z S_z + g_1 \beta (H_x S_x + H_y S_y) + A I_z S_z + B (I_x S_x + I_y S_y), \quad (1)$$

with $S = \frac{1}{2}$ and $I = I_1 + I_2$ where $I_1 = I_2 = \frac{3}{2}$ is the spin of

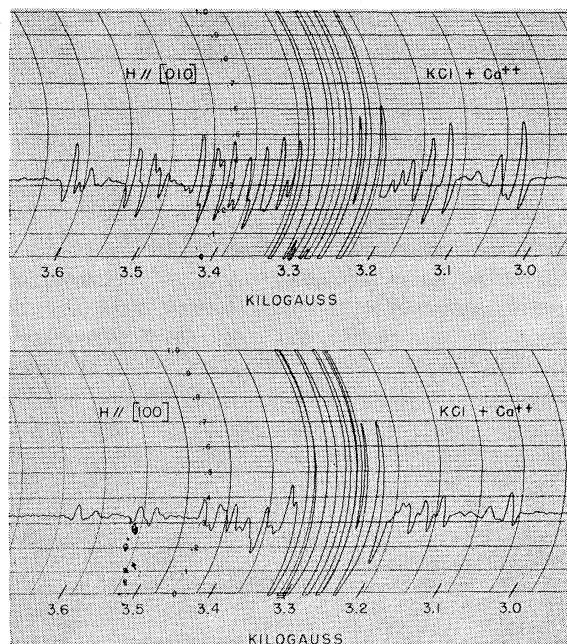


FIG. 2. Paramagnetic resonance spectrum (second derivative of absorption lines) of a KCl:Ca sample x-irradiated for 80 min at 195°K and bleached for 15 min at 77°K with [100] polarized light lying in the 323-m μ optical absorption band, (a) with $H \parallel [010]$ and (b) with $H \parallel [100]$; measured at 77°K.

⁵ C. J. Delbecq and P. H. Yuster (unpublished).

the chlorine nucleus. The allowed transitions $(\frac{1}{2}, m) \leftrightarrow (-\frac{1}{2}, m)$ occur when⁶

$$h\nu = g\beta H + Km + (B^2/4g\beta H_0)[(A^2 + K^2)/K^2] \times [I(I+1) - m^2], \quad (2)$$

where $K^2 g^2 = A^2 g_{11}^2 \cos^2 \theta + B^2 g_1^2 \sin^2 \theta$ and θ is the angle between the external magnetic field H and the axis of the molecule ion; H_0 is the field at which resonance would occur in the absence of a hfs. The measured constants of the spin Hamiltonian for the isotopic species 35-35 are $g_{11} = 2.005 \pm 0.002$, $g_1 = 2.04 \pm 0.01$, $A = 89.0 \pm 0.2 \times 10^{-4} \text{ cm}^{-1}$, and $B \approx 13 \times 10^{-4} \text{ cm}^{-1}$. The corresponding measurements for the $\langle 110 \rangle$ oriented centers are¹ $g_{11} = 2.0010$, $g_1 = \frac{1}{2}(g_x + g_y) = 2.0437$, $A = 94.3 \times 10^{-4} \text{ cm}^{-1}$, and $B = 8.4 \times 10^{-4} \text{ cm}^{-1}$.

Crystals of KBr containing alkaline earth ions behave in a similar fashion to those of KCl. Seven groups of lines are observed when the external magnetic field is oriented along a cube edge (Fig. 3). The spectrum is assigned to Br_2^- and is the analog of Cl_2^- spectrum; there are three distinguishable centers, each aligned approximately along a cube edge. Lines with intensities in the ratios 1:2:1 arising from the species 79-79, 79-81, 81-81 are observed in the extreme hfs components; the degeneracy of the inside hyperfine components is lifted in the parallel orientation even in the case of the $\langle 110 \rangle$ oriented Br_2^- centers by the large quadrupole moment of the nuclei and by higher order effects, and in the present case the effect is accentuated by the inequivalence of the nuclei. Of the parameters of the spin Hamiltonian, Eq. (1), only g_{11} and A could be measured; for the 81-81 ion, $g_{11} = 1.991 \pm 0.003$ and $A = 419 \pm 3.0 \times 10^{-4} \text{ cm}^{-1}$. The corresponding measurements on the $\langle 110 \rangle$ oriented centers are¹ $g_{11} = 1.980$ and $A = 420 \times 10^{-4} \text{ cm}^{-1}$.

OPTICAL ABSORPTION SPECTRA

When single crystals of pure KCl and KBr are x-irradiated at 195°K, the optical absorption spectra above 200 μ consist of three bands, the V_2 band in the ultraviolet and the F and K bands in the visible. However, when the samples have been doped with the divalent alkaline earth ions Ca^{++} , Sr^{++} , or Ba^{++} ,

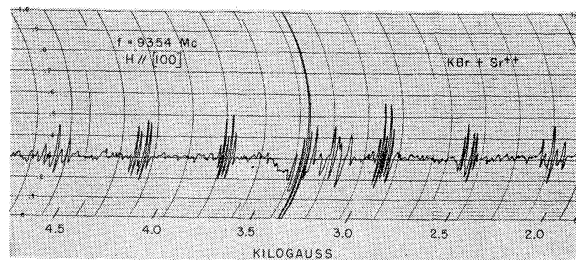


Fig. 3. Paramagnetic resonance spectrum (second derivative of absorption lines) of a KBr:Sr sample quenched from 600°C and x-irradiated at 195°K; measured at 77°K.

⁶ B. Bleaney, Phil. Mag. 42, 441 (1951).

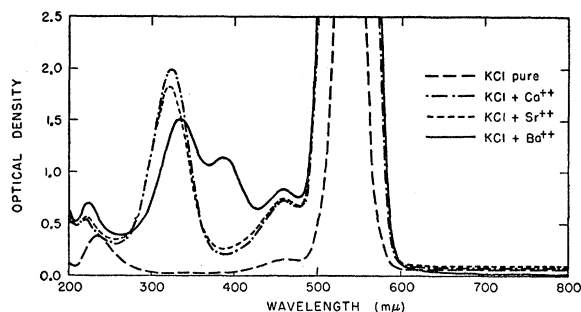


Fig. 4. Optical absorption spectra of KCl samples after 40-min x-irradiation at 195°K; measured at 77°K.

x-irradiation at 195°K produces an additional band in the near ultraviolet.

Figure 4 gives the results of measurements on KCl samples; V_2 absorption occurs at 235 μ , F absorption at 540 μ , and K absorption at 460 μ . The position of the new peak depends upon the nature of the divalent ion. In KCl:Ca the peak occurs at 323 μ , in KCl:Sr at 321 μ and in KCl:Ba at 335 μ . An additional peak is found in KCl:Ba at 390 μ . The crystals containing divalent ions also developed F and K bands upon irradiation as well as a band in the V_2 region having a maximum at 222 μ . There are two significant differences between these bands in the doped and pure crystals. Firstly, the band in the V_2 region appears to have shifted to slightly shorter wavelengths in the doped samples. Secondly, the amount of F absorption produced by the same amount of x-irradiation is far greater in the samples with divalent impurities. The fact that the ratio of F absorption to V_2 absorption is significantly larger in the doped samples indicates that the new peaks in the near ultraviolet are trapped hole centers since the F center is a trapped electron and a positive hole is created simultaneously with each electron upon x-irradiation.

The results for KBr are similar and are shown in Fig. 5. The spectrum of pure KBr shows V_2 absorption near 275 μ , F absorption at 600 μ and K absorption near 530 μ . The position of the new peak found in the doped samples again depends upon the nature of the

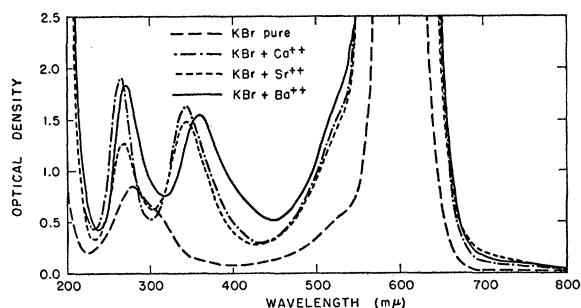


Fig. 5. Optical absorption spectra of KBr samples after 60-min x-irradiation at 195°K; measured at 77°K.

divalent ion. In KBr:Ca the peak occurs at $345\text{ m}\mu$, in KBr:Sr at $345\text{ m}\mu$, and in KBr:Ba at $360\text{ m}\mu$. A second peak in KBr:Ba is indicated at $410\text{ m}\mu$ but is not resolved. The addition of the divalent impurities to KBr produces a shift in the V_2 region peak and a variation in intensity of the band. This absorption increases upon addition of divalent ion; however, the F absorption increases at a greater rate indicating that the impurity induced centers in KBr also involve trapped holes.

All of the samples used to obtain data for Figs. 4 and 5 were 3.0 mm thick and were quenched to room temperature from 650°C before x-irradiation.

Correlation Between Optical and Resonance Spectra

A correlation between the $325\text{-m}\mu$ bands in KCl, the $345\text{-m}\mu$ bands in KBr and the X_2^- resonance spectra has been achieved. Both the optical and resonance absorptions appear when KCl and KBr are doped with the divalent ions and irradiated at a low temperature and their intensities are proportional. The thermal stabilities of the two types of spectra are the same. The following decay temperatures were found: KCl:Ca at 236°K , KCl:Sr at 233°K , KCl:Ba at 231°K , KBr:Ca at 243°K , KBr:Sr at 253°K , and KBr:Ba at 263°K . These temperatures correspond to the inflection points of curves relating optical density or resonance intensity to pulse annealing temperature. A typical plot is given in Fig. 6.

It was found that bleaching with light such that the electric vector is parallel to the $[100]$ direction results in preferential bleaching of those centers aligned along $[100]$. Similar effects have been observed with the $\langle 110 \rangle$ oriented X_2^- ions.^{3,4} Figure 7 gives the results of an experiment on a KCl:Ca crystal which was bleached for 15 minutes at 77°K in the interval 300 to $400\text{ m}\mu$. The solid line shows the optical absorption in both the $[100]$ and $[010]$ directions before bleaching. The dashed lines show the absorption in these directions after bleaching with $[100]$ polarized light. The optical

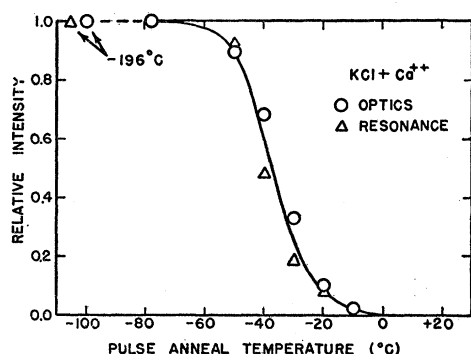


FIG. 6. Thermal stability of Cl_2^- centers in KCl:Ca as determined by disappearance of resonance signal and optical absorption band.

density in the $[100]$ direction is reduced by a factor of more than two while that in the $[010]$ direction has been slightly enhanced due to a reorientation of centers from the $[100]$ direction. The largest ratio of $[010]$ to $[100]$ optical density which could be obtained was about 3 to 1 which may be compared with the value of 20 to 1 achieved with the $\langle 110 \rangle$ oriented centers.³ The low ratio obtained in the present case is largely due to the strained nature of the crystals which depolarizes the light.

Figure 2 shows the paramagnetic resonance spectrum of KCl:Ca after bleaching with $[100]$ polarized light. Figure 2(a) was taken with the external magnetic field parallel to the $[010]$ direction and Fig. 2(b) with the field parallel to the $[100]$ direction. A comparison of these spectra with the spectrum before bleaching showed that the bleaching did not decrease the number of $[010]$ oriented centers while the number of $[100]$ centers was reduced to $\frac{1}{3}$ of its original value. The optical and resonance measurements of the dichroism are therefore consistent. Very little dichroism was observed in the optical or resonance spectra after bleaching with $[110]$ polarized light.

The KBr crystals were badly strained and depolarized light to a degree which made it difficult to bleach preferentially the Br_2^- molecule ions; the maximum ratio of $[010]$ to $[100]$ oriented centers which could be achieved was about 3:2.

Resonance and optical measurements gave identical reorientation temperatures. The following values were found: KCl:Ca(Sr,Ba) at 193°K and KBr:Ca at 223°K . These values may be compared with 173°K for the $\langle 110 \rangle$ oriented Cl_2^- and 143°K for the $\langle 110 \rangle$ oriented Br_2^- .^{3,4}

DISCUSSION

It has been established that the centers giving rise to the $325\text{-m}\mu$ optical absorption band in KCl containing alkaline earth ions, and the $345\text{-m}\mu$ band in KBr

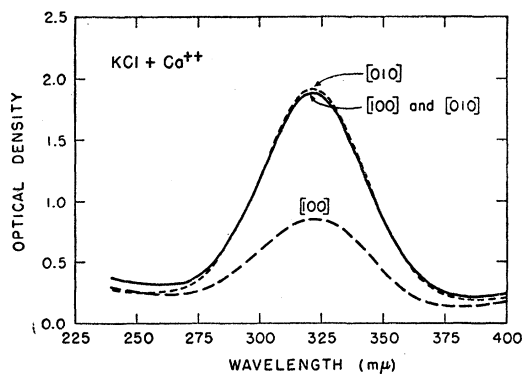


FIG. 7. Dichroism induced in the Cl_2^- optical absorption band in KCl:Ca by bleaching with polarized light at 77°K . Solid line shows absorption in both the $[100]$ and $[010]$ directions after 90-min x-irradiation at 77°K ; dashed lines show absorption after 80 min of irradiation with $[100]$ polarized light lying in the absorption band.

containing the same impurities are Cl_2^- and Br_2^- molecule ions. These ions differ from the Cl_2^- and Br_2^- ions of Castner and Känzig¹ in that they have approximate axial symmetry about a cube edge. Experiments have been carried out with other alkali halides containing alkaline earths and with $\text{KCl}:\text{Cd}$ but the $\langle 100 \rangle$ oriented X_2^- ions have not been found. The centers have not been found in pure crystals or crystals containing good electron traps such as Ag , Tl , or Pb where the $\langle 110 \rangle$ oriented centers are readily formed.

Following Haven⁷ and Dryden and Meakins⁸ we shall assume that the alkaline earth ions enter the lattice substitutionally and that a large fraction of them are associated with positive ion vacancies at the temperature of irradiation (195°K). It is suggested that upon x-irradiation, a halogen ion is ionized and the electron is trapped as an F center; the positive hole is trapped as a V_2 center or as an X_2^- center at a positive ion vacancy. The presence of the vacancy may cause the molecule ion to move out of its normal $\langle 110 \rangle$ alignment and produce approximate alignment along $\langle 100 \rangle$; one possible way in which this may be achieved is illustrated in Fig. 1(b). It can be seen that the environments of the two chlorine nuclei are not now identical. We might expect the anion-to-cation radius ratio of the host alkali halide to be of importance in the formation of the $\langle 100 \rangle$ oriented centers and the fact that we could not produce these centers in KI , NaCl , or NaBr may be due in part to the large value (~ 2) of this ratio in these salts. No variation in the position of the optical absorption band of the $\langle 110 \rangle$ oriented centers was observed in crystals of KCl containing Ag , Tl , or Pb impurities and it was concluded³ that this center was a property of the "pure" lattice. The variation in the position of the optical absorption band with the impurity ion in the present case supports the view that the impurity ion is closely associated with the X_2^- center. The fact that the X_2^- centers were not observed in $\text{KCl}:\text{Cd}$ may be due to the smaller solubility of Cd in KCl .

The vacancy stabilized centers decay at a higher temperature than the $\langle 110 \rangle$ oriented centers and the latter could not be observed at dry ice temperature. When the samples are x-irradiated at liquid nitrogen temperature, V_1 centers are produced in addition to the $\langle 100 \rangle$ oriented X_2^- centers; with the irradiation times used (~ 40 min) the optical or resonance spectra of the $\langle 110 \rangle$ oriented X_2^- centers could not be observed.

The g shifts in the $\langle 110 \rangle$ oriented Cl_2^- spectrum of Castner and Känzig are discussed by them in terms of the theory given by Cohen⁹ and Inui, Harasawa, and

Obata.¹⁰ The ground-state configuration of Cl_2^- is expected to be $(\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2)^2\Sigma_u^+$ and a transition to the state $(\sigma_g\pi_u^4\pi_g^4\sigma_u^2)^2\Sigma_g^+$ is allowed for σ -polarized radiation; this may give rise to the ultraviolet band of the $\langle 100 \rangle$ and $\langle 110 \rangle$ oriented X_2^- centers since it has the correct polarization properties. A very weak transition of the $\langle 110 \rangle$ oriented centers has been observed^{3,4} at about $750 \text{ m}\mu$ but a corresponding transition has not been found in the case of the $\langle 100 \rangle$ oriented centers presumably because of lack of intensity.

The unpaired electron of the ground state of Cl_2^- is in the antibonding $3p\sigma_u$ orbital and the g shifts are determined by the spin-orbit coupling to the $3p\pi_u$ level separated by a distance Δ . Following Inui, Harasawa, and Obata¹⁰ we may write

$$g_{11} = g_0 - \frac{\lambda^2}{\Delta^2(1+\alpha^2)}, \quad g_1 = g_0 - \frac{2\lambda}{\Delta(1+\alpha^2)} - \frac{2\lambda^2}{\Delta^2(1+\alpha^2)},$$

where α determines the fraction of s character of the electron wave function and λ is the spin-orbit coupling constant. The predicted value of $g_{11} - g_0$ is negative ($g_0 = 2.0023$ is the free electron g value) and in the case of the $\langle 110 \rangle$ oriented Cl_2^- center is found to be -0.001 . In the present case the g shift is $+0.003$. The positive shift may arise from the fact that the molecule ions are not aligned accurately along a cube edge; the g value measured with the magnetic field parallel to a cube edge will therefore include a small contribution from g_1 . The observed shift indicates that the molecule ion makes an angle of about 2° with a cube edge. The misalignment results in an increase in the number of possible orientations and hence an increase in the number of distinguishable centers; however, the spectra from the centers distributed around a particular cube edge are not resolved.

Most of the crystals grown contained aggregates of impurity ions which caused cloudiness and scattering of light. Quenching from 650°C to room temperature dispersed the impurity ions in the lattice and the number of X_2^- centers which could be produced was increased by a factor of about 3. However, the strains produced by quenching caused shattering of the crystals, depolarization of polarized light and broadening of the resonance lines. These effects depend on the concentration and size of the impurity and were more pronounced in KBr than in KCl . The small Ca^{2+} ions strain the KBr lattice more severely than Ba^{2+} ions.

The effect of strains and misalignment on the resonance linewidth is reduced in the parallel orientation since the hfs is at a maximum. The effect is expected to be less in KCl because of the smaller hyperfine splitting. With both KCl and KBr a sharpening and increase in amplitude of the lines from the $[100]$ oriented centers occurs when the external magnetic field is moved parallel to the $[100]$ direction. In the

⁷ Y. Haven, *Report of the Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955), p. 261.

⁸ J. S. Dryden and R. J. Meakins, *Discussions Faraday Soc.* 23, 39 (1957).

⁹ M. H. Cohen, *Phys. Rev.* 101, 1432 (1956).

¹⁰ T. Inui, S. Harasawa, and Y. Obata, *J. Phys. Soc. Japan* 11, 612 (1956).

case of KBr:Ba the resonance lines disappear when the magnetic field is 18° off the $[100]$ direction and with KBr:Ca cannot be observed even when the magnetic field is parallel to the $[100]$ direction. It will be noticed in the spectrum of KBr:Sr (Fig. 3) that only lines from centers oriented parallel to the magnetic field are sufficiently narrow to be clearly visible.

In the parallel orientation, the Cl_2^- and Br_2^- linewidths are 9.0 and 12.0 gauss, respectively, as compared with 1.3 and 2.5 gauss for the $\langle 110 \rangle$ oriented centers. Considerations based on dipole-dipole interactions with nuclei of the surrounding ions suggest linewidths of 0.5 and 1.0 gauss, respectively. It has already been shown by Hayes,¹¹ that in the case of the $\langle 110 \rangle$ oriented Cl_2^- center that part of the linewidth arises from interaction with the nuclei of nearest neighbor ions through weak covalency. This effect, the strained nature of the crystals and the misalignment of the centers may well account for the large linewidth in the present case.

¹¹ W. Hayes (unpublished).

The ultraviolet optical absorption band of the X_2^- center in both KCl and KBr occur at shorter wavelength than the bands of the corresponding $\langle 110 \rangle$ oriented centers. (A detailed discussion of the optical spectra of the $\langle 110 \rangle$ oriented F_2^- , Cl_2^- , Br_2^- , and I_2^- is being prepared by Delbecq, Hayes, and Yuster.⁴) This effect is expected to arise largely from the influence of the environment on the excited level of the transition. The effect of environment on the ground state in which paramagnetic resonance is observed should be less and only slight differences in the parameters of the resonance spectra from the two types of center are observed.

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Photoconductivity of Cuprous Oxide in Relation to Its Other Semiconducting Properties*†

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It is shown that at least two of the three known peaks in the photoconductivity *versus* wavelength curve of Cu_2O are strongly dependent on the oxygen content of the material. The peak near $600 \text{ m}\mu$ can be shifted from shorter to longer wavelengths by exposing the sample to relatively low oxygen pressures at 860°C . The peak near $800 \text{ m}\mu$ is found to increase in magnitude relative to the others under these circumstances. This is in apparent contrast to the results of previous investigators. It is further shown that both results are consistent with the values of the high temperature activation energy of the conductivity process, as well as with the change in bandgap as a function of temperature as obtained from optical absorption measurements under the assumption that Cu_2O can be classified as a nonpolar semiconductor.

INTRODUCTION

THE photoconductivity of Cu_2O was first observed by Pfund¹ in 1916 and has since been the subject of considerable investigation.²⁻⁷ The present study is an

outgrowth of research into the cathodoluminescence⁸ of Cu_2O and its relation to the other semiconducting properties of this material.

In general the work on Cu_2O can be divided into two categories. Much work is done on the type of Cu_2O used in rectifiers, where often oxygen in excess of the stoichiometric proportions is deliberately introduced. Other work is done on this material for the purpose of measuring the properties of Cu_2O in which the excess oxygen content is kept at a minimum. In the literature this distinction has only recently been emphasized in the work by Anderson and Greenwood⁹ and by Böttger¹⁰ in regard to the dark conductivity, and in the work by

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¹ A. H. Pfund, Phys. Rev. **7**, 289 (1916).

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⁶ T. Okada and R. Uno, J. Phys. Soc. Japan **4**, 351 (1949).

⁷ G. F. J. Garlick, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 19, p. 377.

⁸ R. Frerichs and F. L. Weichman, J. Appl. Phys. **29**, 710 (1958).

⁹ J. S. Anderson and N. N. Greenwood, Proc. Roy. Soc. (London) **A215**, 353 (1952).

¹⁰ O. Böttger, Ann. phys. **10**, 232 (1952).

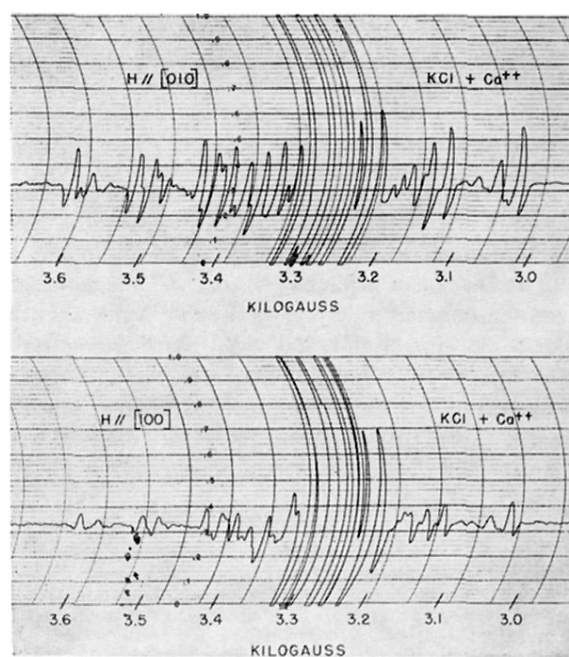


FIG. 2. Paramagnetic resonance spectrum (second derivative of absorption lines) of a KCl:Ca sample x-irradiated for 80 min at 195°K and bleached for 15 min at 77°K with [100] polarized light lying in the 323-m μ optical absorption band, (a) with $H \parallel [010]$ and (b) with $H \parallel [100]$; measured at 77°K.

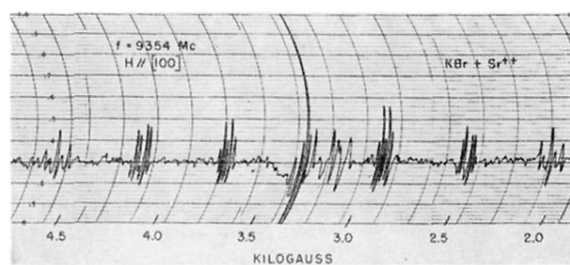


FIG. 3. Paramagnetic resonance spectrum (second derivative of absorption lines) of a KBr:Sr sample quenched from 600°C and x-irradiated at 195°K; measured at 77°K.