entation.[20] However, the magnitude of misorientation has to be of the order of 26° away from the X_3 axis assuming $\phi = 0$.

ACKNOWLEDGMENTS

I wish to thank Professor John C. Jamieson for his encouragement, suggestive questions, and constructive criticism throughout the course of this research. Helmut Zahn was very helpful in the construction of the high-pressure system and the other ancillary devices. Gene Litivak maintained the apparatus during the experimentation. The financial support for this investigation was provided by National Science Foundation grants, the Petroleum Research Fund of the American Chemical Society, and an ARPA grant at the University of Chicago. The support of the U. S. Atomic Energy contract at Cornell University in preparation of the manuscript is gratefully acknowledged.

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[20] C. Y. Wang (private communication) thinks that the apparently high compressibility of his calcite specimen was probably caused by the compression and extrusion of two layers of silver paint, which he put between this particular specimen and the two transducers to serve as the electrical contact for grounding one side of the transducers.

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Optical and Electron-Spin-Resonance Studies of the ICl^- V_K Center in KCl:I[†]

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The ICl^- V_K center, a ⟨110⟩-oriented self-trapped hole center, has been investigated in x-irradiated KCl:I and KCl:I:Pb at low temperatures by optical and electron-spin-resonance techniques. Three optical transitions are identified at 430, 840, and 1000 nm by anisotropic absorption measurements; their observed σ polarizations and relative intensities are consistent with a molecular-orbital model modified for XY^- molecule-ion centers. Pulse-annealing experiments monitored by ESR and correlated with thermoluminescence data and absorption spectrum changes give information on the formation and thermal stability of ICl^-. An improved analysis of the ESR spectrum has been carried out, taking into account deviations from axial symmetry. Perturbation theory calculations are extended to include some terms to fourth order. The observed $|\Delta m| = 1,2$ forbidden transitions are fitted with these equations, allowing a determination of the sign, as well as the magnitude, of the large iodine quadrupole interaction.

I. INTRODUCTION

The V_K center in alkali halides has been extensively studied since its discovery and analysis by Kanzig *et al.*[1] with electron-spin-resonance techniques. The center, produced efficiently by ionizing irradiation at liquid-nitrogen temperatures, is an X_2^- molecule ion (X = halogen) in which a hole is self-trapped between neighboring halogen ions along a ⟨110⟩ crystal direction. Its optical absorption spectra and thermal stability properties were first identified by Delbecq *et al.*[2,3] in carefully correlated optical and ESR experiments. The luminescence from V_K center-electron recombination was observed by Kabler[4] and Murray and Keller.[5,6] More recently, studies of the thermal reorientation and diffusion of V_K holes were made by Keller *et al.*[7,8]

Essentially parallel developments are suggested for XY^- V_K centers in mixed alkali halides. Wilkins and Gabriel[9] observed by means of ESR the FCl^- center in KCl doped with F^- ions. Subsequently, several other XY^- combinations (with the exception of ICl^-) in various host crystal lattices were investigated with ESR by Schoemaker[10,11] and by Dreybrodt and Silber.[12] However, only limited studies of the optical absorption

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[2] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **111**, 1235 (1958).

[3] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1961).

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[5] R. B. Murray and F. J. Keller, Phys. Rev. **137**, A942 (1965).

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[11] D. Schoemaker, C. J. Delbecq, and P. H. Yuster, Bull. Am. Phys. Soc. **9**, 629 (1964); D. Schoemaker, in Proceedings of the International Symposium on Color Centers, Urbana, Ill., 1965, Abstract Nos. 167 and 168 (unpublished).

[12] W. Dreybrodt and D. Silber, Phys. Status Solidi **16**, 215 (1966).

properties of these mixed-halogen centers were made and none at all of their recombination luminescence.

This paper presents a detailed study of one such XY^- center, the ICl^- V_K center in the mixed-crystal systems KCl:I and KCl:I:Pb.[13,14] We have investigated the optical absorption and electron-spin-resonance spectra of the center and have correlated these by means of polarized bleaching experiments. In addition, information on both the formation of ICl^- by trapping of mobile Cl_2^- holes at iodine-ion sites and of its thermal stability has been obtained. The experimental results are presented in Sec. III. Section IV contains an analysis of the ESR spectrum, taking into account deviations from axial symmetry, with an improved determination of the spin-Hamiltonian parameters reported earlier.[14] Perturbation theory calculations, including terms to second order in the large iodine quadrupole interaction, are presented. The observed $|\Delta m|=1$, 2 forbidden transitions are fitted with these equations, allowing a determination of the sign, as well as the magnitude, of the quadrupole interaction. In Sec. V, the thermal and optical absorption properties of the ICl^- center are discussed and comparisons are made with other V_K centers. In the course of this work the luminescence from ICl^--center-electron recombination was identified and is reported elsewhere.[15]

II. EXPERIMENTAL

The mixed alkali-halide crystals KCl:I and KCl:I:Pb and pure KCl were grown by the Kyropoulos method in an argon atmosphere. The starting materials were reagent grade KCl, first treated by bubbling Cl_2 gas through the molten salt principally to remove Br^- impurities, and, as dopants, Harshaw KI and reagent grade $PbCl_2$ where appropriate. The doping content determined by chemical analysis was approximately 0.1 mole% of I^- and 0.05 mole% of Pb^{++}; the initial amount of I^- added to the melt in both cases had been about five times greater, and that of Pb^{++} about ten times greater.

Cleaved crystal pieces for optical experiments were typically 2 mm thick. Those used for ESR measurements were of dimensions $4\times6\times16$ mm^3 with the long axis ground in a [110] orientation. Prior to irradiation, in order to disperse any aggregation of the added impurities, the samples were heated at 500°C in room air for 15 min and quenched to room temperature on a copper block. Color centers were produced by x irradiation at 77°K with a tungsten-target Norelco MG-150 unit (beryllium window filter) operating at 120 kV and 16 mA, and filtered through 1 mm of quartz.

Optical experiments were carried out in a standard conduction cryostat (Supracil quartz windows). Temperature measurements were made with a copper-constantan thermocouple pressed between the crystal and copper sample holder; the measurements at liquid-helium temperatures were augmented with a calibrated 1000-Ω Allen-Bradley carbon resistor attached to the sample holder. Optical absorption spectra were taken with a Cary model 14 recording spectrophotometer. A Rochon polarizer was placed in a rotatable mount in front of the Cary tungsten-lamp source for polarized absorption measurements down to 290 nm. The ICl^- centers were preferentially oriented by polarized irradiation into either their infrared- or uv-absorption bands using, respectively, a Polaroid type HR sheet-film polarizer with a tungsten lamp and monochromator or a type HNP'B polarizer with the 436-nm radiation of an Osram HBO 200-W high-pressure Hg lamp isolated by an interference filter. Thermoluminescence was detected with the full spectral response of an EMI 6255S photomultiplier.

The ESR experiments were performed with a standard x-band, double-bolometer, balanced-bridge spectrometer described elsewhere.[16] A TE_{101} rectangular cavity with one end wall replaced by copper-mesh screen was used. The crystal was held against this mesh permitting both x and optical irradiation while in the cavity. The x irradiation was carried out with the cavity and the waveguide immersed in liquid nitrogen in a small Styrofoam Dewar. Subsequently, the cavity was quickly transferred to the liquid-helium immersion Dewar used for the ESR measurements. Temperatures between 4.2 and 77°K were obtained by surrounding the cavity with a block of Teflon to increase the thermal mass, thus permitting a very slow (~10°K/h) warmup after the liquid helium evaporated. Field measurements (Varian 6-in. magnet) were made with a Harvey-Wells G-502 proton resonance gaussmeter in conjunction with a Beckman 7175N frequency counter. A DeMornay-Bonardi DBG-715-1 wave-meter cavity was used to determine the microwave frequency.

III. EXPERIMENTAL RESULTS

A. Optical Absorption and Thermal Luminescence

Distinct changes in the absorption spectrum (Fig. 1) of x-irradiated KCl:I:Pb are observed upon warming from 77°K. These absorption changes correlate with the thermoluminescent glow peaks (Fig. 2) at about 208 and 250°K that result from the release of trapped charge. In the first transition-temperature region a process of $Cl_2^- \rightarrow ICl^-$ conversion following thermal release of Cl_2^- holes is identified; in the second, the ICl^- holes themselves begin to become thermally unstable.

Figure 1(a) presents the absorption spectrum (above 300 nm) of KCl:I:Pb after 15-min initial x irradiation at 77°K. The spectrum is identical to that obtained in

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[13] L. S. Goldberg and H. Mahr, Bull. Am. Phys. Soc. 11, 246 (1966).

[14] M. L. Meistrich and L. S. Goldberg, Solid State Commun. 4, 469 (1966).

[15] L. S. Goldberg, Phys. Rev. 168, 989 (1968).

[16] W. D. Ohlsen, Ph.D. thesis, Cornell University, 1962 (unpublished).

x-irradiated KCl:Pb by Delbecq *et al.*[2] The broad band peaking at 365 nm consists principally of the 365-nm Cl_2^- absorption in addition to an underlying absorption presumably arising from (Pb^{++}+electron) centers. Warming to 170°K [Fig. 1(b)] results in only a slight decrease in absorption of the combined band at 365 nm and of the *F* band, indicating a small loss of the hole centers by recombination. Two weak thermal glow peaks appear within this temperature region (Fig. 2) but are of no apparent significance.

Several important absorption changes occur [Fig. 1(c)] after warming past the large glow peak at 208°K. An analogous glow peak was observed in the KCl:Pb system by Delbecq *et al.*[2] and by Neubert and Reffner[17] and was identified with the thermal release of Cl_2^- holes and their subsequent recombination with electrons trapped at impurity sites—in this case, principally Pb^{++}. The absorption band peaking at 365 nm [Fig. 1(c)] now shifts to 392 nm with a 30% decrease in height and with a pronounced increased absorption in the long-wavelength edge. This increased absorption arises in part from an ultraviolet absorption band of the ICl^- center, later established by measurements of induced anisotropic absorption to be centered at 430 nm; the bulk of the remaining absorption contributing to the 392-nm band is presumably related to formation of (Pb^{++} +hole) centers. In addition, two infrared bands associated with ICl^-, centered at 840 nm and at about 1000 nm, now appear in a previously transparent region.

The three ICl^- absorption bands disappear [Fig. 1(d)] after further warming past the glow peak at 250°K. The band at 392 nm shifts to 383 nm, midway between the two previous positions, and grows by some 20%. This 383-nm band was partially present after $Cl_2^- \rightarrow ICl^-$ conversion and likely arises from (Pb^{++} +hole) centers; the centers are very stable, remaining even after warming to over 340°K. The glow peak at 250°K (Fig. 2) is considered to be associated with the thermal release of ICl^- holes and seems to be a sensitive marker for the presence (actually the disappearance) of the ICl^- center. A similar 250°K glow peak was also observed in KCl:I, x or uv irradiated at low temperatures, indicating that ICl^- centers had been formed, but it was not seen in x-irradiated pure KCl.

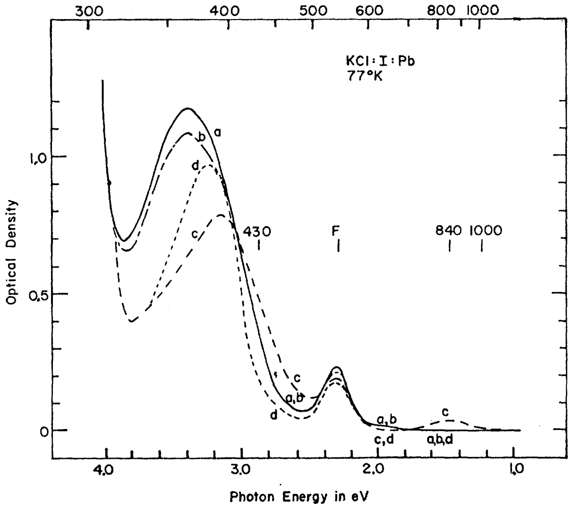

Fig. 1. Absorption spectra at 77°K of 3-mm-thick KCl:I:Pb crystal: (a) after initial x irradiation for 15 min at 77°K; (b) after warming to 170°K; (c) 235°K; (d) 273°K.

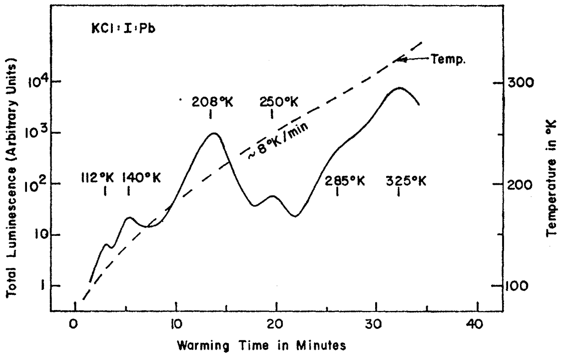

Fig. 2. Thermal glow curve for KCl:I:Pb after x irradiation for ½ h at 77°K. The warming temperature is indicated by the dashed line.

A prominent thermal glow peak also occurs at 325°K in both I^--containing crystals. However, there are no further discernible absorption changes after warming past this temperature, and the source of the glow peak remains unclear.

B. Anisotropic Absorption

Anisotropic absorption studies of ICl^- were made in KCl:I:Pb following preferential orientation of the centers along one of the six equivalent ⟨110⟩ crystal directions by polarized excitation at low temperatures.[18] The centers were prepared by x irradiation at 77°K, brief warming to 230°K to convert $Cl_2^- \rightarrow ICl^-$, and cooling to 11°K for measurement. Excitation with $[1\bar{1}0]$-polarized light at 840 nm, incident along [001], resulted in a growth of the [110]-absorption spectrum and a decrease in the $[1\bar{1}0]$ spectrum. The subtraction of these two spectra defines the anisotropic absorption shown in Fig. 3; any isotropic component is of course excluded.

Three absorption bands of the ICl^- center are identified: two strongly anisotropic bands having the same direction of polarization located at 430 and 840 nm, the former having a noticeably asymmetric line shape, and a very weak, largely isotropic band at about 1000 nm. The relative anisotropic integrated absorption areas of the three bands and the relative isotropic areas of the two infrared bands are given with other absorption data in Table I; it was not possible to determine the isotropic

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[17] T. J. Neubert and J. A. Reffner, J. Chem. Phys. **36**, 2780 (1962).

[18] Details of similar polarized orientation experiments are described in Ref. 3.

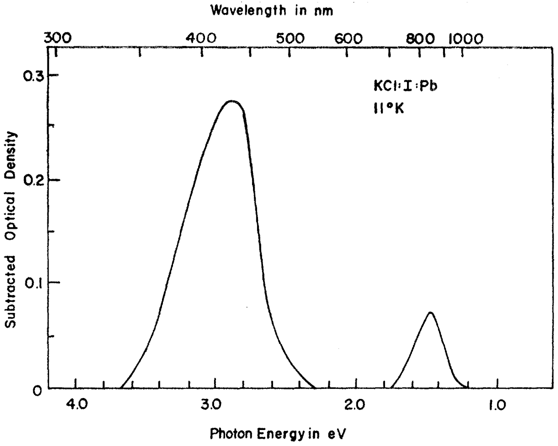

FIG. 3. Anisotropic absorption spectrum of ICl$^-$ in KCl:I:Pb at 11°K. Obtained by subtraction of the spectrum measured with [1$\bar{1}$0]-polarized light from the [110] spectrum after preferential orientation of the ICl$^-$ by [1$\bar{1}$0]-polarized light at 840 nm, incident along [001].

area of the 430-nm band due to other overlapping absorption.

A similar anisotropy could also be induced in the [010] and [100] spectra by excitation with [010] light, substantiating that the ICl$^-$ transition moments have a general ⟨110⟩ orientation. The optical experiments by themselves, however, cannot determine whether the three transitions are σ or π polarized.[19] This ambiguity was removed by ESR experiments in which the orientation of the centers could be directly monitored. Excitation at 430 or 840 nm with [1$\bar{1}$0]-polarized light resulted in the principal axis of the centers being reoriented along [110], thus proving that these transitions are σ polarized. The case for the 1000-nm transition is less definite, but a slight σ polarization is indicated from the anisotropic absorption measurements.

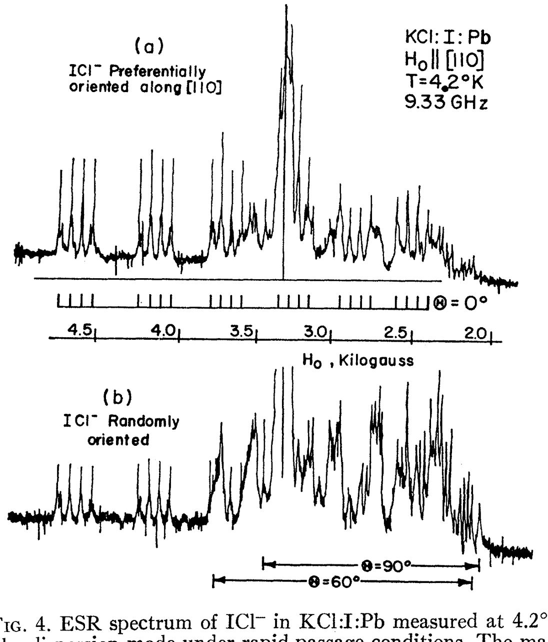

FIG. 4. ESR spectrum of ICl$^-$ in KCl:I:Pb measured at 4.2°K in the dispersion mode under rapid-passage conditions. The magnetic field H_0 is along the [110] direction (a) after irradiation with [1$\bar{1}$0]-polarized light at 436 nm (b) before polarized irradiation. (From Ref. 14.)

A measure of the relative mixing of π polarization into the two σ-anisotropic transitions at 430 and 840 nm was made by determining the degree of anisotropy α_λ that could be induced by polarized excitation at each of these wavelengths. α_λ is defined here as the ratio of intensity of the [110] absorption to that of the [1$\bar{1}$0], monitored always at the 840-nm band (a region of no other overlapping absorption), following saturation with [1$\bar{1}$0]-polarized light at λ. The magnitude of $\alpha_\lambda(\alpha_\lambda>1)$ is a measure of the ratio of σ to π polarization. After about 10 min of polarized 840-nm excitation at 11°K, a maximum reorientation of the ICl$^-$ was obtained, yielding $\alpha_{840}\approx 3$. Similarly, after polarized 430-nm excitation, $\alpha_{430}\approx 10$ was obtained. Although there was some uncertainty in these values due to difficulties in monitoring absorption changes in the small 840-nm band, the results clearly indicate a greater admixture of π polarization into the infrared 840-nm transition than into the ultraviolet 430-nm transition. Similar conclusions were obtained in reorientation experiments monitored by ESR.

Excitation at 430 nm produced a noticeable bleaching of the ICl$^-$ centers, resulting principally in the reformation of Cl_2^-. No significant bleaching was observed with 840-nm excitation.

A preferential orientation of the ICl$^-$ centers could be induced and maintained only at low temperatures near liquid helium. At 11°K the anisotropy obtained in the absorption spectrum remained stable for periods on the order of hours. Upon warming, one-half of the induced anisotropy was lost at 14°K; by 18°K it had completely disappeared.

C. Electron Spin Resonance

Details of initial ESR studies of the ICl$^-$ center in KCl:I:Pb are described in Ref. 14. They confirm that the center consists of a hole self-trapped between an iodine and a chlorine ion occupying adjacent lattice sites along a ⟨110⟩ direction and that there are no other nuclei associated with the center.[20] The spectrum of the

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[19] The polarization of a given transition of an axially symmetric center is assigned as σ or π depending on whether the transition is induced by light having electric vector polarized parallel or perpendicular with respect to the principal axis. For a center with principal axis oriented along the [110] face diagonal, the σ-polarized transition moment lies parallel to [110], and the two mutually orthogonal π-polarized transition moments, π_1 and π_2, lie parallel to [1$\bar{1}$0] and [001], respectively. The transition moment π_1 and π_2 are nonequivalent due to the orthorhombic symmetry of the center; however, in these experiments only the [1$\bar{1}$0]-transition moment π_1 was sampled and is hereafter referred to simply as π.

[20] Schoemaker (Ref. 10) and Dreybrodt and Silber (Ref. 12) report the observation at 77°K of a ⟨110⟩-oriented ICl$^-$ center weakly interacting with a neighboring fluorine nucleus in crystals doped simultaneously with I$^-$ and F$^-$ ions. In neither case, however, do they observe an isolated ICl$^-$ center.

TABLE I. Optical absorption band parameters of the ICl⁻ V_K center in KCl:I:Pb at 11°K. Orientation of ICl⁻: ⟨110⟩. Disorientation temperature: 14°K. Thermal stability temperature: 250°K.

Peak position λ(nm)	Peak position E(eV)	Half-width (eV)	Transition moment polarization	Degree of anisotropy	Relative integrated absorption area Anisotropic	Relative integrated absorption area Isotropic
430	2.88	0.60	σ	$\alpha_{430}\approx 10$	8	···
840	1.48	0.23	σ	$\alpha_{840}\approx 3$	1	1
1000	1.2	0.1	σ	···	0.005	0.1

center has also been observed in x-irradiated KCl:I and KCl:I:Tl and is identical. At 35°K the resonance signal broadens and disappears although the center itself is stable until much higher temperatures.

An analysis of the ESR spectrum is carried out in Sec. IV. In order to simplify the evaluation of the spin-Hamiltonian parameters, the spectrum is analyzed for the special cases when the external magnetic field H_0 is along the major axes of the center. The complexity of the observed spectra resulting from overlapping patterns of centers having different angles Θ between their symmetry axis and H_0 can be greatly reduced by alignment of the centers with polarized light. With the centers preferentially oriented along [110] and with H_0 parallel to that direction, the $\Theta=0°(z)$ spectrum can now be clearly seen [Fig. 4(a)]. By rotating H_0 by 90° parallel to [001], the $\Theta=90°(y)$ spectrum is observed (Fig. 5). And by leaving H_0 parallel to [110] and reorienting the centers along [$1\bar{1}0$], the $\Theta=90°(x)$ spectrum can be observed.

Pulse annealing experiments were performed in KCl:I, KCl:I:Pb, and in pure KCl to determine the thermal stability of the Cl_2^- centers and to monitor the accompanying formation of ICl⁻ when I⁻ ions are present in the lattice. The crystals, x irradiated for 2 h at 77°K, were warmed in successive steps of about 15°K, held constant at each temperature for about one minute, and cooled quickly to 77°K for measurement of the Cl_2^- signal intensity. Correspondingly, in separate measurements, the ICl⁻ signal intensity was measured at 21°K following warming in successive steps of about 40°K. The pulse annealing data are presented in Fig. 6.

In the pulse annealing curves for KCl:I:Pb, the major loss of Cl_2^- begins at about 170°K and increases rapidly in the temperature region around 200°K, as had previously been observed for KCl:Pb.[2,17] This loss of Cl_2^- is accompanied by a sharp increase in the number of ICl⁻, correlating well with optical evidence of ICl⁻ formation. For KCl:I, however, the Cl_2^- annealing behavior is markedly different, proceeding in two distinct stages. At lower temperatures, roughly below 150°K, the number of Cl_2^- decreases by about one-half while only a very small accompanying ICl⁻ growth occurs. This first stage can be compared with the results for pure KCl, also shown in Fig. 6, for which a nearly complete loss of Cl_2^- at low temperatures is observed. In the second stage, at higher temperatures, the Cl_2^- annealing behavior in KCl:I closely follows that obtained for KCl:I:Pb and is likewise accompanied by a marked increase in the number of ICl⁻.

The thermal stability of the ICl⁻ center, indicated in the data of Fig. 6 for both KCl:I:Pb and KCl:I, is also in agreement with optical evidence. The number of ICl⁻ decreases greatly, although not completely, after warming to 270°K. No new resonance is observed after this thermal loss of ICl⁻.

IV. ANALYSIS OF THE ESR SPECTRUM

A more detailed analysis of the ICl⁻ ESR spectrum reported earlier[14] has been performed in a manner simi-

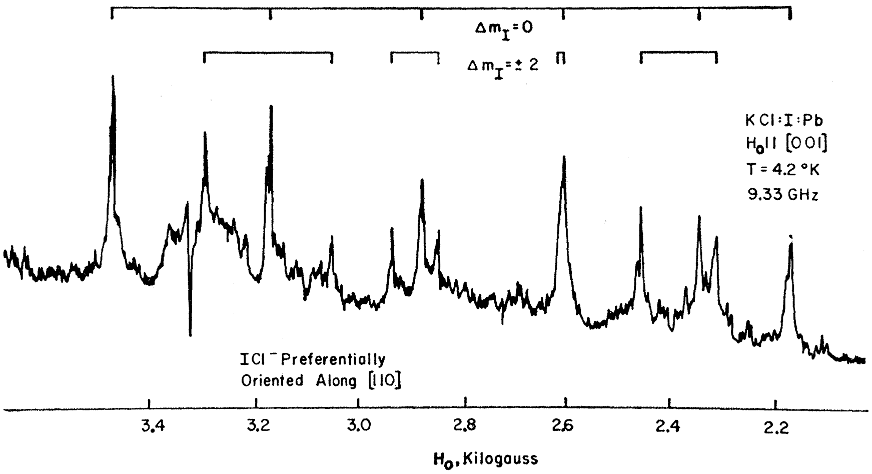

FIG. 5. $\Theta=90°$ spectrum ($\mathbf{H}_0\|y$) of oriented ICl⁻ under the same conditions as in Fig. 4(a). The magnetic field is now along the [001] direction.

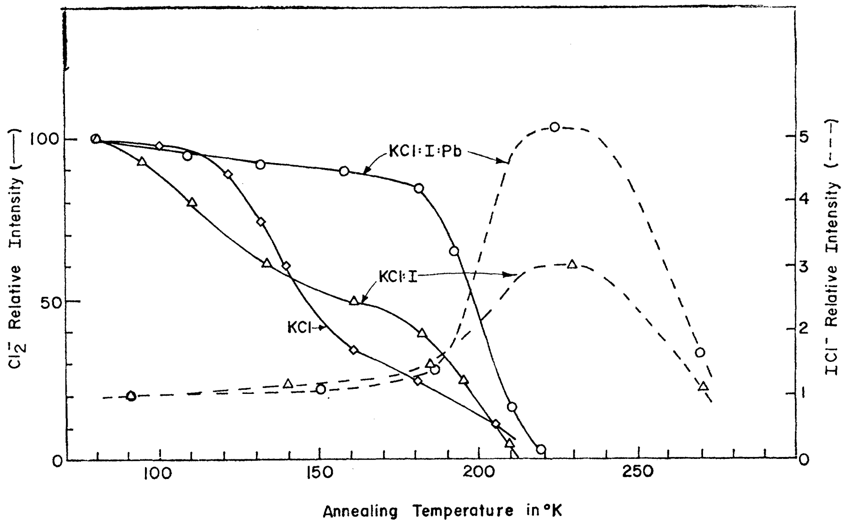

FIG. 6. ESR pulse-annealing data. Signal intensity of (—) Cl_2^- and (- - -) ICl^- centers in KCl:I:Pb, KCl:I, and pure KCl, each initially x-irradiated for 2 h at 77°K.

lar to that used by Schoemaker[10] and Dreybrodt and Silber[12] for other XY^- centers. The ⟨110⟩-oriented ICl^- center lies in a crystal field of orthorhombic symmetry for which the two directions perpendicular to the molecular axis of the center are not equivalent. This center does display a deviation from axial symmetry, and hence a rhombic spin Hamiltonian[21] of the following form is used:

$$\frac{\mathcal{H}}{g_0\beta}=\frac{1}{g_0}\sum_{i=x,y,z} g_iH_iS_i+\sum_{n=1,2}\sum_{i=x,y,z} A_{ni}I_{ni}S_i +Q'[I_{1z}^2-\tfrac{1}{3}I_1(I_1+1)]. \quad (1)$$

The subscripts $n=1$, 2 refer to the I^{127} and Cl^{35} nuclei, respectively; z is the direction of the molecular axis of the center chosen to lie along [110], x the [1$\bar{1}$0], and y the [001] directions perpendicular to the molecular axis. Since the deviation from axial symmetry is small, the hyperfine tensor components A_{1x} and A_{1y} are assumed to have the same sign and only the axial quadrupole interaction term of the iodine nucleus, $Q'=3e^2qQ/4I_1(2I_1-1)$, is used. The chlorine quadrupole interaction is small and will be neglected.

The above Hamiltonian can be most easily evaluated when the external magnetic field lies along the principal axes of the hyperfine and g tensors. Standard perturbation theory and an expansion in terms of the deviation from equal energy denominators as used in earlier papers[10,12] are employed to determine the resonant line positions in these special cases. The field values expressed in gauss are

$$\begin{aligned}H_z(m_1,m_2)=(g_0/g_z)\{&H_0-A_{1z}(1+\epsilon_z)m_1-A_{2z}m_2\\&-\tfrac{1}{4}(A_{1x}+A_{1y})^2[2H_0/(H_0^2-\tfrac{1}{4}A_{1z}^2)][I_1(I_1+1)-m_1^2]\\&-\tfrac{1}{4}(A_{1x}+A_{1y})^2(2Q'm_1/H_0^2)[2I_1(I_1+1)-2m_1^2-1]\\&-\tfrac{1}{4}(A_{1x}+A_{1y})^4(2/H_0^3)[C(m_1)C(m_1-1)]\}, \quad (2)\end{aligned}$$

$$\begin{aligned}H_x(m_1)=\frac{g_0}{g_x}\bigg\{&H_0-A_{1x}(1+\epsilon_x)m_1-\frac{A_{1y}^2+A_{1z}^2}{4H_0}\\&\times[I_1(I_1+1)-m_1^2]+\frac{A_{1x}Q'^2}{8}\bigg[\frac{C(m_1)C(m_1+1)}{A_{1x}^2-[2(m_1+1)Q']^2}\\&-\frac{C(m_1-1)C(m_1-2)}{A_{1x}^2-[2(m_1-1)Q']^2}\bigg]\bigg\}, \quad (3)\end{aligned}$$

and, similarly, for $H_y(m_1)$, with

$$H_0=h\nu/g_0\beta, \quad \epsilon_i=\sum_{i\neq j} A_{1j}^2/8H_0^2,$$

and

$$C(m_1)=I_1(I_1+1)-m_1(m_1+1). \quad (4)$$

The $\Theta=0°$ expression (H_z) is given to fourth order; the $\Theta=90°$ expressions (H_x and H_y) only to second order. Perturbation terms due to the chlorine hyperfine interaction are negligible; in the $\Theta=90°$ expressions even the direct chlorine hyperfine terms can be neglected.

Because of the large quadrupole interaction of the iodine, transitions involving a change in quantum number of both the nucleus and the electron become allowed. As Θ deviates slightly from 0°, the weakly allowed $|\Delta m_1|=1$ transitions become visible (Fig. 2 of Ref. 14); at $\Theta=90°$, the $|\Delta m_1|=2$ transitions are seen (Fig. 5). (These are also referred to as forbidden quadrupole lines.) The positions of the lines could not be fit with

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[21] W. Low, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Suppl. 2.

the equations given by Bleaney,[22] but required a higher-order perturbation calculation.

The $|\Delta m_1|=1$ transitions are considered first. Although these transitions are not allowed when the magnetic field is along a principal axis of the center, by observing these lines at a series of small angles their position at $\Theta=0°$ can be determined by extrapolation. Using the quantum number k (as in Ref. 22) with values $I_1-\frac{1}{2}, I_1-\frac{3}{2}, \cdots, -I_1+\frac{1}{2}$, the $|\Delta m_1|=1$ lines can conveniently be expressed as transitions between levels with $m_1=k\pm\frac{1}{2}$ and $m_1=k\mp\frac{1}{2}$. A second-order calculation shows that the resonant field positions of these lines extrapolated to $\Theta=0°$ for $\Delta m_1=+1$, $\Delta m_s=+1$ and $\Delta m_1=-1$, $\Delta m_s=+1$ are, respectively,

$$\begin{aligned} H_z(k,m_2)&=(g_0/g_z)\Big\{H_0-A_{1z}(1+\epsilon_z)k-A_{2z}m_2-2kQ' \\ &\qquad -\tfrac{1}{4}(A_{1x}+A_{1y})^2\frac{1}{H_0}[2I_1(I_1+1)-2k^2-\tfrac{3}{2}]\Big\}, \\ H_z(k,m_2)&=(g_0/g_z)\Big\{H_0-A_{1z}(1+\epsilon_z)k \\ &\qquad -A_{2z}m_2+2kQ'-\tfrac{1}{4}(A_{1x}+A_{1y})^2\frac{1}{H_0}[2I_1(I_1+1) \\ &\qquad -2(k-\tfrac{1}{2})(k+\tfrac{1}{2})]\Big\}. \end{aligned} \tag{5}$$

In order to describe the $|\Delta m_1|=2$ transitions for the magnetic field at $\Theta=90°$ along either of the two principal directions perpendicular to the molecular-axis of the center, it is convenient to use the quantum numbers m (again as in Ref. 22) with values $I_1-1, I_1-2, \cdots, -I_1+1$. The resonant field position for transitions from ($m_1=m\pm1$, $m_s=\frac{1}{2}$) to ($m_1=m\mp1$, $m_s=-\frac{1}{2}$) are (to second order)

$$\begin{aligned} H_x(m)=\frac{g_0}{g_x}\Big\{&H_0-A_{1x}(1+\epsilon_x)m\pm2mQ' \\ &-\tfrac{1}{4}(A_{1z}\pm A_{1y})^2\left[\frac{C(m+1)+C(m-2)}{H_0}\right] \\ &-\tfrac{1}{4}(A_{1z}\mp A_{1y})^2\left[\frac{C(m)+C(m-1)}{H_0}\right] \\ &+(\tfrac{1}{4}Q')^2\left[\frac{C(m)C(m-1)}{A_{1x}\pm2mQ'}-\frac{C(m)C(m-1)}{A_{1x}\mp2mQ'}\right. \\ &\left.+\frac{C(m+1)C(m+2)}{A_{1x}\mp2(m+2)Q'}-\frac{C(m-2)C(m-3)}{A_{1x}\pm2(m-2)Q'}\right]\Big\}, \end{aligned} \tag{6}$$

and similarly for $H_y(m)$.

TABLE II. Parameters of the spin Hamiltonian of $(I^{127}\ Cl^{35})^-$ in KCl:I:Pb measured at 4.2°K; all values (except g) in gauss. $Q'=-43\pm3$; linewidth (for $\Theta=0°$) ≤3.5.

	z,[110]	x,[1$\bar{1}$0]	y,[001]
g	1.855±0.007	2.392±0.007	2.326±0.008
A_1	394.5±1.5[a]	316±3	283±3
A_2	61.2±1.5[a]	<3	<4

[a] These values were incorrectly quoted in Ref. 14. The numbers given there were (g_0/g_z) times the correct value.

Careful examination of Eq. (6) reveals that the line positions are independent of the sign of A_{1x} (assuming A_{1y} has the same sign), but do depend upon the sign of Q' with respect to A_{1z}. This permits the determination of the sign of Q' from the ESR spectrum.

Using the measured line positions, the three components of g, A_1, and A_2 may be calculated by an iteration procedure from Eqs. (2) and (3). The A_z are positive since the magnetic moments of both I^{127} and Cl^{35} are positive. The A_x and A_y are assumed to be positive by analogy with the BrCl⁻ center for which Schoemaker[10] has shown $A_1>0$. The magnitude of Q' is determined from Eq. (3). In principle, its sign can be obtained from Eq. (2); however, more precise field measurements (to within 1 G) would be required.

The values of the parameters are presented in Table II. These values are then inserted into Eqs. (2), (3), (5), and (6) and the agreement with experiment can be determined. In this manner, the lines of the $\Theta=0°$ spectrum can be fit to within 3 G, the order of the experimental error in this case. The line positions computed from Eq. (3) agree with the spectra for H_0 along x and y to within 12 G. For Θ near 0° only the $|\Delta m_1|=1$ transitions at the high-field end of the spectrum could be clearly seen. Their positions, extrapolated to $\Theta=0°$, agreed with the calculations from Eq. (5) to within 5 G. Taking the sign of Q' as negative, Eq. (6) describes the position of the $|\Delta m_1|=2$ lines to within 14 G; with Q' taken as positive the discrepancies are about five times larger. It is clear that the negative sign for the quadrupole interaction is most consistent with experiment.

The remaining discrepancies in the calculation of the $\Theta=90°$ spectra for both the $|\Delta m_1|=0$ and $|\Delta m_1|=2$ lines arise from third- and fourth-order terms. The magnitudes of these terms are quite appreciable, some being as large as 20 G, thereby questioning the validity of the second-order calculation. However, when the parameters obtained by only considering terms of second order were inserted into the fourth-order expressions, the calculated line positions were shifted by less than 12 G, and, in fact, the fit with the experimental line positions was markedly improved. This indicates that although there are sizeable higher-order terms, they tend to cancel out, and that the second-order expression is quite adequate for calculating the parameters of the ICl⁻ center from the spectra.

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V. DISCUSSION

A. Thermal Properties

In the alkali halides, holes self-trapped in regions of the perfect lattice as V_K centers become mobile upon warming to sufficiently high temperatures. The mobile holes have two possible fates: Either they become retrapped at more stable sites within the lattice or they are destroyed by recombination with electrons trapped at defect or impurity sites. In the present experiments iodine ions residing substitutionally in the KCl host lattice provide efficient sites for hole capture; the new hole center thus formed is a ⟨110⟩-oriented mixed-halogen V_K center, ICl^-.

The process of thermal conversion of $Cl_2^- \rightarrow ICl^-$ is seen to be essentially identical in the two mixed-crystal systems studied. Details of this conversion process are discussed first for KCl:I:Pb. The Cl_2^- holes disappear sharply in the temperature region of 180 to 210°K. The Cl_2^- pulse annealing curve for KCl:I:Pb (Fig. 6) agrees with previous observations in KCl:Pb[2,17] for which it has been shown[8] that above its reorientation temperature of about 170°K the Cl_2^- hole begins to diffuse away by nearest-neighbor jumps. Three events follow the thermal release of Cl_2^- holes in KCl:I:Pb: (1) Hole capture at iodine-ion sites increases the number of ICl^- centers by at least a factor of 5 from the amount initially present after x irradiation. (2) Hole recombination with trapped electrons occurs, principally at (Pb^{++} + electron) sites, and results in the large thermoluminescent glow peak at 208°K. (3) A small degree of hole capture at the Pb^{++}-impurity sites forms some (Pb^{++}+hole) centers indicated by optical absorption increases in the region at 383 nm. (After thermal release of ICl^- holes at higher temperatures, a marked absorption-band growth at this wavelength occurs; these hole centers remain stable until considerably higher temperatures.)

In KCl:I a curious two-stage Cl_2^- annealing behavior is found (Fig. 6). It appears to combine the behavior one would obtain separately for the case of pure KCl and for that of the Pb^{++}-doped crystal. The first, low-temperature stage, in which about one-half of the Cl_2^- decay with little increase in ICl^-, is comparable with the pure-KCl behavior for which a nearly complete loss of Cl_2^- occurs by about 140°K. In the second, higher-temperature stage, analogous to that observed in KCl:I:Pb, the remaining half of the Cl_2^- holes disappear and the number of ICl^- increase by a factor of 3. In addition, a glow peak occurs near 208°K.

The anomolous low-temperature loss of Cl_2^- in pure KCl had previously been discussed by Delbecq, Smaller, and Yuster.[2] They noted that there is no significant thermal mobility of the Cl_2^- in doped crystals below 170°K and that the stability of the center appears intrinsic to a pure lattice environment and not a result of nearby impurities. Thus, they interpreted the low-temperature loss as an annihilation of stable Cl_2^- holes by electrons released from a small number of low-lying traps in this temperature region. The results here, using the I^- ions as probes of the Cl_2^- hole mobility, confirm this interpretation. Differences apparent in the low-temperature annealing of Cl_2^- in KCl:I and KCl can be attributed to formation of shallow electron traps differing in both depth and concentration.

The ICl^- center itself is thermally more stable than Cl_2^-; the release of the hole trapped between the I^- and Cl^- ions is marked in both KCl:I:Pb and KCl:I by a glow peak at 250°K. However, the rate of loss of ICl^- does not reach a sharp maximum at that temperature, as a small number of centers still remain after warming to 270°K. Schoemaker[11] has reported that in KCl:Br:Pb the thermal decay of ⟨110⟩-oriented $BrCl^-$ centers results in formation of a second, bent-angle ⟨110⟩ $BrCl^-$ center which is believed to be associated with a nearby positive-ion vacancy. However, in KCl:I:Pb no evidence is found of an analogous perturbed ICl^- center.

The disorientation temperature of the ICl^- is the lowest of all V_K centers observed. A preferential orientation can be maintained only below 14°K, as compared to 100°K for $BrCl^-$ [11] and 170°K for Cl_2^-.[2] Two effects likely contribute to this extremely low disorientation temperature for ICl^-: (1) The iodine ion, because of its large size disparity, must remain near the center of the lattice site in the KCl host lattice. Hence, relatively small thermal vibrations are sufficient to bring it closer to other Cl^- ions, and the hole may then undergo a transition bonding the iodine to a different Cl^- ion.[23] (2) A contributing, although perhaps less important effect is that the hole is more localized on the iodine (as seen in the ESR hyperfine spectrum) than in the case of $BrCl^-$ or Cl_2^-. Consequently, the overlap of the hole wave function among states bonding to different Cl^- ions is greater for ICl^-, thereby enhancing the transition rate and hence reorientation.

B. Optical Absorption

The observed optical absorption spectrum of the ICl^- center is analogous to that of X_2^- centers. Delbecq, Hayes, and Yuster[3] have discussed the optical absorption of the homonuclear X_2^- molecule-ion in terms of a molecular-orbital scheme. The ground-state electronic configuration is described by $\cdots\sigma_g{}^2\pi_u{}^4\pi_g{}^4\sigma_u{}^1({}^2\Sigma_u{}^+)$, and the excited states, in order of increasing energy, by $\cdots\sigma_g{}^2\pi_u{}^4\pi_g{}^3\sigma_u{}^2({}^2\Pi_g)$, $\cdots\sigma_g{}^2\pi_u{}^3\pi_g{}^4\sigma_u{}^2({}^2\Pi_u)$, and $\cdots\sigma_g{}^1 \times\pi_u{}^4\pi_g{}^4\sigma_u{}^2({}^2\Sigma_g{}^+)$. The twofold orbital degeneracies of the ${}^2\Pi$ states are removed by the orthorhombic crystal field. Parity allowed electric-dipole transitions are of the type $u \rightarrow g$: ${}^2\Sigma_u{}^+ \rightarrow {}^2\Sigma_g{}^+$ is allowed for σ-polarized and

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[23] The recent work of Murray and Keller (Ref. 6) has demonstrated the importance of lattice spacing on the thermal activation energy required for V_K motion: In three alkali iodides studied, the smaller the nearest-neighbor iodine separation, the lower was the observed activation energy for V_K motion.

${}^2\Sigma_u{}^+ \rightarrow {}^2\Pi_g$ for π-polarized light, respectively. In generalizing to the case for a heteronuclear XY^- molecule-ion, the lack of inversion symmetry makes the g and u labeling of orbitals no longer strictly valid. Nevertheless, under the assumption that the two effective nuclear charges are not too greatly different, the characterization of the ground- and excited-state electronic configurations will be the same as for X_2^-, except that the g and u labels are omitted. The corresponding electric-dipole transition selection rules will be weakened and hold only approximately. Schoemaker,[10] in studies of FX^- centers, introduced the indices 1 and 2 to distinguish the various orbitals. Following this notation, the ground state is $\cdots\sigma_1{}^2\pi_1{}^4\pi_2{}^4\sigma_2{}^1({}^2\Sigma_1{}^+)$ and, similarly, for the corresponding excited states ${}^2\Pi_1$, ${}^2\Pi_2$, and ${}^2\Sigma_2{}^+$.

The strongly σ-polarized 430-nm band of the ICl⁻ is assigned here to the ${}^2\Sigma_1{}^+ \rightarrow {}^2\Sigma_2{}^+$ transition. The two σ-polarized infrared bands at 840 nm and at about 1000 nm are assigned, respectively, to the ${}^2\Sigma_1{}^+ \rightarrow {}^2\Pi_{1a}$ and ${}^2\Sigma_1{}^+ \rightarrow {}^2\Pi_{1b}$ transitions; the indices a and b distinguish the two levels of the ${}^2\Pi_1$ state split by the crystal field and by spin-orbit coupling. There is no evidence of a ${}^2\Sigma_1{}^+ \rightarrow {}^2\Pi_2$ transition, forbidden for a homonuclear molecule as a $u \rightarrow u$ transition.

Although the perturbation calculation of the g factor for Cl_2^- by Inui *et al.*[24] is not strictly valid in the case of ICl⁻, his Eqs. (6b) and (6c) can be used to estimate the splitting between the ${}^2\Pi_{1a}$ and ${}^2\Pi_{1b}$ levels (namely, $\Delta_1-\Delta_2$) from the anisotropy of $g_\perp$. Using the experimentally determined values for g_x, g_y, and Δ_1, $\Delta_1-\Delta_2$ is computed to be 1200 cm^{-1}. This result is of the same order as the 1900 cm^{-1} splitting between the 840 nm (11 900 cm^{-1}) and the 1000 nm (10 000 cm^{-1}) bands. Thus the assignments of the two infrared transitions are consistent with the ESR data.

The predominant σ polarization of the 840-nm transition, in addition to its appreciable intensity relative to that at 430 nm, suggests a large admixture of ${}^2\Sigma_2{}^+$ into ${}^2\Pi_{1a}$ via spin-orbit coupling. A considerably lesser amount of admixture into ${}^2\Pi_{1b}$ would be required to account for the very weak intensity and near isotropy of the 1000-nm transition. The polarization and intensity behavior of the two infrared bands is qualitatively similar to that observed for the Br_2^- and I_2^- centers[3]; in both cases the effect of the large spin-orbit coupling constant of these halogens is significant. For the ICl⁻ center other effects of the appreciable iodine spin-orbit coupling can be noted in the ESR spectrum by the relatively large g shifts and by the large magnitude of the perpendicular components of the iodine hyperfine-structure constant.

Excitation in the 430-nm band leads to a decrease in the ICl⁻ concentration and the re-formation of Cl_2^- centers. No such effect is observed for 840-nm excitation. This loss of an ICl⁻ hole upon excitation at 430 nm is considered to indicate a delocalization of the ${}^2\Sigma_2{}^+$ state.

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