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Low-Temperature Recombination Luminescence in Alkali Halide Crystals*

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Luminescence observed upon low-temperature x-ray excitation of alkali-halide crystals has been identified as due to radiative electron-hole recombination in the perfect lattice. In KCl the emission spectrum is a single band, while in KBr, KI, and NaCl there are two bands. In crystals containing self-trapped holes, optical excitation of electron-excess defects such as F centers causes transfer of electrons to holes with emission of recombination luminescence identical to that excited directly by x-ray irradiation. If the holes have been preferentially oriented, the optically excited luminescence from KCl and KBr exhibits partial polarization characteristic of the transitions involved. The origin of the recombination luminescence is revealed through these polarization properties, together with results on optical excitation and bleaching spectra, temperature dependence, excitation efficiency, and impurity independence. The relevance of this work to the process of electron tunneling from excited F centers is discussed from an elementary point of view. The bleaching of F and F' centers through the absorption of recombination luminescence is shown to be a potentially important factor in determining the growth rates of the various centers during high-energy irradiation.

INTRODUCTION

It is known that high-energy irradiation of an alkali-halide crystal below a characteristic temperature in the range 100–200°K produces stable self-trapped holes in the lattice.[1] The holes are at least several lattice spacings distant from and independent of other imperfections. Mobile electrons created pairwise with the holes are captured by point defects in the lattice, and the number of electron traps evidently determines the number of self-trapped holes which may be created by the irradiation.[2] Trapping of the hole occurs through the formation of a covalent bond between the halogen atom and an adjacent halide ion, which move together to form an X_2^- molecule-ion with axis along a [110] direction. This configuration is commonly known as the V_k center and gives rise to optical absorption bands, the major one occurring in the spectral range 3–4 eV.[2] Absorption of light by a V_k center may cause it to change its axis from one [110] direction to another, and polarized light may be used to largely depopulate any particular orientation.

In studies of electron-hole interactions in alkali-halide lattices at low temperature, it is advantageous to exploit the above properties of holes. The use of this approach in the present work furnishes substantial evidence associating certain characteristic emission bands with radiative electron-hole recombination. For instance, the ejection of electrons from traps in KCl or KBr containing preferentially oriented V_k centers excites luminescence which reflects the symmetry of the V_k centers.

The most extensive and successful prior efforts to associate luminescence from alklai halides with intrinsic electron-hole recombination are those of Teegarden.[3,4] The alkali iodides, particularly KI, were investigated at temperatures down to 93°K. In KI, ultraviolet illumination in the region of the exciton absorption excited with high efficiency an emission band centered about 3.3 eV. Also, after ultraviolet irradiation, a rapidly decaying burst of the 3.3-eV luminescence occurred upon exciting in the F absorption band. The results were consistent with an intrinsic recombination model, but a link with V_k centers was not established.

The usefulness of alkali iodides as scintillation materials has led to a number of investigations of their emission spectra under ionizing radiation.[5] An emission band which is supposedly characteristic of the perfect lattice and whose intensity increases with decreasing temperature has been observed in several of these crystals and, though it has been reasonable to associate the band with electron-hole recombination, direct evidence has been lacking. Several weak emission bands, including two which bear some similarity to those of the present work, have been recently noted in KBr under x-ray excitation at liquid-nitrogen temperature.[6] They have not been studied or interpreted, however.[6a]

EXPERIMENTAL

All experiments were carried out at either 4°K, 77°K, or room temperature in a Dewar with optical and x-ray windows. Crystals were freshly cleaved, and measured approximately 10×4×4 mm³. A 50 kV

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* A preliminary account of this work was presented at the March, 1964 meeting of the American Physical Society [Bull. Am. Phys. Soc. 9, 241 (1964)].

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

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

[3] K. J. Teegarden, Phys. Rev. **105**, 1222 (1957).

[4] K. Teegarden and R. Weeks, Phys. Chem. Solids **10**, 211 (1959).

[5] See e.g., W. J. Van Sciver, Phys. Rev. **120**, 1193 (1960); N. N. Vasil'eva and Z. L. Morgenshtern, Opt. i Spektroskopiya **12**, 86 (1962) [English transl.: Opt. Spectry. **12**, 41 (1962)]; R. Gwin and R. B. Murray, Phys. Rev. **131**, 508 (1963).

[6] R. Fieschi, E. Panizza, and P. Scaramelli (to be published).

[6a] *Note added in proof*. S. Wakita and M. Ueta, J. Phys. Soc. Japan **19**, 924 (1964) have recently photographed luminescence spectra similar to those of the present work. Certain of their conclusions differ from those here, however.

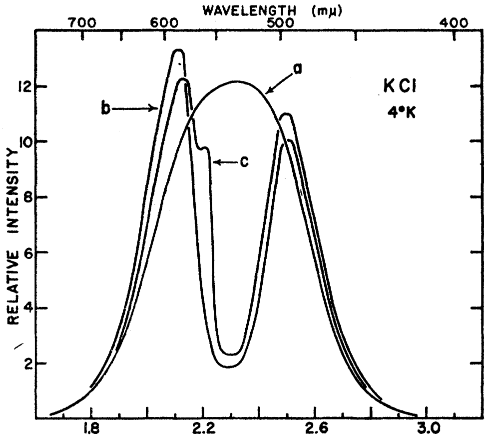

FIG. 1. Emission specta of KCl at 4°K. Curve (a), initial, under x-ray excitation; (b) x-ray excitation, after 0.5-h x-ray dose; (c) 2.21-eV photon excitation after x-ray irradiation. Relative intensity scales for (a) and (b) are approximately equivalent. Spectra have been corrected for monochromator dispersion and photomultiplier response.

TABLE I. Properties of recombination emission bands at 4°K.

Crystal	Band peak (eV)	Half-width (eV)	Percent polarization	1st Exciton absorption (eV) at 77°K[a]
KCl	2.31	0.58	−30	7.76
KBr	2.27	0.40	−20	6.77
	4.42	0.41	+50	
KI	3.33	0.37	$-13<P<0$	5.80
	4.0			
NaCl	3.36	0.67		7.96
	5.38	0.63		

[a] See Ref. 18.

constant potential tungsten-target tube furnished the x rays, which were filtered through approximately 1 mm of aluminum; a tube current of 1 mA usually gave easily measurable luminescent spectra at 4°K. Appropriate combinations of grating monochromators, optical filters, quartz lenses, and tungsten and mercury arc light sources were used for exciting and measuring the spectra, which were detected with a 1P28 or 7326 photomultiplier tube and recorded. The luminescence was always observed at right angles to the direction of the exciting beam of light or x rays. A Glan prism or a sheet Polaroid was used for polarizing light to orient V_k centers; the orienting light was always incident on the face of the crystal through which the luminescence was observed. Absorption spectra were measured with a Cary Model 14 spectrophotometer. All emission spectra shown are corrected for monochromator dispersion and photomultiplier response.

RESULTS

A. KCl

Curve (a) of Fig. 1 is the initial[7] emission spectrum of Harshaw KCl at 4°K under low-intensity x-ray excitation. The band is structureless at a resolution of 4 mμ. Its characteristic parameters are given in Table I, along with those of the emission bands of the other alkali halides studied. In the spectral range 1.5–6 eV, pure KCl at 4°K emits no other luminescence of consequence. After an x-ray dose sufficient to create an average F-center density of approximately 5×10^{16} cm^{-3}, the spectrum has become curve (b). The marked self-absorption arises from the F band at 2.29 eV. The relative intensity scales of curves (a) and (b) are approximately the same, but the slight apparent increase of intensity of (b) relative to (a), evident at the high- and low-energy edges, is not necessarily an indication of a change in the rate of emission.

The intensity of luminescence is proportional to the intensity of excitation. Response to changes of x-ray intensity takes place in less than 0.1 sec; this is an upper limit, and the true response time may be orders of magnitude smaller.

A rough measurement of the efficiency of x-ray excitation of the luminescence gave the result that emission of one photon requires absorption of 40 eV of x-ray energy.[8] This means about 0.5 photon is emitted per electron-hole pair created by the x rays, assuming that an average of 20 eV of absorbed x-ray energy are required to create a pair. This estimate is probably accurate to within a factor of 2.

Following x-ray irradiation, the crystal of Fig. 1, still at 4°K, was illuminated with light in the F band at 2.21 eV. The resulting luminescence is displayed in curve (c), the intensity scale being different from that which applies to curves (a) and (b). The small shoulder on the inside of the curve is due to scattered exciting light. The exicting light was incident on the crystal in the direction opposite to that of the x rays and thus passed first through the region of the crystal which was colored the least. Therefore, a relatively larger fraction of exciting light than of x rays was absorbed in regions of the crystal where the self absorption due to the F and K bands was a minimum, allowing relatively more luminescence to escape at the high-energy side of the emission band for F-light excitation and accounting for the slight differences between curves (b) and (c). Within the limits of the experiment, then, x-ray and F-light excitation yield identical emission spectra.

The excitation spectrum for the luminescence of curve (c) followed the absorption spectrum in the region of the F and K bands, with sensitivity also evident in the higher excited states of the F center,

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[7] "Initial" is used to imply times before the emission spectra have become affected by the accumulating color center self-absorption.

[8] V. H. Ritz, Phys. Rev. **133**, A1452 (1964).

i.e., the L bands.[9] When the coloration had been produced by x-ray irradiation at 77°K, where F' centers are formed, an additional band correlating with the F' absorption band was apparent in the 4°K excitation spectrum. Under continued F-light illumination the emission intensity decreased to zero. This observation, coupled with the fact that photons of a given energy excite luminescent photons of higher energy, clearly points to the decay of some metastable state of the x-rayed crystal.

These experiments were performed on pure crystals from the Harshaw Chemical Company and on the following KCl crystals grown in this laboratory: pure and also Tl-doped Optovac Company material regrown under dry argon[10]; a crystal heavily doped with Pb; reagent grade KCl zone-refined under an HCl atmosphere to remove oxygen. Among these samples, there were no significant differences in spectrum or magnitude of the luminescence at 4°K.

If the sequence of experiments with nominally pure material yielding the data of Fig. 1 at 4°K is carried out instead at room temperature, the luminescence is negligible; at 77°K the emission band appears at an intensity three orders of magnitude below that at 4°K. If a KCl crystal is colored by x rays at room temperature and cooled immediately to 4°K, the luminescence excited by F light is negligible. However, if the crystal is colored at 77°K and excited with F light at 4°K, the luminescence of curve (c), Fig. 1, appears with intensity comparable to that resulting from an equivalent 4°K x irradiation. One may note that, of the major V centers created by x-ray irradiation, only the V_k is formed in comparable concentrations at 4 and 77°K and is unstable at room temperature.

Having colored either a pure or a doped crystal at 4 or 77°K, brief illumination with F light at 4°K produces luminescence and bleaches a small fraction of the F centers. In the V-band spectral region, the measured spectrum of the absorption which has been bleached follows closely the absorption spectrum of V_k centers alone, which peaks at 3.39 eV. Thus, in the initial stage of bleaching where the luminescence is diminishing rapidly, the absorption spectra indicate primarily a mutual annihilation of F and V_k centers. Other investigators have obtained this same result and, in addition, have observed that F- and H-center annihilation predominates in the later stages of bleaching.[11] However, even after the bleach into the F band has reduced the luminescence to negligible magnitude, a substantial fraction of the V_k centers and most of the F centers remain.

Evidence linking the polarization properties of the luminescence with the symmetry of V_k centers was obtained as follows. It is known that a large fraction (>0.9) of V_k centers can be aligned in, say, the $[\bar{1}10]$ direction by illumination with polarized V_k light of around 3 eV and with electric vector $[\bar{1}10]$.[2] This orienting procedure was carried out at 4°K on both pure and Tl-doped KCl with V_k light incident in the $[001]$ direction, and maximum orientation was achieved. Upon subsequent excitation with unpolarized F light, a polarization of -30% was measured in the luminescence emitted along $[00\bar{1}]$.[12] That is, if V_k centers are aligned along $[\bar{1}10]$, the luminescence of Fig. 1 is partially polarized with electric vector along $[110]$. This result is essentially independent of whether the emission is observed on the high- or low-energy side of the F-center absorption "dip" in curve (c). Also, dichroic absorption of a magnitude sufficient to affect the emission is not present. Thus the luminescence clearly involves V_k centers and electrons and occurs during their disappearance.

Considering the evidence as a whole, we are led to conclude that the luminescence of Fig. 1 is due directly to electrons recombining with self-trapped holes in the perfect lattice.

B. KBr

The initial luminescence from Harshaw KBr under x-ray irradiation at 4°K appears in two distinct bands. Figure 2 displays the spectrum, along with those of the other alkali halides investigated. Aside from this duality, the behavior of KBr is very similar to that of KCl. Except for the gradual onset of some color center self-absorption, the luminescence is independent of time.

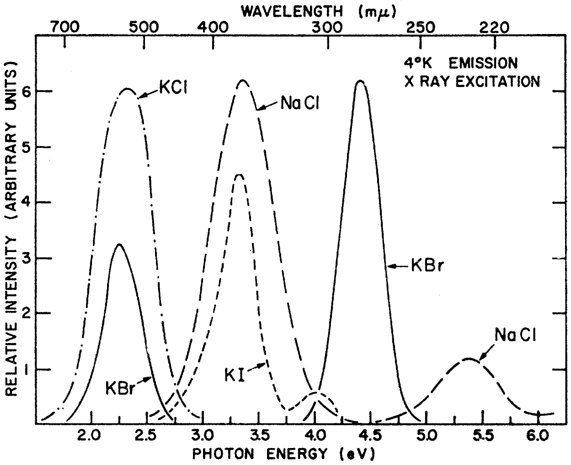

FIG. 2. Initial emission spectra under x-ray excitation at 4°K. Relative intensity scales for different crystals are not necessarily equivalent. Spectra have been corrected for monochromator dispersion and photomultiplier response.

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[9] F. Lüty, Z. Physik **160**, 1 (1960); C. C. Klick and M. N. Kabler, Phys. Rev. **131**, 1075 (1963).

[10] D. A. Patterson, Rev. Sci. Instr. **33**, 831 (1962).

[11] W. D. Compton, Summer School on Solid State Physics, Mol, Belgium, 1963 (to be published).

[12] 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 to the direction along which the V_k centers are aligned, respectively. With the geometry being used, the parallel direction is chosen $[\bar{1}10]$ and the perpendicular direction $[110]$.

The efficiency for conversion of absorbed x-ray energy to luminescence is again high, comparable to that measured for KCl.

After a moderate x-ray dose at 4 or 77°K, excitation with light in the trapped-electron absorption bands (F, F', K, etc.) at 4°K produces the same luminescent spectrum as does x-ray excitation. With a crystal x-rayed at 4°K to create roughly 5×10^{16} cm^{-3} F centers and a smaller but undertermined concentration of V_k centers, a measurement of the initial quantum efficiency gave 0.03 photon emitted in each of the two bands per photon absorbed in the F band. During continued illumination, the rate of decay of emission intensity is the same for both bands. Elimination of the luminescence corresponds to the destruction of roughly one-third of the F band and the composite V_k and H band. Although the latter two bands nearly coincide in KBr (3.22 and 3.26 eV, respectively), in analogy with KCl it is reasonable to presume that the early bleaching involves mainly V_k and F centers.

The variation of the recombination luminescence in KBr with temperature also parallels that for KCl. Under x-ray excitation, the heights of the high- and low-energy peaks at 77°K are, respectively, 0.02 and 0.005 times their heights at 4°K. This implies that the excited state producing the higher energy emission is more stable thermally. Optical excitation produces luminescence only when V_k centers are known to be present.

The polarization properties of the recombination luminescence were determined by aligning the V_k centers along a particular [110] direction, using the same methods and geometry as with KCl. The maximum polarization obtained was -20% for the 2.27-eV band and $+50\%$ for the 4.42-eV band. That is, the electric vector of the latter band is parallel to the axis of the V_k center, while that of the former is perpendicular to the V_k axis as was the case for the KCl luminescence. It should be noted that, of the nonequivalent $[\bar{1}10]$ and [100] transition moments perpendicular to the axis of the center, the experiments with aligned V_k centers employ only one geometry and sample only the $[\bar{1}10]$ moment. However, the spectrum of the emission polarized along this moment is indistinguishable from that for randomly oriented V_k centers with which all moments are sampled. This implies that the [100] transition moment does not give rise to a distinct emission band, at least over the observed spectral range.

KBr lightly doped with Ag exhibits the same polarization properties as does the pure material.

C. NaCl

At 4°K, Harshaw NaCl under x-ray excitation also yields luminescence in two well-resolved bands, Fig. 2. Again, the efficiency for conversion of x-ray energy to luminescence is high and the time dependence is negligible. The same two emission bands with the same relative intensities are excited by F-light illumination of a crystal x-rayed at low temperature. Tl-doped NaCl behaves similarly.

It is known from ESR measurements that V_k centers are produced in NaCl x-rayed at low temperatures.[1] However, the optical absorption band or bands associated with this center do not seem to have been identified. A heavy x-ray irradiation at 4°K produced a broad shoulder on the high-energy side of the F band with approximately one-third its height. This shoulder is in the 3.4-eV region, where one would expect the V_k band to lie. The concentration of F centers was about 8×10^{15} cm^{-3}, the coloration being relatively inefficient at this temperature.[8,13] The bleaching spectrum resulting from F-light illumination was similar in shape to the initial absorption spectrum. This result may be interpreted as associating at least part of the shoulder with the V_k band, in analogy with other alkali halides. A cursory attempt to align V_k centers with polarized light at 3.4 eV failed to produce measurable polarization of either band of luminescence; it is not certain, however, that alignment was achieved.

D. KI

Two intrinsic emission bands appear in KI under x-ray excitation at 4°K. The spectrum is shown in Fig. 2. X-ray excitation efficiency is such that a substantial fraction of the electron-hole pairs formed undergo radiative recombination. This is consistent with the quantum efficiency of 0.5-1.0 measured by Teegarden with ultraviolet excitation at 113°K.[3] Crystals which have been given moderate exposure to x rays at temperatures where V_k centers are stable emit a spectrum similar to that of Fig. 2 upon optical excitation in the F band or in a very broad band around 1.3 eV. The absorption of the latter band is too slight to measure. It appears to traverse a spectral range from about 1 eV into the visible, and probably corresponds to a band postulated by Hersh to explain certain bleaching properties of KI:Tl.[14]

The Semi-Elements Company KI crystals used in the present work contained thallium impurity, as evidenced by its characteristic 2.9-eV emission band which broadens slightly the low-energy side of the 3.33-eV band in Fig. 2. Correcting for the thallium emission, the 3.33-eV band shape is closely Gaussian with half-width 0.37 eV. This becomes 0.6 eV at[15] 83°K and 0.7 eV at[4] 93°K, according to other workers. A number of narrow oxygen emission bands were also observed,[16] but their peak intensities were less than 3% that of the recombination luminescence.

Continued x-ray irradiation at low temperature

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[13] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

[14] H. N. Hersh, J. Chem. Phys. **31**, 909 (1959).

[15] R. Fieschi and G. Spinolo, Nuovo Cimento **23**, 738 (1962).

[16] J. Rolfe, J. Chem. Phys. **40**, 1664 (1964).

produced V_k absorption bands at 1.55 and 3.08 eV,[2,14] and a very weak F band at 1.88 eV. These bands could be bleached by F light (although the relative number of F centers was so small that total bleaching of them caused only a small drop in the V_k bands), a result again indicative of mutual annihilation of F and V_k centers.

It was possible to orient the V_k centers in the usual way with polarized 3-eV light at 4°K. However, measurements of the emission polarization were hindered by overlap of the dichroic V_k absorption with the emission. The present experiments allow one to say only that the maximum polarization of the emission at 3.3 eV is probably between zero and -13%.

DISCUSSION

Although the present experiments were concerned with the polarization properties of the luminescence mainly as evidence bearing on the intrinsic recombination radiation hypothesis, these properties contain some information regarding the bound states of an electron-hole pair. The diatomic-molecule model is evidently applicable for the classification of states, and the possible electronic configurations are those of a rare-gas molecule.[17] With only the limited luminescence data to take into account, the orthorhombic crystalline field around the molecule may be ignored; this is because only one transition moment perpendicular to the axis of the V_k center has been observed.

It is clear that the two-band emission spectra are not due to a transition from a high excited state to an intermediate state followed by a transition from the intermediate state to the ground state, since the sum of the energies of the most energetic photons of the two bands is too large in comparison with the first exciton absorption energy,[18] given for convenience in Table I. Thus we have to deal with transitions from two distinct excited states to the ground state.

Previous authors have assumed a $\sigma_g{}^2\pi_u{}^4\pi_g{}^4\sigma_u({}^2\Sigma_u{}^+)$ ground-state configuration for the V_k center,[1,2] and it is reasonable to expect the addition of an electron to result in a $\sigma_g{}^2\pi_u{}^4\pi_g{}^4\sigma_u{}^2({}^1\Sigma_g{}^+)$ ground state, as for the rare-gas molecule. There is no net covalent bonding in this state, and the ions will relax immediately to restore the perfect ionic lattice. The predominance of π polarization of the KCl and lower energy KBr emission bands suggests a transition from a Π_u state, the excited electron being in a π_g orbital. This is an allowed dipole transition, whereas $\Pi_g \rightarrow \Sigma_g$ would be forbidden. Σ_u with a σ_g excited electron is indicated as the excited state which initiates the 4.42-eV emission in KBr, the $\Sigma_u \rightarrow \Sigma_g$ charge-transfer transition being allowed for σ-polarized light. Because of spin-orbit coupling, these Π_u and Σ_u states will not be pure, but will have other states mixed with them. In particular, Π_u may contain a substantial amount of some Σ_u state. This mixing would have the effect of decreasing the degree of π polarization in the luminescence from this state, in agreement with the relatively small polarizations observed. Furthermore, the spin-orbit coupling, being larger for the heavier atoms, might be expected to diminish the percentage of π polarization along the sequence from KCl to KBr to KI. Table I shows this to be the case. Alternatively, the amount of polarization might be curtailed by the occasional reorientation of a V_k center as the ions relax with the trapped electron prior to the luminescent transition. One would surmise that this possibility is less likely, since it is reasonable to expect the ionic relaxation during the trapping of an electron into the excited states to be small compared with the relaxation of the ground state after a luminescent transition.

The spectral position of the peak of the high-energy emission band changes with the host crystal in much the same manner as do the peaks of the well-known absorption bands. For instance, the ratio of the higher emission energy to the first exciton absorption energy is constant to within about 5%. However, the relative intensity of this emission band varies widely and without apparent order from NaCl to KBr to KI, and there is no indication that the band exists in KCl. By contrast, the intensities of the low-energy emission bands of the four materials are comparable, but their peak energies do not vary in any obviously regular way with the physical properties of the host crystal. Explanation of this behavior requires further experimental and theoretical analysis. However, from a localized mode viewpoint,[19] one may remark that the large Stokes shifts and strong thermal quenching allow the possibility of the configuration coordinate curves for the Π_u and Σ_u excited states intersecting at some point which varies slightly from one crystal to another. If the intersection comes close to the minimum of the Σ_u state, nonradiative transitions from this state to the Π_u state will prevail and diminish or eliminate optical $\Sigma_u \rightarrow \Sigma_g$ transitions. Also, slight shifts in the coordinate of the minimum of the Π_u states relative to the Σ_u and Σ_g states may cause substantial changes in the $\Pi_u \rightarrow \Sigma_g$ transition energies.

It is known that thermal quenching of the F-center infrared luminescence in the vicinity of 100°K arises from thermal excitation of the electron from the excited state into the conduction band before it can return to to the ground state.[20] This type of process is probably not responsible for the quenching of recombination luminescence, since V_k centers are still effective electron traps at temperatures where the recombination lumines-

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[17] G. Herzberg, *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), 2nd ed.

[18] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

[19] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962).

[20] R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).

cence has diminished by more than two orders of magnitude.[21] The results are more nearly consistent with a well-known model involving thermal excitation of the electron up to a point where the ground- and excited-state configuration coordinate curves intersect, allowing the electron to cross over into the ground state without producing the characteristic luminescence.[19]

It is easy enough to visualize the process whereby recombination luminescence is excited by illumination in the F' or L absorption bands, since this is known to give rise to conduction electrons at all temperatures. The situation is more complex, however, for F-band excitation at low temperatures, because the excited state of the F center is thought to lie 0.10–0.15 eV below the conduction band.[20] On the basis of optical bleaching data, a number of previous investigators have suggested the occurrence of electron tunneling from the F-center excited state to a localized excited state of some other center, without the electron entering the conduction band.

Following this line of thought, one may determine the maximum $F-V_k$ separation distance over which tunneling is taking place in the present experiments, assuming that initially there is no *microscopic* correlation between the locations of F and V_k centers. Macroscopic correlation does, of course, exist. In the course of bleaching with 2.21-eV photons, the KCl crystal of Fig. 1 was emitting at 10% the initial intensity when 40% of the F centers and about 50% of the V_k centers had been annihilated. Ignoring the variation of concentration due to nonuniform absorption of x rays, at the start of bleaching there were 5×10^{16} cm^{-3} F centers and roughly 2.5×10^{16} cm^{-3} V_k centers. The latter number involves the assumption that V_k and F centers have the same oscillator strength[21] and includes the effect of the V_k-center anisotropy and the overlap of the H-center absorption band. At this F-center concentration, there is a 50% probability that a V_k center has an F center within a radius of 150 Å. Although filtered x rays were used, the coloration was not uniform in the direction of the x-ray beam; when account is taken of the variation of concentration, the radius becomes 140 Å. Tunneling must be occurring over at least this distance if there is no microscopic correlation between F- and V_k-center locations.

An independent measure of the maximum tunneling distance is desirable for purposes of comparison. However, the only available relevant data concerns tunneling to the conduction band. Specifically, it has been shown by Lütty[22] that an applied electric field of about 2×10^5 V-cm^{-1} will ionize significant numbers of optically excited F centers in additively colored KCl at tempertaures in the vicinity of 10°K.[23] This information can be utilized in the present problem if the Coulomb field of a V_k center is assumed to affect the excited F electron in the same way as the externally applied field. While bound to its vacancy, the electron can gain from the applied field E a maximum energy eEd/K, where d is a measure of the diameter of the excited-state wave function and K is the appropriate dielectric constant. One then asks at what separation r $(r>d/2)$ between the F center and a V_k center can the bound electron gain the same energy from the field of the V_k center as it could from the applied field. Equating these energies

$$\frac{e}{K(r-d/2)}-\frac{e}{K(r+d/2)}=\frac{eEd}{K}.$$

Solving this equation for r, using the value of E sufficient to cause tunneling to the conduction band, one obtains 85 Å$<r<$100 Å when $0<d<100$ Å, a range including the physically reasonable values of d for the KCl F center. Though this calculation has circumvented details of the tunneling process which could be important, it is probably reliable enough to exclude the possibility of tunneling over $F-V_k$ separations of 140 Å. Since this value is the minimum required to explain the present experiments under the assumption of no microscopic correlation between F and V_k centers, one is led to conclude that F and V_k centers are, on the average, located closer together than this assumption would indicate. Our conclusion is not unreasonable physically since, as Compton has suggested,[11] an electron-hole pair is more likely to recombine if it is created far away from other centers capable of trapping the electron.

Having recognized the existence of strong luminescence during high-energy irradiation at low temperature, it is natural to inquire into possible effects on the coloration process due to absorption of the luminescence by the various centers. A qualitative measure of the importance of absorption by a given center might be taken to be the bleaching rate of that center relative to its net rate of growth. The bleaching rate will depend upon the rate of absorption of luminescence by the center and the bleaching efficiency of the center. On this basis, F and F' centers appear most likely to be affected directly.

The present measurements indicate that, for KCl and KBr under x-ray irradiation at 4°K, roughly 100 luminescent photons are emitted for each F center created. The lower energy emission bands of Fig. 2 overlap the F' absorption bands to a large degree, and the optical bleaching efficiency of the F' center is known to be near unity for crystals colored at low

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[21] J. D. Kingsley, Phys. Rev. **122**, 772 (1961).

[22] F. Lüty, Z. Physik **153**, 247 (1958); *Halbleiterprobleme* (Friedrick Vieweg und Sohn, Braunschweig, 1960), Vol. VI, p. 276.

[23] R. N. Euwema and R. Smoluchowski, Phys. Rev. **133**, A1724 (1964).

temperature.[19,21] Thus a peak optical density (averaged over all directions in the crystal) of the order of 0.01 in the F'absorption band will result in an F'-center bleaching rate roughly equal to the net F-center creation rate at 4°K. Also, at low optical densities, the F'-center bleaching rate will be roughly proportional to the concentration. The bleaching rate will also vary linearly with the intensity of luminescence, and it will be recalled that this intensity is several orders of magnitude lower at 80°K than at 5°K. In KCl and KBr, x-ray irradiation at 80°K is known to produce about $\frac{1}{5}$ as many F' centers as F centers,[21] whereas irradiation at 5°K yields essentially no F' centers.[24] Assuming that the rate of trapping of electrons by F centers (the F'-center creation rate) is not markedly different at these two temperatures, the reasonable conclusion is that recombination luminescence is responsible for keeping the net F'-center creation rate essentially zero at 5°K.

Estimates of the anticipated bleaching rate for F centers are less certain, because accurate measurements of the optical bleaching efficiencies are not available. For KBr, the present work sets a lower limit of 0.06 for the bleaching efficiency; this is a minimum since only those F centers whose destruction gives rise to a recombination photon are counted. A guess of 0.1 for the efficiency in KCl and KBr at 4°K is probably the best that one can do. Taking rough account of the spectral overlap of the emission bands with the F-center absorption, computation shows that, to give an F-center bleaching rate comparable to the *net* F-center creation rate, peak F-band optical densities (averaged over all directions in the crystal) of 0.3 for KCl and 1.0 for KBr are necessary. These numbers should be taken as no more than order-of-magnitude estimates.

As in the case of F' centers, one would expect effects of the absorption of luminescence to appear as decreases in the F-center concentration with decreasing temperatures of irradiation, relative now to the α-center concentration. A relative decrease is, in fact, observed; the ratios of F-center concentration to α-center concentration for 4°K x-ray irradiation are about 0.25 in KCl and 0.17 in KBr,[25] while for 77°K irradiation the ratios are greater than one. These ratios do not vary appreciably with concentration, which might be taken to indicate that the inverse process, i.e., the trapping of electrons by α centers, varies with concentration in roughly the same way as the bleaching. Heretofore, in order to explain the persistently high α-center growth rate at 4°K, it was necessary to suppose that a large fraction of these centers as formed were stable against electron capture during irradiation.[22,25] The present work reveals a mechanism whereby it is possible to relax this restriction to some degree, depending upon the results of more accurate measurements of the rates of F-center bleaching through absorption of recombination luminescence.

SUMMARY

The principal result of this work has been the establishment beyond reasonable doubt of intrinsic electron-hole recombination in the perfect lattice as the source of certain efficient emission bands in alkali halides at low temperature. This is the first recognition of the origin of these bands in KBr, KCl, and NaCl, and is also evidently the first observation of the bands themselves in the latter two crystals. The main features upon which our argument rests are the polarization properties of the luminescence, its independence of impurities, and the high efficiency of excitation. In addition, the optical excitation and bleaching spectra and the temperature dependence are consistent only with the V_k center as an activator.

The observed energies, symmetries, and intensities of the various electron-hole decay transitions will require further theoretical analysis for clarification. For instance, it is notable that an alkali-halide crystal should exhibit two strong, well-separated recombination emission bands. Also, the Stokes shifts are quite large, particularly for KCl. Another item demanding attention is the process of transfer of an electron from the F-center excited state to the V_k center.

Estimates based on the present work indicate that the bleaching of F and F' centers by recombination luminescence during high-energy irradiation at low temperature can have sizable effects upon the color center production rates. Processes of electron transfer among the various defects may be of greater importance than has been supposed in the past.

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