centers. A forthcoming paper[46] will discuss the variation in α/F ratio shown in Fig. 9 and show that it is possible to account for this variation in terms of the competing processes of F-center bleaching by the luminescence and electron trapping by alpha centers.

V. SUMMARY

The principal results of this investigation may be summarized as follows:

1. The growth curves (α, F, "H," 2300-Å band and total vacancies) are not linear with dose.
2. The vacancy-production efficiency is slightly dose-rate dependent, but the α/F ratio is not.
3. The α/F ratio is not constant as the irradiation progresses, but it varies in the same way for all types or "qualities" of radiation.
4. The quality dependence of vacancy production follows the same trend reported previously for F centers.
5. Mechanisms involving the single ionization of two adjacent halide ions are the most probable cause of low-temperature vacancy production.

ACKNOWLEDGMENTS

The author thanks M. N. Kabler for many stimulating discussions, H. Rabin for very kindly reading the manuscript, and S. Slawson for preparing the crystals used in the orientation-dependence study.

---

[46] V. H. Ritz and M. N. Kabler (to be published).

PHYSICAL REVIEW VOLUME 142, NUMBER 2 FEBRUARY 1966

V_K Center in NH_4Br and NH_4Cl Single Crystals

Frank W. Patten and Michael J. Marrone
U. S. Naval Research Laboratory, Washington, D. C.

(Received 27 September 1965)

The EPR spectrum of Br_2^- in NH_4Br single crystals has been observed and fitted with an axial spin Hamiltonian. Optical transitions of the V_K center in NH_4Br and NH_4Cl have been identified and an interpretation of the radiation-induced 380-mμ absorption band, first observed by Rüchardt in both ammonium halides, is presented. These measurements show that the V_K center in the ammonium halides is essentially the same as in the alkali halides. A description is given of a procedure for determining the polarization of the two observed Br_2^- optical transitions, and they are both found to be largely σ-polarized. These polarizations can be explained by the generally accepted energy-level scheme.

INTRODUCTION

The ammonium halides offer the possibility of an interesting extension of the work done on radiation-induced defect centers in the alkali halides. Structural investigations have been performed on single crystals of NH_4Cl, NH_4Br, and NH_4I using the techniques of x-ray diffraction, infrared absorption, and nuclear magnetic resonance.[1] Each of these materials has three structure modifications in different temperature intervals[2]: a high-temperature phase in which the crystal structure is of the NaCl type, an intermediate-temperature phase within which the crystal structure is of the CsCl type, and a low-temperature phase resulting from an order-disorder transition due to reorientation of the ammonium ion.[3] At liquid-nitrogen temperature the ammonium ions are ordered in each material. The NH_4Cl crystal is of the CsCl structure, while NH_4Br and NH_4I have a distortion along one axis which makes the space lattice tetragonal.

Rüchardt[4] first observed radiation-induced optical absorption bands in pure and doped single crystals of NH_4Cl and NH_4Br at temperatures below 200°K. He ascribed an intense band occurring at 380 mμ (3.26 eV) in both the chloride and bromide to the NH_4^0 ion, which could result from an electron being stripped from a Cl^- ion and trapped by NH_4^+. Another small absorption band in the uv was not identified.

Zeller, Vannotti, and Känzig[5] have reported observing the electron paramagnetic resonance (EPR) absorption of Cl_2^- (termed the V_K center) in single crystals of NH_4Cl irradiated at liquid-nitrogen temperature. They found that the ground-state wave function for the unpaired electron of the Cl_2^- molecule ion differed little from NH_4Cl to NaCl. The local symmetry is higher in the ammonium halides because the Cl_2^- molecules are oriented along the $\langle 100\rangle$, as opposed to

---

[1] References to this work are contained in the two papers by Itoh, R. Kusaka, and Y. Saito, J. Phys. Soc. Japan **17**, 463, 481 (1962).

[2] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Vol. I.

[3] H. A. Levy and S. W. Peterson, Phys. Rev. **86**, 766 (1952).

[4] H. Rüchardt, Z. Physik **134**, 554 (1953).

[5] H. R. Zeller, L. Vannotti, and W. Känzig, Phys. Kondens. Materie **2**, 133 (1964).

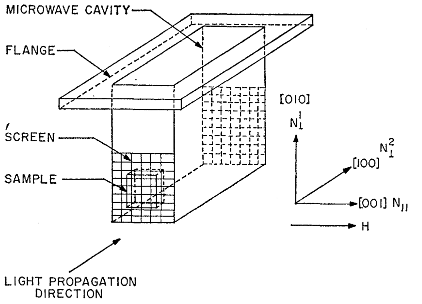

FIG. 1. Sample arrangement in the optical-microwave cavity and crystal axes orientation.

⟨110⟩ in the alkali halides, where these directions refer to the cubic axes.

The purpose of this work is to report the EPR observation of the Br_2^- center in NH_4Br single crystals and the identification of optical absorptions due to the V_K center in NH_4Br and NH_4Cl.

EXPERIMENTAL PROCEDURE

Single crystals of NH_4Cl, ND_4Cl, and NH_4Br were grown from saturated aqueous solution with urea added to stimulate a cubic crystal habit. Starting from saturation at about 40°C, the solution was placed in a closed vessel which was further immersed in a water bath regulated to within 0.01°C. The temperature was then lowered by about 0.1°C per day over a period of weeks. Though the NH_4Cl crystals were colorless, the NH_4Br crystals grown in this manner were colored slightly yellow, probably due to dissociated bromine; NH_4Br crystals grown at 20°C by slow evaporation of the solvent are colorless. NH_4I single crystals were also grown, but they invariably became polycrystalline masses when cooled to liquid nitrogen temperature, and could not be used. The crystals could not be cleaved. Instead, they were cut to size with a string saw and the rough surfaces were water-polished to smoothness. Chemical analysis for halogen content showed that the crystals were close to (better than 1%) stoichiometric composition. It was not possible to detect the presence of urea impurity using NMR and infrared (ir) absorption techniques.

The EPR data were taken with a conventional hybrid-T bridge spectrometer with crystal and superheterodyne detection, operating at both X and K-band frequencies. The low-temperature Dewar was of the "cold finger" type, with the sample mounted on an end or side wall of a rectangular TE_{012} mode microwave cavity which was cooled by conduction through a copper block in direct contact with the cryogenic fluid. The cavity wall on which the sample was mounted was an aluminum plate, flashed with a copper film, through which samples could be conveniently x rayed at low temperatures. Also, opposite sections of the cavity side wall were replaced with metallic screens for optical measurements on the sample while in the microwave Dewar. A diagram of this combination optical-EPR cavity with the sample arrangement is shown in Fig. 1. The sample was mounted on one of the screens and the remaining screen area was painted with an indium-gallium mixture to aid thermal conduction from the sample to the cold cavity walls. With this arrangement, the sample temperature was about 50°K with liquid helium in the Dewar.

The optical apparatus consisted of a Cary Model 14 MR spectrophotometer and a Dewar of conventional design with CaF_2 optical windows and a Be x-ray window. Polaroid sheet (type HR and HN) and interference filters were used for bleaching and absorption measurements with polarized light. The source of irradiating light was a tungsten lamp. The two interference filters used in these experiments were a 447-mμ filter, with peak transmission at 447 mμ and a half-band width of 13 mμ, and an 804-mμ filter with a half-band width of 14 mμ.

All irradiations were done with a Machlett OEG-60 x-ray tube with a tungsten target, operated at 50 kV dc and 40 mA. Samples were located from 5 to 7 cm from the target and exposure times were from 15 min to 1 h.

RESULTS

1. V_K Center—EPR

When single crystals of NH_4Cl and NH_4Br are irradiated with x rays at liquid nitrogen temperature or below, the x-ray induced EPR spectra are a superposition of three separate patterns. One of these is due to the V_K or X_2^- center,[6] where X represents a halogen atom. An interpretation of the second spectrum is discussed in Sec. 4; the third spectrum will not be treated in this paper.

Because the crystal structure is that of CsCl, the X_2^- bond axis is expected to lie along any of the three ⟨100⟩ crystal axes in a site of tetragonal symmetry, as opposed to orthorhombic symmetry in the alkali halides. Neglecting quadrupole effects, the data for both crystals can be fitted to an axial spin Hamiltonian:

$$\mathcal{H}=g_{\parallel}\beta H_zS_z+g_{\perp}\beta(H_xS_x+H_yS_y)+AI_zS_z+B(I_xS_x+I_yS_y), \quad (1)$$

with $S=\frac{1}{2}$, $I=I_1+I_2$, and $I_1=I_2=\frac{3}{2}$, and with the principal axes of the center along the ⟨100⟩. The unpaired spin density is the same on both nuclei, but there are two isotopes with different magnetic moments to consider for each halide. Bleaney[7] has derived the formula for the allowed transitions $(\frac{1}{2},m)\leftrightarrow(-\frac{1}{2},m)$ for all angles of applied magnetic field with respect to the symmetry axis. The measured constants in Eq. (1) for the isotopic combination $(Br^{81}-Br^{81})^-$ in NH_4Br are given in Table I, along with the values obtained by

---

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

[7] B. Bleaney, Phil. Mag. 42, 441 (1951).

TABLE I. Spin Hamiltonian constants for $(Cl^{35}-Cl^{35})^-$ and $(Br^{81}-Br^{81})^-$ in the ammonium halides, compared with the alkali halides.

Material	g_x $g_\perp$ g_y	$g_z(g_\parallel)$	A / $g_0\beta$ (gauss)	B / $g_0\beta$ (gauss)	Line-width (gauss)
NH_4Br	2.181	1.980	431	81	20
	±0.004	±0.002	±2	±10	±2
KBr[a]	2.179 2.175	1.980	455	80	2.8
NH_4Cl[b]	2.0437	2.0011	97.6	10	4.1
KCl[a]	2.0428 2.0447	2.0010	101	9	1.34

[a] Reference 6. [b] Reference 5.

Zeller *et al.*[5] for $(Cl^{35}-Cl^{35})^-$ in NH_4Cl; these are compared with values obtained by Castner and Känzig[6] for the V_K center in the corresponding alkali halides.

2. V_K Center—Optical

Delbecq, Hayes, and Yuster[8] have identified the optical absorption spectra of the V_K center in several alkali halides by correlating the changes produced in the optical and paramagnetic resonance spectra after irradiation with polarized light. Similar techniques have been used to identify optical absorptions for Cl_2^- and Br_2^- in the ammonium halides.

a. NH_4Br. Unirradiated NH_4Br single crystals were examined and found to be free of optical absorption bands in the spectral region from the fundamental absorption edge at 200 to 1200 mμ[9]; strong absorptions occur at longer wavelengths because of the NH_4^+ ion vibrations. The crystals were exposed to x rays at liquid nitrogen and liquid helium temperatures (approximately 80 and 10°K, respectively, in the optical Dewar). Since the results at both temperatures were qualitatively similar, only data obtained at liquid helium temperature will be presented. The absorption spectrum for most crystals contained a single intense band at 380 mμ, the band first observed by Rüchardt.[4] However, some NH_4Br starting materials resulted in crystals exhibiting additional x-ray induced bands which, as will be shown, are due to the V_K center. One of the latter spectra is shown in Fig. 2; absorption bands are apparent at 400 and 800 mμ. An optical density of 0.4 could be produced at 800 mμ in a sample 2 mm thick after 15 min x-irradiation.

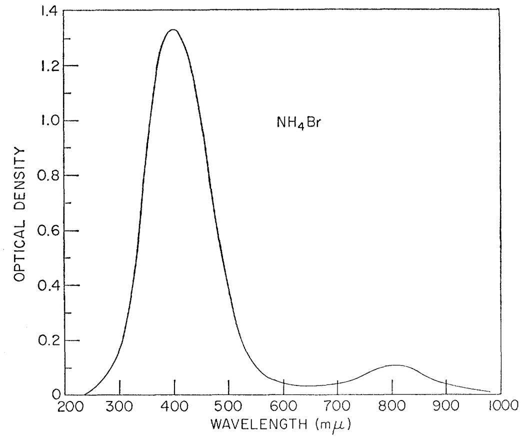

FIG. 2. Optical absorption spectrum in an NH_4Br single crystal x irradiated and measured at liquid-helium temperature.

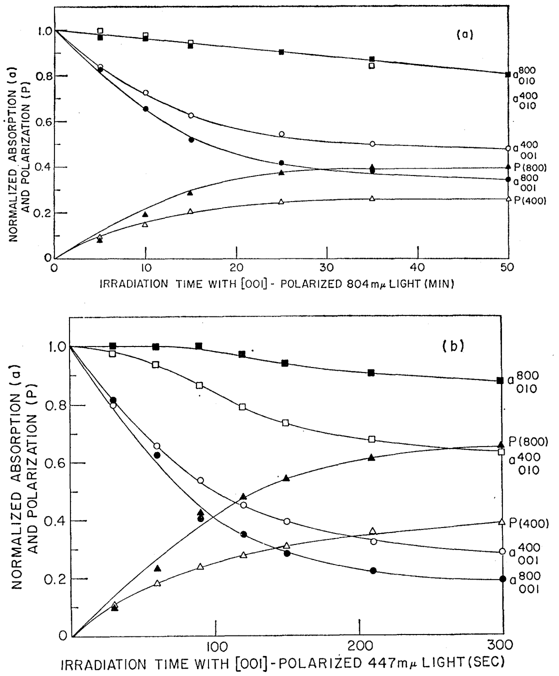

FIG. 3. Normalized absorptions, a_{001}^λ and a_{010}^λ, measured with [001]- and [010]-polarized light and polarization P at $\lambda=400$ and 800 mμ in NH_4Br at liquid-helium temperature, as a function of irradiation time with [001]-polarized light at (a) 804 mμ and (b) 447 mμ.

A ⟨100⟩ dichroism was produced in the 800-mμ absorption band by irradiating with [001]-polarized light[10] at 804 mμ. As a measure of the amount of dichroism produced within an absorption band, the polarization P is defined as

$$P(\lambda)=(a_{010}^\lambda-a_{001}^\lambda)/(a_{010}^\lambda+a_{001}^\lambda),$$

where a_{001}^λ is the ratio of optical density after irradiation with polarized light to the initial value before irradiation, both measured with [001]-polarized light at the peak of the absorption band, λ; a_{010}^λ is similarly defined. The absorption ratios a_{001}^λ and a_{010}^λ are referred to as "normalized absorptions" and are shown as a function of irradiating time in Fig. 3a.

---

[8] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1960).

[9] Absorptions, which vary greatly depending on crystal-growth conditions and starting material, are found at 350 and 390 mμ in some unirradiated ammonium bromide single crystals.

[10] All directions refer to the cube axes of the ammonium halide crystals. We will use the convention that [001]-polarized light means light with the electric vector polarized along the [001] direction. In these experiments, both irradiating light and measuring light have their direction of propagation along [100].

The anisotropic absorption is defined as the difference of normalized absorptions, $(a_{010}^{\lambda}-a_{001}^{\lambda})$; the position and half-width of the anisotropic absorption were found to be identical with the 800-mμ band.

After irradiating with [011]-polarized light at 804 mμ, no dichroism was observed for measuring light polarized along the orthogonal [001] and [01̄1] directions. Therefore, part, and possibly all, of the 800 mμ band is due to a center with a ⟨100⟩ transition moment.[11]

Similar experiments were performed on the band at 400 mμ to determine whether it, or a portion of it, could be due to a transition with a ⟨100⟩ electric dipole moment. Dichroism was induced in the band by irradiating at 447 mμ with [001]-polarized light, Fig. 3b. The anisotropic absorption had a peak at 400 mμ with a half-width of 0.80 eV; this width is about 0.2 eV less than that of the original absorption band. Irradiating at the same wavelength with [011]-polarized light produced no ⟨110⟩ dichroism.

⟨100⟩ dichroism could be produced in the 400-mμ band by irradiating with [001]-polarized light into the 800-mμ band, and ⟨100⟩ dichroism could be produced in the 800-mμ band by irradiating with [001]-polarized light into the 400-mμ band. These data are also shown in Figs. 3a and 3b. This indicates that the 400- and 800-mμ bands likely arise from the same center.

Using 804-mμ unpolarized light it was possible to bleach the 800-mμ band completely, along with part of the 400-mμ band. The remaining absorption band at 380 mμ had a half-width of about 1.0 eV. The difference curve obtained from the 400-mμ band before and after bleaching corresponded well with the anisotropic absorption band observed at 400 mμ. Assuming that the portion of the band at 400 mμ not due to a ⟨100⟩ transition moment is unaffected by the 804-mμ irradiation, the ratio of areas of the 400-mμ band to the 800-mμ band was found to be about 40:1 (Table II).[12]

In order to relate these dichroic absorption bands to the V_K center observed by EPR, simultaneous optical-EPR experiments were conducted on NH_4Br single crystals while mounted in the microwave cavity. After irradiating for successive time intervals with polarized light, the optical and EPR measurements both exhibited the same dichroism. Since these experiments relate to another measurement as well, they will be more fully explained later.

b. NH_4Cl. A similar set of experiments was performed on single crystals of NH_4Cl x rayed and observed at liquid helium temperature, with the following results: (1) Radiation-induced bands were observed at 380 and 790 mμ. (2) The band at 790 mμ, whose peak optical density after x raying for 6 h was 0.3 in a 3-mm-thick sample, and whose half-width was 0.37 eV, exhibited little or no ⟨100⟩ dichroism upon polarized 804- or 447-mμ irradiation. (3) A portion of the 380-mμ band showed ⟨100⟩ dichroism upon irradiation with polarized 447-mμ light. The anisotropic absorption exhibited a peak at 375 mμ with half-width about 1.0 eV; the remaining isotropic band, again with a 1.0-eV half-width, peaked at 385 mμ. (4) It was possible to partially bleach the band at 375 mμ with 804-mμ light. (5) A correlation was achieved between the dichroism of the 375-mμ band and the dichroism of the EPR spectrum of the V_K center. (6) A correlation was obtained between the bleaching rates of the 790-mμ absorption band and the EPR spectrum of the V_K center. Thus the evidence is consistent with the bands at 375 and 790 mμ being transitions of the V_K center.

TABLE II. Optical-absorption results for the V_K center in the ammonium halides and corresponding alkali halides.

Material	Absorption band peak position (mμ)	(eV)	Relative area of band	Half-width
NH_4Br	400	3.10	40	0.80
	800	1.55	1	0.27
KBr[a]	385	3.22	47	0.73
	750	1.65	1	0.26
NH_4Cl	375	3.31	100	1.0
	790	1.57	1	0.37
KCl[a]	365	3.40	100	0.81
	750	1.65	1	0.37

[a] Reference 8.

The optical data for the V_K center in both ammonium halides is tabulated in Table II, where a comparison is made with the results for the V_K center in the alkali halides.

3. Second Center

The x-ray-induced band at 380 mμ in both ammonium halides, first seen by Rüchardt, is thus shown to be a superposition of two bands, one of which is due to the V_K center. In NH_4Br crystals grown from reagent grade material, the V_K center absorption at 400 mμ was completely overshadowed by the intense band at 380 mμ. The fact that the bands shown in Fig. 2 are primarily the V_K center bands (the ratio of the amplitude of the V_K center band at 400 mμ to the amplitude of the other band at 380 mμ is about 3:1) would appear to be due to accidental impurities in NH_4Br which greatly enhance the production of V_K centers. In the NH_4Cl crystals studied, also grown from reagent grade materials, the amplitudes of the V_K center band at 375 mμ and the band at 385 mμ were approximately equal; the two bands coalesced to form the single band observed at 380 mμ.

Thermal annealing experiments, in which the samples were gradually warmed from 80 to 225°K, showed a correspondence between the disappearance of the

---

[11] W. D. Compton and H. Rabin, *Solid State Physics* (Academic Press Inc., New York, 1965), Vol. 16, p. 138.

[12] Delbecq, Hayes, and Yuster (Ref. 8) found a third band at 900 mμ for the V_K center in KBr. In NH_4Br there did not appear to be an additional absorption band on the long-wavelength side of the 800-mμ band, though a peak of 0.7 optical density was attained at 800 mμ.

NH_4Br 380-mμ band and the NH_4Cl 385-mμ band, at temperatures above 150°K, with the disappearance of a second paramagnetic species in each material whose EPR spectrum was superimposed on the V_K center spectrum. Irradiation with [001]- and [011]-polarized light at 447 mμ produced no dichroism either in the 380- and 385-mμ bands or in the EPR spectrum of the second species in NH_4Br and NH_4Cl.

The EPR spectrum of this second species has been found to be consistent with the molecule NH_3X, where X represents a halogen atom. The NH_3X axis lies along a ⟨111⟩ direction. There is good self-consistency among the spectra observed in single crystals of NH_4Cl, ND_4Cl, and NH_4Br, based on relative values of magnetic moment and unpaired spin density at the nuclei for hydrogen-deuterium and chlorine-bromine. A detailed analysis of this species will not be made here.[13]

4. Polarization of the Br_2^- Optical Transitions

It is of interest to learn whether the V_K center optical absorption bands are due to σ- or π-polarized transitions,[14] or mixtures of both, since this places symmetry restrictions on the initial- and final-state wave functions for the transitions. It can be seen that an optical polarization experiment, such as that discussed in Sec. 2, cannot unambiguously determine the polarization of a transition giving rise to one of the V_K bands without *a priori* knowledge of the dichroism produced by the irradiating light, i.e., the polarization of the transition induced by the irradiating light. Another complication that must be taken into account is the relative amounts of reorientation and annihilation of the V_K centers by the irradiating light. Since an EPR experiment can determine the relative numbers of centers along the three ⟨100⟩ crystal axes, a combination optical-EPR experiment has been performed to determine the polarization of the transition giving rise to the 800-mμ band in NH_4Br. The uv transition of the V_K center in NH_4Br could not be examined by this procedure because the presence of the overlapping 380-mμ band would confuse the results; however, knowing the polarization of the 800-mμ transition, one can determine the polarization of the 400-mμ transition solely from the optical dichroism data.

The sample arrangement and crystal axes orientation are as shown in Fig. 1; $N_{\parallel}$ represents the number of V_K centers with bond axis aligned along the magnetic field **H**, and $N_{\perp}=N_{\perp}^1+N_{\perp}^2$ represents the number with axis perpendicular to the field. An EPR measurement determines $N_{\parallel}/N_{\parallel}^0$ and $N_{\perp}/N_{\perp}^0$, the parallel and perpendicular populations relative to their initial values. The sample was irradiated for different time intervals with 804-mμ light with the electric vector polarized parallel to the magnetic field ([001]-polarized light), and after each interval optical and EPR measurements were made. The results of these measurements are shown in Fig. 4a.

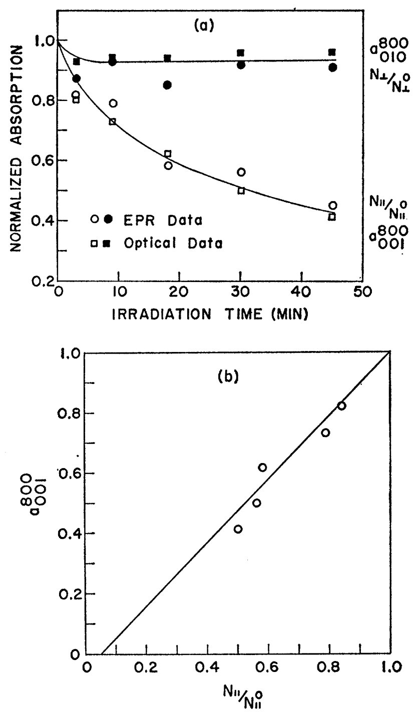

FIG. 4. (a) Combined optical and EPR amplitudes in NH_4Br at liquid-helium temperature for centers along and perpendicular to the [001] direction, versus irradiating time with [001]-polarized light at 804 mμ. (b) Plot of a_{001}^{800} versus $N_{\parallel}/N_{\parallel}^0$ [data taken from Fig. 4(a)].

The near coincidence of the data for a_{001}^{800} and $N_{\parallel}/N_{\parallel}^0$, as well as for a_{010}^{800} and $N_{\perp}/N_{\perp}^0$, indicates that the 800-mμ transition is largely σ polarized. A numerical estimate may be obtained by following the procedure given in the Appendix and plotting a_{001}^{800} versus $N_{\parallel}/N_{\parallel}^0$ to determine a linear relation (Fig. 4b); the value of the ordinate intercept leads to the result that the 800-mμ transition is entirely σ polarized, with a 10% maximum error.

The saturation polarization of the 400- and 800-mμ bands in NH_4Br after irradiation with [001]-polarized light at 804 mμ is observed, from Fig. 3a, to be 0.26 and 0.39, respectively. Both V_K absorption bands were then eliminated from this sample by sustained unpolarized bleaching at 804 mμ, in order to find the amplitude of the unaffected 380-mμ band. Using this value, the V_K absorption bands at 400 and 800 mμ were determined to have saturation polarizations of 0.36 and 0.39, respectively; it is concluded that both V_K center transitions have the same polarization (within 8%). Therefore, both V_K center absorption bands in NH_4Br are largely due to σ-polarized transitions.

---

[13] F. W. Patten and M. J. Marrone (to be published).

[14] σ- and π-polarized transitions are those allowed for light with the electric vector parallel and perpendicular, respectively, to the bond axis. Since a ⟨100⟩ oriented center lies at a site of tetragonal symmetry, the two transition moments perpendicular to the axis are equivalent.

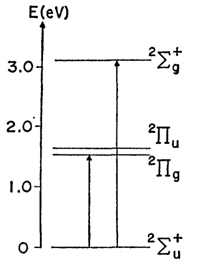

FIG. 5. Energy-level scheme for the V_K center in NH_4Br showing the allowed transitions.

It may now be concluded from the data of Figs. 3 and 4 that the net effect of irradiating at liquid helium temperature with either 447- or 804-mμ light is annihilation rather than reorientation of V_K centers in NH_4Br. Annihilation is also the predominant effect when bleaching at liquid-nitrogen temperature. However, the saturation polarization at liquid-nitrogen temperature was about $\frac{2}{3}$ the value obtained at liquid-helium temperature because bleaching of a_{010}^{800} was greater at the higher temperature.

DISCUSSION

The energy-level scheme for the V_K center has been based on molecular orbitals formed from a linear combination of atomic p orbitals.[15,16] This leads to a ground state $\sigma_g^2\pi_u^4\pi_g^4\sigma_u({}^2\Sigma_u^+)$, and excited states $\sigma_g^2\pi_u^4\pi_g^3\sigma_u^2({}^2\Pi_g)$, $\sigma_g^2\pi_u^3\pi_g^4\sigma_u^2({}^2\Pi_u)$ and $\sigma_g\pi_u^4\pi_g^4\sigma_u^2({}^2\Sigma_g^+)$. Since the site symmetry of the V_K center is tetragonal in the ammonium halides, the double degeneracy of each of the Π states is not removed by the crystalline field. The optical transitions are expected to be ${}^2\Sigma_u^+\rightarrow{}^2\Sigma_g^+$ (in the uv) with σ polarization, and ${}^2\Sigma_u^+\rightarrow{}^2\Pi_g$ (in the ir) with π polarization[8] (Fig. 5).

Spin-orbit coupling causes some mixing between states of the same parity. The amount of ${}^2\Pi_u$ admixture into the ground ${}^2\Sigma_u^+$ state can be determined from the variation of the ESR g factor from the free-spin value, using the g-factor calculation of Inui, Harasawa, and Obata.[16] With the data given in Table I, the ${}^2\Pi_u$ state for the NH_4Br V_K center is found[17] to lie 12 500 cm^{-1} (1.55 eV) above the ground state and there is about 7% admixture of the ${}^2\Pi_u$ state into the ground state. The energy-level scheme and optical transitions for Br_2^- are shown in Fig. 5.

Mixing of the ${}^2\Sigma_g^+$ and ${}^2\Pi_g$ states will also occur by the same process. Since the infrared transition for Br_2^- has been shown to be largely σ-polarized, it is reasonable to conclude that the ${}^2\Sigma_g^+$ admixture into the ${}^2\Pi_g$ state makes a much larger contribution to the transition moment of the infrared absorption than does the remaining ${}^2\Pi_g$. Letting δ represent the amount of ${}^2\Sigma_g^+$ admixture into the ${}^2\Pi_g$ state for the NH_4Br V_K center, its value can be determined from the data of Table II by relating the Einstein probability of absorption, B, to the oscillator strength of the transition, f, for both the ir and uv absorptions:

$$\frac{B_{\rm ir}}{B_{\rm uv}}=\frac{|\langle{}^2\Sigma_u^+|er|{}^2\Pi_g+\delta{}^2\Sigma_g^+\rangle|^2}{|\langle{}^2\Sigma_u^+|er|{}^2\Sigma_g^++\delta{}^2\Pi_g\rangle|^2}\approx|\delta|^2,$$

and

$$B_{\rm ir}/B_{\rm uv}\approx\lambda_{\rm ir}f_{\rm ir}/\lambda_{\rm uv}f_{\rm uv}\approx\lambda_{\rm ir}A_{\rm ir}/\lambda_{\rm uv}A_{\rm uv},$$

where λ and A refer to the wavelength and relative area of the ir and uv transitions. We have neglected the ${}^2\Pi_u$ contribution to the ground state. Then

$$|\delta|\approx(\lambda_{\rm ir}A_{\rm ir}/\lambda_{\rm uv}A_{\rm uv})^{1/2}=(1/20)^{1/2}.$$

This result predicts about 20% admixture of the ${}^2\Sigma_g^+$ state into the ${}^2\Pi_g$ state.

ACKNOWLEDGMENTS

The authors wish to thank J. H. Schulman for stimulating their interest in the ammonium halides and M. N. Kabler for many informative and critical discussions. The authors are grateful for the assistance of other members of the Materials Sciences Staff, in particular that of I. Schneider.

APPENDIX

With crystal axes orientation as shown in Fig. 1 and irradiating light at 804 mμ polarized along [001], the following additional quantities are defined:

$\alpha_\sigma=\sigma$-polarized fraction of the transition,

$\alpha_\pi=\pi$-polarized fraction of the transition,

$x(t)=N_{\parallel}(t)/N_{\parallel}^0,$

$\epsilon(t)=N_{\perp}^1(t)/N_{\parallel}^0=N_{\perp}^2(t)/N_{\parallel}^0,$

$y(t)=a_{001}^{\lambda}(t).$

Then

$$y(t)=\frac{\alpha_\sigma N_{\parallel}(t)+\alpha_\pi[N_{\perp}^1(t)+N_{\perp}^2(t)]}{\alpha_\sigma N_{\parallel}^0+\alpha_\pi N_{\perp}^0}=\frac{\alpha_\sigma x(t)+2\alpha_\pi\epsilon(t)}{\alpha_\sigma+2\alpha_\pi}.$$

Solving for the ratio of π to σ components:

$$\alpha_\pi/\alpha_\sigma=(x-y)/2(y-\epsilon)=C(\text{constant}).$$

The experimental results (Fig. 4a) show that one may take $\epsilon=1$, to obtain a linear equation:

$$y=x/(2C+1)+2C/(2C+1).$$

The ratio of π- to σ-polarized fraction of the transition, averaged over all experimental points, may be found from either the slope or ordinate intercept.

---

[15] M. H. Cohen, Phys. Rev. **101**, 1432 (1956).

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

[17] Reference 16, Eqs. (4) and (6). The following values were used: $\Delta g_{\perp}=0.177$, $\lambda=-2450$ cm^{-1}, and $1/(1+a^2)=0.57$.