

Recombination Luminescence from Self-Trapped Excitons in Ammonium Halide Crystals

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(Received 12 August 1968)

Luminescence due to intrinsic self-trapped exciton annihilation has been observed in ammonium halide single crystals under x irradiation at low temperatures. A broad emission band appears at 4.86 eV for NH_4Cl , 4.20 eV for NH_4Br , and 3.74 eV for NH_4I . The source of the luminescence is identified primarily through an experiment which relates the polarization of the luminescence to the orientation of self-trapped holes or V_k centers. As in the alkali halides, the self-trapped exciton may be characterized as a bound pair of nearest-neighbor halide ions in an excited state. The transition in NH_4Cl is σ -polarized with respect to the pair axis, and its lifetime under pulsed x -ray excitation is on the order of 10^{-8} sec. The NH_4Br emission band consists of two overlapping transitions. There is a fast σ -polarized component similar to that found in the chloride. The other component is π -polarized and has a longer lifetime of 7.7×10^{-7} sec. Comparison is made between these transitions and similar transitions previously observed in the alkali halides. It is concluded that the self-trapped exciton states are essentially the same in the two materials; in particular, a triplet state evidently initiates the long-lived emission band.

INTRODUCTION

NONACTIVATED alkali-halide crystals luminesce strongly under high-energy excitation at low temperatures. This luminescence has been studied extensively, particularly in the iodides,¹ and in the past several years has been shown to be due to intrinsic radiative decay of self-trapped excitons. The exciton traps itself in an ionic configuration evidently similar to that of the well-known self-trapped hole or V_k center, and self-trapped exciton luminescence can readily be produced by causing electrons to recombine with previously created V_k centers.²⁻⁴ Although the V_k center is itself a stable defect at low temperatures, the self-trapped exciton is a metastable excited state of the crystal and decays spontaneously to restore the perfect lattice. The present work was undertaken to observe and identify intrinsic luminescence in the ammonium halides and to compare the properties of this luminescence with those of the luminescence in alkali halides.⁵

Stable radiation-induced defects or color centers, which are for the most part analogous to those observed in the alkali halides, are now known to occur in the ammonium halides. The self-trapped hole, or V_k center, has been identified in NH_4Cl by means of EPR by Zeller, Vannotti, and Känzig.⁶ EPR and also optical-absorption bands of the V_k center in NH_4Cl and NH_4Br have been reported by Patten and Marrone.⁷ The hole may be regarded as being localized on a pair of nearest-

neighbor halide ions which are drawn together by a covalent bond to form an X_2^- molecular ion. Information concerning the V_k center is important for the present investigation because it provides the means of identifying the luminescent center and furnishes a useful model for the hole in the self-trapped exciton.

A summary of the relevant structures of ammonium-halide crystals is appropriate here.⁸ NH_4Cl has the CsCl structure below 184°C. A λ -point transformation at about -30°C leads to an ordering of the NH_4^+ ion orientations; below this temperature the space group is T_d^1 and the point symmetry about either the N or the Cl is T_d . V_k centers, which consist of nearest-neighbor Cl^- -ion pairs, lie along the $\langle 100 \rangle$ directions; the point symmetry of the V_k -center sites is D_{2d} . NH_4Br also has the CsCl structure at room temperature. Its λ -point transformation at about -38°C results, however, in a tetragonal lattice, space group D_{4h}^7 . The point symmetry about the NH_4^+ ion is D_{2d} ; that about the Br^- ion is C_{4v} . (This structure is identical to that of PH_4I , in which V_k centers have also been observed recently.⁹) Two distinct types of nearest-neighbor Br^- -ion pairs are possible. One, along the c axis, yields a V_k center of C_{4v} symmetry. The other, lying almost in $\langle 110 \rangle$ directions, produces a V_k center of C_{2h} symmetry with the axis of the center being perpendicular to the $\langle 110 \rangle$ symmetry rotation axis. It should be noted that, aside from the relative orientations of the NH_4^+ ions, the Br^- ions are displaced only about $0.03a_0$ from CsCl lattice positions. Thus for certain experiments, and in particular the previous V_k -center work,^{6,7} the actual tetragonal lattice is not evident, cubic symmetry is an adequate approximation, and NH_4Br appears structurally equivalent to NH_4Cl . NH_4I has the NaCl structure at room temperature, and around -18°C changes to the CsCl structure. The

¹ See K. Teegarden, in *Luminescence of Inorganic Solids*, edited by P. Goldberg (Academic Press Inc., New York, 1966), Chap. 2.

² M. N. Kabler, Phys. Rev. **136**, A1296 (1964).

³ R. B. Murray and F. J. Keller, Phys. Rev. **137**, A942 (1965); **153**, 993 (1967).

⁴ M. N. Kabler and D. A. Patterson, Phys. Rev. Letters **19**, 652 (1967).

⁵ A preliminary account of this work was presented by M. J. Marrone and M. N. Kabler, Bull. Am. Phys. Soc. **13**, 420 (1968).

⁶ H. R. Zeller, L. Vannotti, and W. Känzig, Phys. Kondensierten Materie **2**, 133 (1964).

⁷ F. W. Patten and M. J. Marrone, Phys. Rev. **142**, 513 (1966).

⁸ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Vol. 1.

⁹ C. L. Marquardt, J. Chem. Phys. **48**, 994 (1968).

λ -point transition results in a tetragonal lattice with site symmetries identical to those of NH_4Br . By way of comparison, alkali halides generally assume the NaCl structure and their V_k centers have $\langle 110 \rangle$ axes and D_{2h} point symmetry.

EXPERIMENTAL PROCEDURE

The crystals used in these experiments were grown at room temperature from aqueous solution containing urea to stimulate growth in a cubic habit. The starting materials were Fisher, Mallinckrodt, or Merck analytical reagent grade chemicals, and no impurities or luminescent activators were intentionally added. Although weak impurity absorption bands at 250 and 295 nm in NH_4Cl and at 250 and 375 nm in NH_4Br were sometimes apparent, these bands were never present with sufficient optical density to cause any appreciable distortion in the radiation-induced emission or absorption spectra. Because the crystals could not be cleaved, most samples were removed from solution when they reached a convenient size for optical measurements (typically $9 \times 9 \times 2$ mm). The faces were then water polished so that the edges remained $\langle 100 \rangle$ directions. Upon cooling, the NH_4Cl and NH_4Br crystals remained transparent and free of cracks. However, the NH_4I crystals cracked severely and became translucent when cooled past the -18°C phase change from the NaCl to the CsCl structure. The loss of transparency proved a serious handicap and limited the data obtained for NH_4I .

All experiments were carried out at liquid-nitrogen temperature (LNT) or liquid-helium temperature (LHeT) in a rotatable-base Dewar with quartz optical windows and a beryllium x-ray window. The optical-absorption measurements were made with a Cary Model 14 MR spectrophotometer. The apparatus for recording the emission spectra consisted of a grating monochromator, quartz lenses, and an EMI 9558 QB photomultiplier tube. The relative spectral response of the entire emission-detection system was measured by means of a quartz-iodine tungsten-filament lamp calibrated through the National Bureau of Standards. The emission spectra are fully corrected and are given in units of photons per unit energy. In most cases the monochromator bandpass was 7.4 nm.

The x-ray excitation of luminescence was accomplished with a constant potential tungsten target x-ray tube operated at 50 kV dc. A typical tube current of 1 mA with x rays filtered through 2 mm of aluminum gave sufficient luminescent intensity. The source used for optical excitation was a tungsten lamp imaged through a grating monochromator. Experiments involving polarized light were performed with a Polacoat ultraviolet polarizing filter (type PL40), a Polaroid sheet (type HR or HN), or a Glan-Thompson prism.

Measurements of radiative lifetimes were made using pulsed x-ray excitation from a tungsten target bom-

barded by 500-kV electrons.¹⁰ The pulse width was approximately 5 nsec, giving adequate time resolution. The luminescent pulses were transmitted through a grating monochromator and detected with an Amperex PA56U photomultiplier system which fed directly into a Tektronix 585A oscilloscope.

RESULTS

A. Absorption Bands of the V_k Center

The optical absorption bands due to the V_k or X_2^- center in NH_4Cl and NH_4Br have been described previously.⁷ A brief review of those data relevant to the identification of the recombination luminescence is given here. Curve a of Fig. 1 illustrates a typical absorption spectrum of an NH_4Br crystal after x irradiation at LHeT. Although none of the crystals has been doped with electron-trapping impurities to enhance the production of stable V_k centers, the NH_4Cl and NH_4Br crystals grown from all three starting materials yielded substantial concentrations of V_k centers upon x irradiation. Optical dichroism can be produced in the V_k absorption bands by bleaching with plane polarized light. Curve b of Fig. 1 shows the dichroic absorption of the Br_2^- center in NH_4Br .¹¹ As noted above, although NH_4Br is tetragonal below -38°C the actual departure from the CsCl structure is small and the dichroic spectra are consistent with V_k centers lying along $\langle 100 \rangle$ cube axes parallel to the sample edges. The V_k absorption spectrum for NH_4Cl is similar to that for NH_4Br , although the anisotropy of the infrared transition is so small that it is difficult to detect in the dichroic spectrum.

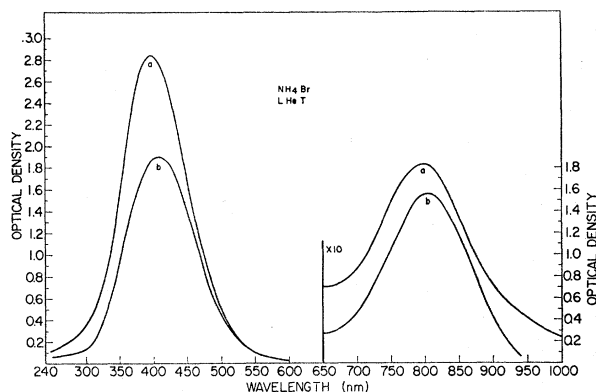


FIG. 1. (a) X-ray-induced absorption in NH_4Br at liquid He temperature. (b) Anisotropic absorption of the Br_2^- center obtained by subtracting the optical density measured with $[001]$ -polarized light from that measured with $[010]$ -polarized light after bleaching with $[001]$ -polarized 400-nm light. For $\lambda > 650$ nm, the optical density has been multiplied by 10.

¹⁰ Electron pulses obtained from a Field Emission Corp. Febetron 706 pulsed electron accelerator.

¹¹ The dichroic absorption is obtained by subtracting the optical density measured with $[001]$ -polarized light from that measured with $[010]$ -polarized light after bleaching with $[001]$ -polarized light.

The V_k bands were always the major component apparent in the absorption spectra. However, another band, tentatively ascribed to a NH_3Cl or NH_3Br center,⁷ was generally found at about 375 nm in the chloride and 395 nm in the bromide superimposed on the ultraviolet V_k band. After bleaching in the infrared V_k band until most of the V_k centers were destroyed, it was found that the NH_3X center contributed less than 25% of the initial absorption in the ultraviolet region. Moreover, it did not appear that bleaching with polarized light produced any dichroism in the NH_3X band. Thus, for the purposes of the present work, a measure of the number of V_k centers oriented along one [100] direction relative to another is given by the dichroic absorption. V_k centers in NH_4I were not investigated because of the sample difficulties caused by the -18°C phase change.

B. X-Ray Excited Luminescence

X-ray excitation at LNT consistently produced a single prominent emission band in all samples of the three ammonium halides. For reasons to be set forth, this emission is believed to be intrinsic electron-hole recombination luminescence. Figure 2 shows the emission bands prior to the growth of radiation-induced absorption sufficient to distort them significantly. Although absolute efficiency measurements were not made, the conversion of absorbed x-ray energy to luminescence appears to be an efficient process, as it is in the alkali halides. At LHeT, the luminescent efficiencies for NH_4Cl and NH_4Br were approximately the same as at LNT. Because of the uncertainty in the temperature of polycrystalline samples, NH_4I was investigated only at LNT. In NH_4Cl and NH_4Br , thermal quenching of the luminescence occurred in the vicinity of 90°K . No intrinsic luminescence was observed at room temperature for any of the ammonium halides.

In NH_4Cl and NH_4Br there appeared an additional band, not shown in Fig. 2, in the region of 400 nm for both crystals. The initial magnitude of this band at LHeT varied from sample to sample between 1 and 50% that of the intrinsic band. Also, a similar band could be excited in the unirradiated crystal at room temperature with light in the 270–290 nm range. These two facts suggest that at least most of this 400-nm emission is due to an impurity. In addition, illumination of irradiated crystals near 650 nm produced transient intrinsic emission but none of the 400-nm emission. This will be described in detail in the next section. The 400-nm band will henceforth be ignored, since there is no evidence that it is intrinsic.

C. Optically Excited Luminescence

The following experiment was performed to determine if, as in the alkali halides, the optical release of

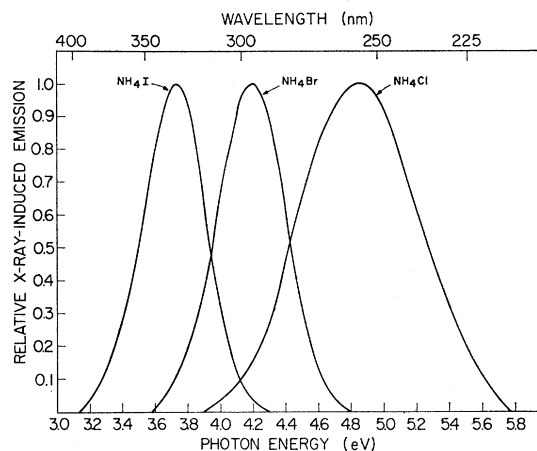


Fig. 2. Emission spectra under x-ray excitation for NH_4Cl and NH_4Br single crystals at liquid He temperature and for NH_4I polycrystalline samples at liquid N_2 temperature. The spectra have been corrected for the response of the detection system and the ordinate has been adjusted to give the relative number of emitted photons per unit energy.

electrons trapped during prior irradiation would annihilate V_k centers and give rise to intrinsic recombination luminescence. Crystals were exposed to x rays at LHeT to produce V_k centers and electrons, the electrons presumably becoming trapped at imperfections. Monochromatic exciting light was then scanned through the spectral range 300–1200 nm. Red light was found to excite the intrinsic emission bands in NH_4Cl and NH_4Br ; no other excitation or emission bands were observed. These excitation bands, shown in Fig. 3, proved too weak to observe in absorption. The emission spectra appeared identical to those of Fig. 2, although the measurement accuracy was somewhat limited by the rapid decay of the luminescent intensity upon sustained illumination. Only 5–10% of the V_k centers could ultimately be bleached by the red light. Although

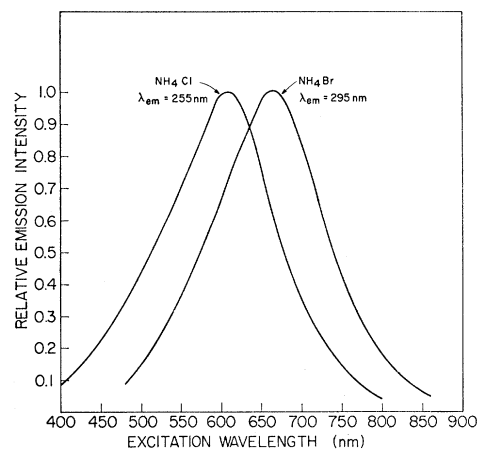


Fig. 3. Optical excitation spectra for the NH_4Cl 255-nm emission, and the NH_4Br 295-nm emission after the crystals had been x irradiated at liquid He temperature.

the nature of these optical excitation bands is unknown, it is reasonable to attribute them to imperfections or impurities which had trapped electrons. Absorption by light then results in the electrons being released to recombine with V_k centers, giving luminescence indistinguishable from that which is excited directly with high-energy radiation. The location of those electrons complementary to the remaining 90–95% of the V_k centers is unknown, because they produce no identifiable optical absorption or excitation in the spectral range investigated. NH₄I at LNT also had a weak excitation band at about 690 nm which was similar to those for the chloride and bromide. In considering the nature of the excitation bands in all three crystals, it may be noted that the peak positions do not follow a Mollwo-Ivey relation with the lattice parameter, as does the F band in alkali halides, for example.¹²

D. Polarized Luminescence

In order to confirm the identity of the luminescent center, a crystal of NH₄Cl was irradiated with x rays at LHeT and the resulting V_k centers were oriented with 380-nm light polarized along a cube axis. The degree of orientation achieved was greater than 70% as estimated from the dichroic V_k absorption. The luminescence at 255 nm under subsequent x irradiation exhibited an initial polarization of +20% throughout the band.¹³ This polarization must have been due to irradiation-produced internal photoelectrons annihilating some of the oriented V_k centers. Thus evidently the NH₄Cl band in Fig. 2 is due to intrinsic electron-hole recombination, the hole being self-trapped throughout the process. The sense of the polarization indicates that the emission is at least primarily a σ transition.¹⁴ The magnitude of the polarization cannot be regarded as significant, since the fraction of the x-ray-produced electrons which annihilated oriented holes was not determined. The partially overlapping dichroic absorption of the oriented V_k centers was determined to have been insufficient to affect the result; in fact, the polarization of the luminescence if caused by the overlapping absorption would have been negative, while the observed polarization was positive.

An experiment similar to the above was carried out with an NH₄Cl crystal using optical instead of x-ray excitation. The maximum polarization of the 255-nm luminescence under 605-nm excitation was +35%. Although the magnitude of the polarization is again not highly significant, it is apparent that the effect is more pronounced for the case of optical excitation,

¹² J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962), p. 52.

¹³ Polarization is defined by $P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$, where I_{\parallel} and I_{\perp} are the intensities of the emission with electric vector parallel and perpendicular, respectively, to the direction along which the V_k centers are aligned.

¹⁴ σ - and π -polarized transitions are those for which the electric vector of the emitted light is parallel and perpendicular, respectively, to the bond axis.

where more of the electrons recombine with oriented V_k centers.

Polarized luminescence under steady-state excitation proved more difficult to achieve in NH₄Br for two reasons. First, the magnitude of the effect appeared to be smaller, and second, the correction due to spectral overlap with the dichroic 400-nm V_k band was greater and always had to be included. Both x-ray and optical-excitation experiments like those described above yielded a polarization of -5% for the 295-nm NH₄Br emission. As described in the next section, this low value for the polarization was due to the fact that the emission consisted of two overlapping components of opposite polarization.

E. Lifetime Measurements

The decay of the intrinsic emission in NH₄Br and NH₄Cl after pulsed x-ray excitation was measured at LHeT. The 295-nm band in NH₄Br was found to consist of two time components. About 85% of the total emission was associated with an approximately exponential component of lifetime 0.77 ± 0.04 μ sec; the remainder had a lifetime of between 5 and 10 nsec. The spectra of both components were essentially the same as that for steady-state excitation, with the possibility that the peak for the fast component might have been at slightly lower energy. The polarization of the two decay components was measured after V_k centers had been introduced into the crystal and oriented. The slow component was found to correspond to a π transition moment, while the fast component was associated with a σ transition moment. Because both components exhibited partial polarization when the V_k centers were oriented, they both must have originated from intrinsic electron-hole recombination. Since one component was σ -polarized and the other π -polarized, two distinct excited states were evidently involved even though the emission spectra were approximately equivalent. The previously mentioned polarization value of -5% measured under steady-state optical excitation was found to be consistent with the relative intensities of the two oppositely polarized components.

Under conditions similar to those above, the decay of the NH₄Cl emission at 255 nm indicated a single component of lifetime between 5 and 10 nsec. Its spectrum agreed with that of Fig. 2. The presence of weak components having the same spectrum but longer lifetimes was not ruled out experimentally. However, the initial instantaneous photomultiplier current due to such components was at least six orders of magnitude less than that of the peak of the 5–10 nsec component. Lifetime measurements were not made for NH₄I.

DISCUSSION

The principal results which support the conclusion that the emission bands of Fig. 2 are intrinsic luminescence associated with electrons recombining with self-

trapped holes are summarized as follows: (1) The consistent appearance under x-ray excitation at LHeT of a single strong emission band in crystals grown from a variety of starting materials is taken as an indication the band arises from a transition characteristic of the pure crystal and is not associated with an impurity. (2) Although the excitation bands of Fig. 3 are not coincident with any of the known V_k absorptions, illumination into these bands destroys V_k centers and gives rise to luminescence whose wavelength is shorter than that of the exciting light. That is, the luminescence has a negative Stokes shift. (3) In crystals containing preferentially oriented V_k centers, a correspondence is found between the symmetry of the oriented centers and the polarization properties of the luminescence. Since the polarization of the luminescence would in general be lost if V_k centers migrated to and annihilated some other defect, the emission bands associated with the optical excitation bands of Fig. 3 are ascribed to electrons recombining with stationary V_k centers. The same mechanism is evidently responsible for the x-ray excited luminescence, inasmuch as the optical and x-ray excitation yield identical emission spectra and, in the presence of oriented V_k centers, polarized luminescence is also observed under x-ray excitation. The data on NH_4I are alone not sufficient to identify the source of its luminescence. However, since its properties which have been measured are quite similar to those of the other crystals, the NH_4I luminescence is tentatively assumed to be intrinsic.

This procedure for identifying the luminescent center is essentially that followed previously with the alkali halides.² Other relevant experiments have been performed on alkali halides; in particular, ultraviolet excitation in the spectral region of the exciton absorption bands has been shown to give luminescence with spectra similar to those resulting from high-energy irradiation and from electron- V_k -center recombination.¹ This kind of correlation, which can in principle relate particular exciton band states to particular self-trapped exciton states, has not yet been attempted for ammonium halides. It is worth pointing out that the self-trapped-exciton concept is nevertheless applicable in the present case, since in the limit of small lattice relaxation a given state of the V_k -center-electron bound pair would in principle be expected to go over into some exciton band state, which might or might not be apparent in optical-absorption or excitation spectra.

In order to compare in more detail the ammonium-halide luminescent properties with those of the alkali halides, it is useful to recall certain general features of the latter emission.²⁻⁴ In NaCl, KBr, RbBr, KI, and RbI at low temperatures, both σ and π self-trapped exciton transitions have been identified. In each material the σ transition is allowed and occurs at a higher photon energy than the π transition, which is

TABLE I. Luminescent transitions of self-trapped excitons in ammonium and alkali halides at liquid He temperature (liquid N_2 temperature for NH_4I). r_0 is the nearest-neighbor halide-ion separation in the appropriate perfect lattice. The two r_0 values given for NH_4Br and NH_4I apply to the two distinct halide-ion pairs in the tetragonal lattice.

| | Polarization | $h\nu$ (eV) | τ (sec) | r_0 (Å) ^a |
|------------------------|--------------|-------------|-----------------------------|------------------------|
| NH_4Cl | σ | 4.86 | $5-10 \times 10^{-9}$ | 3.82 |
| NaCl | σ | 5.6 | $\approx 5 \times 10^{-9}$ | 3.94 |
| | π | 3.38 | 2.95×10^{-4} | |
| NH_4Br | σ | 4.2 | $5-10 \times 10^{-9}$ | 4.03, 4.04 |
| | π | 4.20 | 7.7×10^{-7} | |
| NaBr | π | 4.60 | 4.9×10^{-7} | 4.18 |
| KBr | σ | 4.42 | $\approx 9 \times 10^{-9}$ | 4.63 |
| | π | 2.27 | 1.3×10^{-4} | |
| RbBr | σ | 4.20 | $\approx 11 \times 10^{-9}$ | 4.84 |
| | π | 2.10 | 1.8×10^{-4} | |
| NH_4I | \dots | (3.74) | \dots | 4.37, 4.37 |
| NaI | π | 4.20 | 9×10^{-8b} | 5.54 |

^a R. W. G. Wyckoff (Ref. 8); r_0 values extrapolated to LNT on the basis of thermal expansion.

^b W. Van Sciver and L. Bogart (Ref. 15).

forbidden. In NaI, NaBr, KCl, and RbCl only a forbidden π transition has thus far been observed. It has proved possible to account adequately for the lifetimes and polarizations of the two transitions in terms of electronic states of a simple diatomic molecule comprising a V_k center plus an electron.^{2,4} According to this analysis, the σ transition is ${}^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ and the π transition is ${}^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$. Both excited states have the hole or V_k -center core in its lowest state, $\sigma_u n p^2 \Sigma_u^+$, and the electron in a $\sigma_g(n+1)s$ orbital. The forbiddenness of the π transition is broken by the spin-orbit coupling of the hole, which mixes a higher ${}^1\Pi_u$ state into ${}^3\Sigma_u^+$.

Table I¹⁵ contains the present values for the ammonium-halide transition energies $h\nu$ and lifetimes τ , along with similar data for several of the alkali halides. It may be seen, first of all, that the σ -transition energies and lifetimes for NH_4Cl and NH_4Br are comparable to those shown for NaCl, KBr, and RbBr (also to the KI and RbI values not shown). Thus with regard to the σ transitions, the self-trapped exciton has essentially the same behavior in the alkali and ammonium halides.

A potentially more informative comparison involves the π transition, which unfortunately was identified in the case of ammonium halides only in NH_4Br . The four bromide π transitions in Table I show a rather strong correlation between $h\nu_\pi$ and τ_π , with NH_4Br bearing a close resemblance to NaBr. This association of large $h\nu_\pi$ with a small τ_π for a given halide is apparent also in alkali chloride and iodide data and has been incorporated into the arguments whereby the ${}^3\Sigma_u^+$ excited-state assignment was deduced.⁴ The details of these arguments will not be repeated here. Instead a brief description of the physical basis for the observed correlation of τ_π with $h\nu_\pi$ is given.

The spin-orbit coupling parameter involved in the ${}^1\Pi_u$ - ${}^3\Sigma_u^+$ mixing is that of the halogen. However, the

¹⁵ W. Van Sciver and L. Bogart, IRE Trans. Nucl. Sci. 5, 90 (1958).

separation of these states also affects the mixing and hence τ_π ; the greater the axial relaxation, the greater the separation and thus the greater τ_π . This is because the splittings of the *p*-like atomic orbitals, the main constituents of the trapped hole orbitals, increase with increasing departure from the symmetry of the lattice. The axial relaxation mode is also evidently responsible for most of the observed Stokes shift. Thus $h\nu_\pi$ and τ_π are each correlated with axial relaxation in such a way that as the relaxation increases, $h\nu_\pi$ decreases and τ_π increases. In addition, the $h\nu_\pi$ - τ_π relationship is reinforced by the fact that the Einstein spontaneous emission probability is proportional to $(h\nu_\pi)^3$. These correlations were taken to indicate that the relaxation was increasing in the sequence Na to K to Rb, for a given halogen.

The closeness of the $h\nu_\pi$ and τ_π values for NH₄Br to those for NaBr is thus consistent with the simple suppositions that the nature of the states and the magnitudes of the axial relaxations are the same for both and that the detailed differences in crystal field brought about by the NH₄⁺ ions are unimportant in comparison with the diatomic molecular field. (This is the reason for specifying in the Introduction the point symmetries of V_k centers or self-trapped excitons.) The present data are possibly compatible with other more elaborate explanations in which the relaxations differ but the crystal fields somehow compensate. One might, for example, conceive of a situation in which the π transition would be forbidden not by multiplicity but by the spatial symmetry of the states; the correlations in Table I would then result from other physical relationships not immediately apparent. However, the existing analysis readily accommodates the ammonium-halide data, and it would therefore appear that the data lend support to the following tentative conclusions about the nature of self-trapped exciton states in halide

lattices: (1) The observed self-trapped exciton states are the same in ammonium and alkali halides; as previously proposed, they may be designated approximately as $^1\Sigma_u^+$ for the σ transition and $^3\Sigma_u^+$ for the π transition. (2) Aside from establishing the Madelung potential well in which the V_k -center-electron pair is stabilized, the crystal fields are relatively unimportant. (3) For a given halide, the relative axial relaxation is the primary factor determining both $h\nu_\pi$ and τ_π .

Concerning (3) above, the separation r_0 of halide ions in the perfect lattice is the zero of relaxation relative to which the separations for the self-trapped configurations take effect. Since the latter separations are not accurately known, the r_0 values alone are included in Table I. It is interesting to note that r_0 for an ammonium halide is very near r_0 for the corresponding alkali halide. The evident similarities in transition energies and lifetimes may suggest that r_0 for a given crystal is somehow related to the relaxed halide-ion separations for that crystal. This matter will be considered further in a future discussion.¹⁶

There is as yet no firm explanation for the fact that in some crystals only one of the two transitions, σ or π , is observed. It may be that the absent state does not self-trap or that it undergoes rapid nonradiative transition to the other excited state or directly to the ground state. Additional work is necessary in order to clarify this matter.

ACKNOWLEDGMENTS

The authors wish to thank R. G. Fuller and D. A. Patterson for assistance in making some of the lifetime measurements, M. H. Reilly, C. L. Marquardt, and F. W. Patten for helpful discussions, and C. C. Klick for a critical reading of the manuscript.

¹⁶ M. N. Kabler and M. H. Reilly (unpublished).