

EPR and optical absorption of a self-trapped hole in Rb_2ZnCl_4 crystals

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A self-trapped hole (V_k center) has been identified by means of electron paramagnetic resonance in single crystals of Rb_2ZnCl_4 x-irradiated at 77 K. This center presents a broad (~ 0.8 eV) absorption band at 385 nm which is anisotropic and σ polarized. The thermal and optical bleaching of the V_k centers has been studied through EPR and optical experiments.

I. INTRODUCTION

The processes and defects induced by ionizing radiation in simple halide crystals AX (A monovalent cation, X halogen anion) are well known at present and a number of review articles are available.¹⁻⁴ Progressively less is known in dihalide BX_2 (B divalent cation³⁻¹⁰) and trihalide ABX_3 (Refs 11-13) crystals, although it appears that photolytic damage is closely related in all these materials. The situation is much worse for tetrahalide A_2BX_4 crystals; Martín *et al.*¹⁴ have studied the x-ray-induced luminescence and the thermoluminescence of Rb_2ZnCl_4 , K_2ZnCl_4 , and Cs_2CdBr_4 crystals and have attributed the observed emission to intrinsic electron-hole recombination processes. The same authors¹⁵ have studied the optical absorption bands induced by low-temperature (10 K) x-irradiation in Rb_2ZnCl_4 , K_2ZnCl_4 , and $[(\text{CH}_3)_4\text{N}]_2\text{ZnCl}_4$ crystals as well as their thermal and optical stability. The authors have pointed out that a broadband at 370 nm which appears both in Rb_2ZnCl_4 and K_2ZnCl_4 samples has features of a V_k -type center, although a confirmation is needed.

The V_k center consists of a hole equally shared by two neighboring halide ions forming an X_2^- molecular ion. This defect has been identified in alkali halides,¹⁶ dihalides,^{7,16-19} and trihalides,^{16,20} and is of particular interest since it is thought to be the precursor to the production of Frenkel pairs by radiolysis. Thus, it is important to identify and characterize unambiguously the V_k center in the A_2BX_4 lattices in order to have a more complete picture of the radiation-damage mechanisms in halide crystals.

This paper presents for the first time the EPR spectrum associated to V_k centers produced by x-irradiation at 77 K in Rb_2ZnCl_4 . Also we have investigated the dichroic optical absorption of these self-trapped holes and have correlated both techniques by means of thermal and optical bleaching experiments.

Rb_2ZnCl_4 is paraelectric at high temperature with spatial group D_{2h}^{16} ($Pnam$) and lattice parameters $a=9.257$ Å, $b=12.726$ Å, $c=7.282$ Å; at 302 K it passes through an incommensurate phase; and at 189 K the unit cell triples along the a direction, becoming commensurate ferroelectric²¹ with spatial group C_{2v}^9 ($Pna2_1$). In this work, the crystallographic axes have been chosen according to

Günter *et al.*²² in such a manner that $b \simeq 3c > a > c$ in the high-temperature phase.

II. EXPERIMENTAL DETAILS

Rb_2ZnCl_4 crystals were grown by the Czochralski method under controlled atmosphere. The starting material was obtained from aqueous solutions and it was treated as described in Ref. 22. The samples for EPR or optical spectroscopy were cut and polished to the adequate size after orientation by means of x-ray diffraction.

X-irradiation was carried out at 77 K through a 2 mm thick aluminum filter using a kristalloflex 2 H Siemens apparatus with a tungsten target operating at 50 kV and 30 mA.

EPR measurements were performed with a Varian E-12, x-band spectrometer at 100 kHz field modulation. The temperature of the sample was controlled by a gas-flow temperature controller Varian E-257. Microwave frequency was measured with an HP 5342 A frequency counter. Absolute magnetic field measurements were achieved with a Bruker NMR gaussmeter ER 035 M.

Optical absorption measurements were made in a conventional cryostat with a Cary 17 spectrophotometer. A Glan-Thompson prism was used for polarized absorption measurements.

Optical bleaching was made by illuminating the sample inside the cryostat or the EPR cavity by means of a high-intensity Bausch & Lomb monochromator and a xenon lamp. Bleaching with polarized light was achieved by intercalating a Glan-Thompson prism between the sample and the monochromator. The thermal stability of the absorption bands and EPR spectrum was studied by means of an isochronal pulsed annealing technique, keeping samples for 2 min at each temperature.

III. RESULTS AND DISCUSSION

A. EPR spectra

Figure 1 shows the EPR spectrum measured at 85 K of a sample of Rb_2ZnCl_4 x-irradiated at LNT with the dc magnetic field parallel to the crystallographic c axis. The resemblance of this spectrum to those of V_k centers in alkali halides is remarkable.²³ The spectrum shows seven almost equally spaced lines with intensity ratios

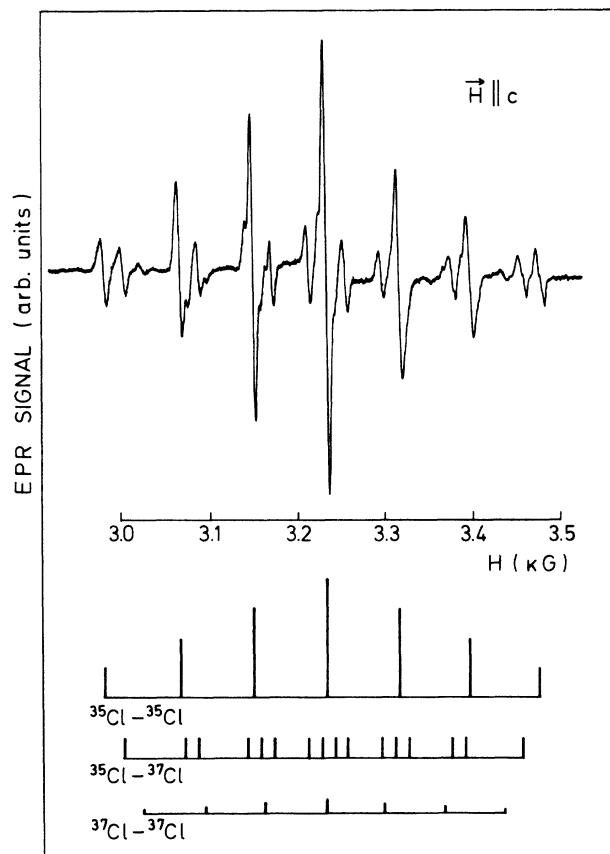


FIG. 1. EPR spectrum, measured at 85 K, with the external magnetic field along the crystalline c axis, of a Rb_2ZnCl_4 sample x-irradiated for 3 h at 77 K. The lower part of the figure shows the relative intensity and the position of the hyperfine lines for the three types of pairs of chlorine nuclei.

1:2:3:4:3:2:1, which is the typical feature of an electron or hole interacting with two equivalent nuclei of spin $\frac{3}{2}$ (Ref. 23). In our crystal, the most obvious candidate is a pair of chlorine nuclei. As ^{35}Cl is about $\frac{3}{4}$ abundant and has somewhat larger nuclear magnetic moment than ^{37}Cl which is $\frac{1}{4}$ abundant, there are three types of pairs: ^{35}Cl - ^{35}Cl , ^{35}Cl - ^{37}Cl , and ^{37}Cl - ^{37}Cl with relative abundance $\frac{9}{16}$, $\frac{6}{16}$, and $\frac{1}{16}$, respectively. The seven main lines observed are due to ^{35}Cl - ^{35}Cl pairs, the ^{35}Cl - ^{37}Cl pairs produce 16 lines of equal intensity (marked in Fig. 1) due to the non-equivalence of the two nuclei, and the ^{37}Cl - ^{37}Cl pairs produce a spectrum similar to that of ^{35}Cl - ^{35}Cl pairs, although with lower splitting (also schematized in Fig. 1). The position of the isotope lines is consistent with the magnetic moments and their intensity agrees with the isotope abundance. Moreover, the spectrum should arise from an electron deficiency (i.e., a hole) center, since an excess electron is unlikely to be at a pair of negative halide ions. This is also confirmed by the positive g shift (see below). Therefore, we ascribe the spectrum to a Cl_2^- molecular ion. From now on we will name this defect the V center.

It is known that the hyperfine splitting of a Cl_2^- molecular ion strongly depends upon the angle between

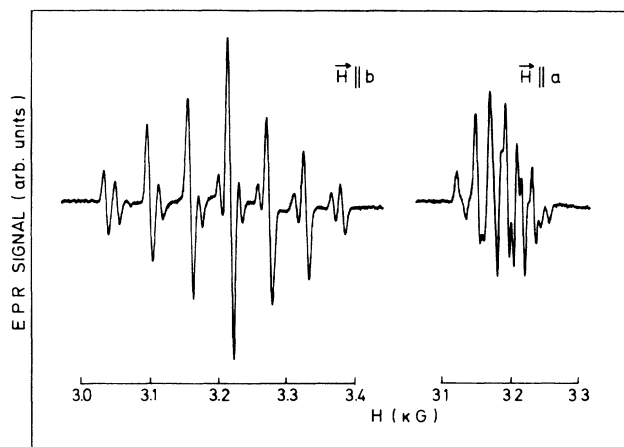


FIG. 2. EPR spectra, measured at 85 K with the external magnetic field parallel to either the a or b axes, of Rb_2ZnCl_4 samples x-irradiated at 77 K.

the molecular axis and the magnetic field in such a manner that the splitting decreases by increasing the angle.²³ When the sample is rotated in the ac or bc planes, it is observed that each line in the spectrum splits into two. This indicates that when the magnetic field \mathbf{H} lies into the ac or bc planes, there are two nonequivalent sets of axes for the defect. For \mathbf{H} parallel to either the crystallographic a or b axes the two sets of lines collapse again into one as it is shown in Fig. 2. Therefore, the orientations of the axis of the Cl_2^- molecule in the lattice are symmetric with respect to the ab , ac , and bc planes. The directions of the main axis (the molecular axis) of the defect can be inferred from the angular variation shown in Fig. 3. The axis is 9.5° out of the bc plane from a line at 35° from the c axis of the lattice, as can be seen in Fig. 4. This location gives rise to four different spectra of the V center for a general orientation of \mathbf{H} which reduce to two when \mathbf{H} lies into the ab , bc , or ac planes, and to just one for \mathbf{H} parallel to the a , b , or c axes.

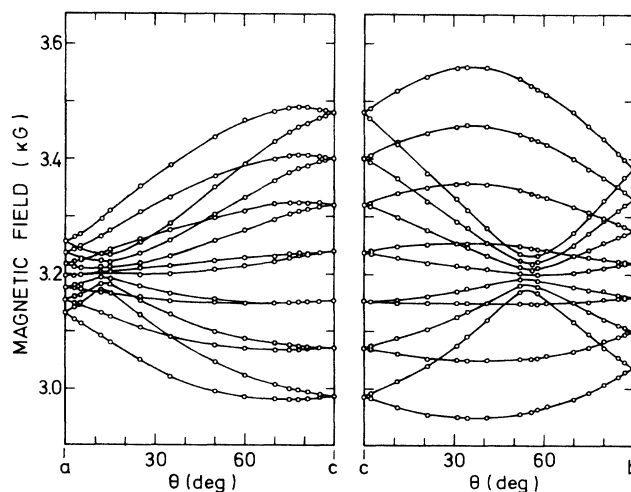


FIG. 3. Angular dependence of the EPR spectrum of the V center with \mathbf{H} in the ac and the bc planes.

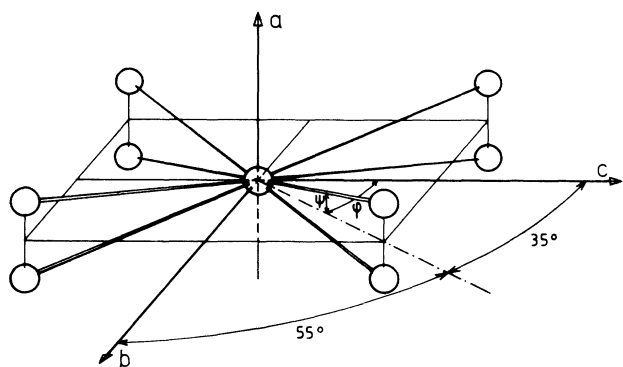


FIG. 4. Orientations of the main axis of the V center with respect to the crystalline axes.

As can be seen in Fig. 3, the seven main lines do not show splitting for any orientation of magnetic field. Thus, one must conclude that the defect is axially symmetric to a very good approximation and that the two nuclei are equivalent. An orthorhombic symmetry²⁴ or a "bending" of the molecular bond²⁰ would lead to a splitting of degenerate levels and the central hyperfine lines would split for some orientations of \mathbf{H} . Therefore, the spin Hamiltonian used to analyze^{25,26} the V -center spectra is (usual notation)

$$\begin{aligned} \mathcal{H}/g_0\beta_0 = & (1/g_0)[g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] \\ & + \sum_{K=1}^2 [A_{\parallel}S_zI_{z,k} + A_{\perp}(S_xI_{x,k} + S_yI_{y,k})] \\ & + P \sum_{K=1}^2 I_{z,k}^2 - (g_N\beta_N/g_0\beta_0)\mathbf{H} \cdot \sum_{K=1}^2 \mathbf{I}_k. \end{aligned}$$

The values obtained for the spin-Hamiltonian parameters from the fitting to the observed spectra are given in Table I. It must be pointed out that the quadrupolar parameter P could not be determined because the expected weakly allowed transitions ΔM_1 or $\Delta M_2 = \pm 1$ quoted by Schoemaker^{25,26} were not found in our crystals.

B. Optical absorption and kinetic aspects

A study of the optical absorption bands induced by low-temperature x-irradiation in Rb_2ZnCl_4 as well as in

other tetrahalides has been published recently.¹⁵ The absorption spectrum of Rb_2ZnCl_4 crystals show three bands at 210, 322, and ~ 370 nm. The latter one presents a large width (~ 0.8 eV) and markedly overlaps the band at 322 nm. In this work, the anisotropy of the absorption bands has been investigated in order to establish correlations between the optical absorption bands and the EPR spectrum due to Cl_2^- centers.

Absorption spectra were measured using light with propagation vector parallel to one of the lattice axes and with electric vector \mathbf{E} parallel to the other two axes. As an example, Fig. 5 shows the absorption spectra measured with light propagation along the b axis and with electric vector \mathbf{E} parallel to the a or c axis. It is clearly observed that the band at ~ 370 nm presents much higher absorption for \mathbf{E} parallel to the c axis than for \mathbf{E} parallel to the a axis, i.e., $\alpha_c > \alpha_a$, where α is the absorption coefficient. The subtraction of both curves gives the anisotropic absorption which peaks at 385 nm (Fig. 5). Similar experiments made with light propagating along the a and c axis, not plotted here for the sake of brevity, show that $\alpha_c > \alpha_b$ and $\alpha_b > \alpha_a$. This behavior would be the expected one for Cl_2^- centers oriented as shown in Fig. 4 if one assumes that the absorption of the Cl_2^- molecule is σ polarized, i.e., the optical transition is permitted for light with electric vector parallel to the molecular axis. Table II lists the positions and widths of the main absorption bands of different Cl_2^- centers in alkali chlorides and dichlorides. The values agree very well with our data: 385 nm and 0.8 eV. Moreover, all the absorptions quoted in Table II are anisotropic and, in a higher or lower degree, σ polarized. These similarities allow us to tentatively assign the 385 nm band to the same V center responsible for the EPR spectra discussed above.

In order to confirm this proposition, we have studied the optical and thermal bleaching of both the optical absorption and EPR spectrum. In a previous paper,¹⁵ it has been ascertained that by illuminating the irradiated sample at 10 K with 380 nm light both the 385 and 210 nm bands strongly decrease, whereas the band at 322 nm remains essentially unchanged. In fact, 5 min of bleaching makes the 385 nm band almost disappear. On the other hand, 5 min of illumination with 380 nm light at 90 K inside the EPR cavity, leaves the Cl_2^- spectrum almost unobservable.

TABLE I. Spin-Hamiltonian parameters for the Cl_2^- center in Rb_2ZnCl_4 (measured at 85 K) and the V_K center in other chlorine compounds (measured at 77 K). All parameters except g are given in G. ΔH is the linewidth between the peaks of the first derivative.

Material	g_{\parallel}	g_{\perp}	$^{35}A_{\parallel}$	$^{35}A_{\perp}$	ΔH	Ref.
Rb_2ZnCl_4	2.0013 ± 0.0005	2.0338 ± 0.0015	103.3 ± 0.1	12.0 ± 0.5	8.0 ± 0.5	This work
RbCl	2.00150 ± 0.00010	2.0430 ± 0.0002	101.92 ± 0.05	12.55	9.0 ± 0.5	26
KCl	2.00145 ± 0.00005	2.0434 ± 0.0001	101.31 ± 0.05	12.13	1.4 ± 0.1	26
NaCl	2.00132 ± 0.00010	2.0458 ± 0.0002	98.71 ± 0.05	9.04	5.6 ± 0.5	26
LiCl	2.00140 ± 0.00010	2.0500 ± 0.0002	95.54 ± 0.05	6.23	5.6 ± 0.5	26
SrCl_2	2.0020 ± 0.0004	2.0326 ± 0.0015	98.60 ± 0.25	10.3 ± 1.5		17
BaCl_2	2.0021 ± 0.0002	2.0444 ± 0.0005	97.7 ± 0.2	10.0 ± 2		19

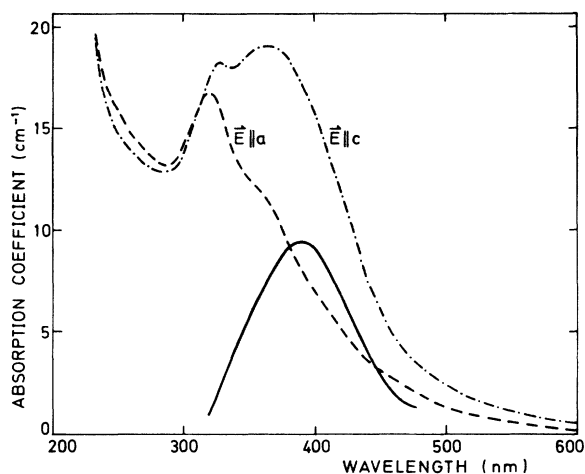


FIG. 5. Absorption spectra measured at 10 K with polarized light propagating along the b axis and with the electric vector \mathbf{E} parallel to either the a or c axis of a Rb_2ZnCl_4 sample x-irradiated for 3 h at 10 K. The continuous line shows the anisotropic absorption spectrum of the V centers.

The thermally induced pulsed annealing of the absorption bands and the EPR spectrum is plotted in Fig. 6. Most of the absorption at 385 nm annihilates near 110 K where the EPR spectrum of V centers strongly decays.

This parallel behavior confirms that both the 385 nm band and the EPR spectrum are produced by the same defect, the V center.

C. Model for the V center and conclusions

In order to establish a model for the V center, we have looked for directions of Cl^- pairs in the lattice of Rb_2ZnCl_4 that almost coincide with the orientations of the molecular axis of the V center determined by EPR and drawn in Fig. 4. Only a family of Cl^- pairs in the Rb_2ZnCl_4 lattice has very approximately the desired orientation (see Fig. 7). It must be noted that, below 189 K, the ZnCl_4^{2-} tetrahedra have various similar but not identical orientations in the lattice.²¹ This gives three different, although similar, sets of orientations for the Cl^- - Cl^- pair. The corresponding values for the φ and ψ angles, defined according to Fig. 4, are given in Table III. As these values are close to those corresponding to the V center obtained from the angular variation of the EPR spectrum, we propose the model for the center, which is

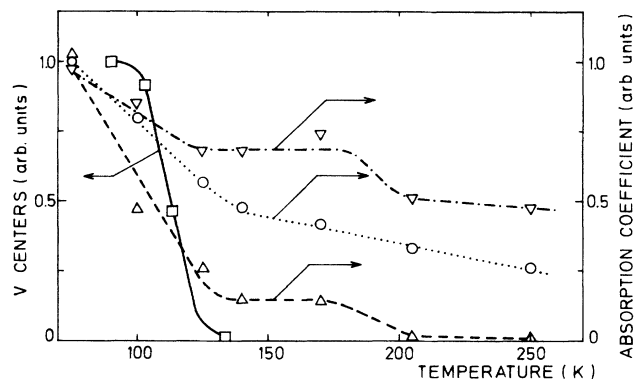


FIG. 6. Evolution with temperature of V centers (\square) as measured by EPR, and of the absorption bands at 385 (\triangle), 322 (\circ), and 210 nm (∇), for x-irradiated Rb_2ZnCl_4 samples.

depicted schematically in Fig. 7. The two Cl^- ions share a hole, and the center can be considered a self-trapped hole; consequently, it should be named V_k center.

Moreover, there are a number of arguments to propose that the detected Cl_2^- center is a self-trapped hole and not an H center, i.e., an interstitial halogen atom, namely, the following.

(i) In case of an H center, the Cl_2^- molecule should occupy a single Cl^- site. Then, the orientation of the molecular axis would be different to that observed or, likely, a different hyperfine structure, due to more than two Cl nuclei, would be observed.

(ii) The values for the position (385 nm) and width (0.8 eV) of the absorption band agree better than those for V_k centers in other materials than with those for H centers (see Table II).

(iii) The evolution of the 385 nm band with irradiation dose, measured in a previous work,¹⁵ presents saturation for ~ 2 h irradiation. This behavior is typical for a self-trapped hole center, and has been observed in alkali halides,²⁴ dihalides,⁹ and trihalides.²⁰

(iv) The high efficiency of the optical bleaching is also a characteristic behavior for a center with net charge, i.e., for a V_k center.

The distances between the two chlorine nuclei in the unperturbed lattice of Rb_2ZnCl_4 for the three sets of orientations are included in Table III. They are very similar to the Cl^- - Cl^- distance in the unperturbed lattice of KCl (4.44 Å) (Ref. 23) or NaCl (3.98 Å).²³ As the

TABLE II. Experimental absorption energies (nm) and linewidths (eV) of the UV band for different Cl_2^- centers in alkali chlorides and dichlorides.

Material	V_k	V_F	$V_{KA}(\text{Na})$	$V_{KA}(\text{Li})$	H	$H_A(\text{Na})$	$H_A(\text{Li})$
LiCl	394(1.47) ^a						
NaCl	378(1.12) ^a	373(—) ^c			330(~ 0.7) ^d		
KCl	366(0.81) ^a	360(0.74) ^c	355(0.85) ^c	352(0.79) ^c	335(0.66) ^c	357(0.65) ^c	354(0.70) ^c
RbCl	365(0.76) ^a			365(—) ^c			
SrCl_2	397(~ 0.8) ^b			379(~ 0.8) ^b			

^aFrom Ref. 27.

^bFrom Ref. 8.

^cFrom Ref. 26.

^dFrom Ref. 28.

^eFrom Ref. 4.

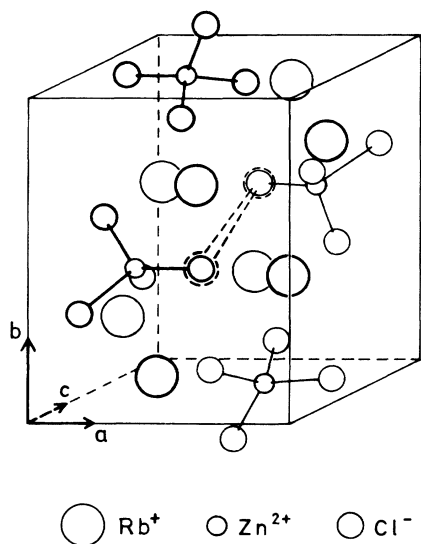


FIG. 7. Schematic model for the V_k center in the simplified crystal structure of Rb_2ZnCl_4 . The Rb atoms and ZnCl_4 groups drawn with thick lines lie on $\frac{1}{4}c$ and thin lines on $\frac{3}{4}c$.

value of the hyperfine parameter is very similar to those for the V_k centers in other materials (see Table I), it is expected that the internuclear distance of the Cl_2^- molecule be lower than in the Rb_2ZnCl_4 lattice, i.e., the two nuclei must pull together considerably as in single halides, dihalides, and trihalides. Thus, it is reasonable, in view of this relaxation, that in spite of the fact that there are three sets of orientations of the Cl^- - Cl^- pair in the unperturbed lattice, only one orientation of the Cl_2^- molecular axis appears in the EPR spectrum. In fact, as can be observed in Fig. 3, a deviation of 2° causes an appreciable splitting of the hyperfine lines. Therefore, the differences among the three possible orientations of the axis of the V_k centers in Rb_2ZnCl_4 , if any, should be considerably lower than in the perfect lattice.

Finally, it should be mentioned that we have attempted to make selective bleaching in both the optical and EPR spectrum by illuminating with polarized light almost parallel to the axis of a set of defects and perpendicular to the axis of another set, as it has been done in the study of Cl_2^- centers in alkali halides,^{29,30} dihalides,^{7,8} and trihalides.³¹ For example, by illuminating with light propagating along the a axis polarized at 35° from b axis, one should bleach the centers with their molecular axis at 55° from the b axis and leave unbleached the centers whose molecular axis is at -55° from b axis (see Fig. 4); thus, a clear difference should appear between the optical absorption spectra measured with polarized light at 55° and -55° from b axis. Clear differences should also be

TABLE III. Values of the φ and ψ angles for the three sets of perfect lattice orientations of the Cl^- - Cl^- pair, shown in Fig. 7. The values obtained for the V center are given for comparison. The distance between the chlorine nuclei for each set is also included (from Ref. 21).

	φ	ψ	Cl^- - Cl^- distance Å
Set 1	27.55°	5.23°	4.101
Set 2	28.51°	5.03°	4.238
Set 3	29.70°	5.22°	4.084
V center	35.0°	9.5°	

observed in the EPR spectrum, where one set of lines (those corresponding to centers at 55° from b) should diminish and the other set of lines (those corresponding to centers at -55° from b) should remain unchanged. At variance with those predictions our experiments produced a similar and strong decrease for both orientations of defects in the optical absorption as well as in EPR spectra. This result is apparently contradictory to the observed anisotropy in the optical absorption spectrum mentioned previously. We believe that the annihilation of both the 385 nm band and the EPR spectrum by optical bleaching is not due to the onset of mobility of the V_k centers. It should be attributed to the release of electrons from traps which recombine with the self-trapped holes. Besides, the absorption bands of the electronic centers should be isotropic and widely overlap the 385 nm band due to the V_k centers, which is clearly anisotropic. In this case, the optical absorption spectrum will show anisotropy, as observed, when measured with the very weak light of the spectrophotometer which does not produce an appreciable bleaching. On the other hand, the optical bleaching, which is made with the intense light of a xenon lamp, will produce a strong release of electrons which will annihilate the V_k centers irrespectively of their orientations. This hypothesis is supported by the fact that the optical absorption spectrum measured with \mathbf{E} almost perpendicular to the axis of the V_k centers (Fig. 5) shows a remaining isotropic absorption in the 350–450 nm range. This absorption which is not observed after bleaching with unpolarized light should be related to electronic centers.

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¹Ch. B. Lushchik, J. K. Vitol, and M. A. Elango, *Usp. Fiz. Nauk* **122**, 223 (1977) [*Sov. Phys. Usp.* **20**, 489 (1977)].

²R. T. Williams, *Semicond. Insulators*, **3**, 251 (1978).

³N. Itoh, *Adv. Phys.* **31**, 491 (1982).

⁴N. Itoh, *Cryst. Lattice Defects Amorph. Mat.* **12**, 103 (1985).

⁵H. W. den Hartog and J. Arends, *Phys. Status Solidi* **22**, 131 (1967); **23**, 713 (1967).

⁶W. A. Sibley and O. E. Facey, *Phys. Rev.* **174**, 1076 (1968).

- ⁷J. H. Beaumont, W. Hayes, D. L. Kirk, and G. P. Summers, *Proc. R. Soc. London A* **315**, 69 (1970).
- ⁸W. Hayes, R. F. Lambourn, G. Rangarajan, and I. M. Ritchie, *J. Phys. C* **6**, 27 (1973).
- ⁹P. J. Call, W. Hayes, J. P. Stott, and A. E. Hughes, *J. Phys. C* **7**, 2417 (1974).
- ¹⁰R. Alcalá, J. Casas González, and P. J. Alonso, *J. Lumin.* **26**, 141 (1981).
- ¹¹C. R. Riley and W. A. Sibley, *Phys. Rev. B* **1**, 2789 (1970).
- ¹²R. Alcalá, N. Koumvakalis, and W. A. Sibley, *Phys. Status Solidi A* **30**, 449 (1975).
- ¹³N. Koumvakalis and W. A. Sibley, *Phys. Rev. B* **13**, 4509 (1976).
- ¹⁴A. Martín, F. J. López, E. Diéguez, F. Agulló-López, and H. Arend, *Phys. Status Solidi B* **138**, 245 (1986).
- ¹⁵A. Martín, F. J. López, E. Diéguez, F. Agulló-López, and H. Arend, *Cryst. Lattice Defects Amorph. Mat.* **17**, 69 (1987).
- ¹⁶M. N. Kabler, in *Point Defects in Solids*, edited by J. H. Crawford, Jr., and L. F. Slifkin (Plenum, New York, 1972).
- ¹⁷H. Bill, H. Suter, and R. Lacroix, *Phys. Lett.* **22**, 241 (1966).
- ¹⁸M. Moreno, *Solid State Commun.* **16**, 1239 (1975).
- ¹⁹B. Houlier, *Solid State Commun.* **17**, 263 (1975).
- ²⁰T. P. P. Hall, *B. J. Appl. Phys.* **17**, 1011 (1966).
- ²¹M. Quilichini and J. Pannetier, *Acta Crystallogr. B* **39**, 657 (1983).
- ²²P. Günter, R. Sanctuary, F. Rohner, H. Arend, and W. Seidenbusch, *Solid State Commun.* **37**, 883 (1981).
- ²³T. G. Castner and W. Känzig, *J. Phys. Chem. Solids* **3**, 178 (1957).
- ²⁴W. Känzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1958).
- ²⁵D. Schoemaker, *Phys. Rev.* **174**, 1060 (1968).
- ²⁶D. Schoemaker, *Phys. Rev. B* **7**, 786 (1973).
- ²⁷A. N. Jette, T. L. Gilbert, and T. P. Das, *Phys. Rev.* **184**, 884 (1969).
- ²⁸W. H. Duerig and J. J. Markham, *Phys. Rev.* **88**, 1043 (1952).
- ²⁹C. J. Delbeck, B. Smaller, and P. H. Yuster, *Phys. Rev.* **111**, 1235 (1958).
- ³⁰C. J. Delbeck, W. Hayes, and P. H. Yuster, *Phys. Rev.* **121**, 1043 (1961).
- ³¹J. T. Lewis, J. L. Kolopus, E. Sonder, and M. M. Abraham, *Phys. Rev. B* **7**, 810 (1973).