is oriented parallel to the microwave electric field but still in a [100] direction, data of the form shown by the dashed curves in Fig. 6 is obtained. The experimental data agrees very well with the results calculated with the four ellipsoid model and discussed above. The small line which was calculated to exist at twice the cyclotron field was never observed. This is not surprising in view of its small intensity and the low $\omega\tau$ when the temperature was raised to obtain a high carrier concentration.

Hall effect and plasma measurements on a small sphere of n-type indium antimonide also have shown good agreement with theory. In this case we have an isotropic mass and, as expected, no longitudinal magnetoplasma resistance was observed.

CONCLUSIONS

These measurements have demonstrated the validity of the simple drift-velocity treatment of magnetoplasma effects in small samples, even when more than one type of carrier is present and when tensor masses are involved. In particular, it has been demonstrated that when more than one type of carrier is present a mode of oscillation exists wherein the carriers can move in such a way that the majority carrier tends to short out the plasma effects of the minority. When the sample size becomes comparable with the wavelength of the radia-

tion in the sample, or when the sample is placed in a nonuniform field, the simple theory does not explain the phenomena. In such cases other resonances can be observed.[16] Since resonances may be observed which are independent of carrier concentration or sample shape over a large range, and yet are not at the cyclotron field of any carrier in the material, the usual checks to assure that cyclotron resonances are unperturbed by plasma effects may in some cases be insufficient.

The very good correspondence between the carrier concentrations determined by Hall measurements and by plasma measurements provide an additional check on the Hall effect as a means of measuring carrier concentration. Indeed, one can imagine certain circumstances where the measurement of carrier concentration by microwave magnetoplasma methods may be more convenient than the usual Hall effect techniques.

ACKNOWLEDGMENTS

[16] M. Cardona and B. Rosenblum (to be published).

Recombination Luminescence in Alkali Halides*

T. Timusk† AND W. Martienssen‡
*Department of Physics and the Laboratory of Atomic and Solid State Physics,
Cornell University, Ithaca, New York*
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A new type of luminescence in nominally pure alkali halide crystals was studied. At room temperature the excitation was most efficient in the wavelength region that has been associated with band-to-band transitions. It is suggested that the emission results from the capture of a hole by an F center. In agreement with this model the emission (430 mμ in KCl) is the same as that which is observed when a crystal containing α centers is irradiated in the α band at low temperature. From the thresholds of the excitation spectra the following band gaps are derived: NaCl, 8.0 eV; KCl, 8.1 eV; KBr, 7.3 eV; and KI, 5.8 eV. A comparison with external photoelectric thresholds as obtained by other investigators yields the electron affinities: NaCl, 0.8 eV; KCl, 0.6 eV; KBr, 0.9 eV; and KI, 1.6 eV.

INTRODUCTION

THE optical absorption spectra of the alkali halides have a peculiar shoulder or step[1] about one electron volt above the absorption edge. No photoconductivity has been observed at the absorption edge itself

and the entire region of strong absorption between the edge and the step is photoelectrically inert. It seems to be associated with the production of excitons and will be called the exciton region in this paper. Above the step, it has been suggested by Taft and Philipp[2] from a study of the external photoemission, band-to-band transitions should begin to take place.

Recently we reported briefly on a new type of luminescence in pure alkali halides at room temperature.[3] It

[1] H. Fesefeld, Z. Physik 64, 623 (1930); W. Martienssen, J. Phys. Chem. Solids 2, 257 (1957); J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. 116, 1099 (1959).

[2] E. A. Taft and H. R. Philipp, J. Phys. Chem. Solids 3, 1 (1957).
[3] T. Timusk, J. Phys. Chem. Solids 18, 265 (1961).

was found that the emission could be excited only with photons of energy higher than the step, the suggested point of onset of band-to-band transitions. In view of this we proposed that the luminescence was the result of recombination of free electrons and holes at some center. In this paper we will give a more detailed description of the observations and will present a tentative model for the emission process.

Observation of luminescence in the fundamental absorption region of the alkali halides is not new. It has been known for some time that luminescence can be excited with high efficiency in this general region in crystals that have received small additions of thallium. Current interest in the fundamental absorption has led to further study of this luminescence.[4-6] It has been found that the thallium-activated crystals show a sharp increase in quantum efficiency of emission if excited with energies just beyond the step in the absorption spectrum. The assumption is that free electrons and holes are generated at the step and give their energy of recombination to the activator ion which then emits its characteristic luminescence.

A different type of luminescence has been studied in in undoped alkali iodides.[7,8] The excitation is strong throughout the fundamental absorption region of the pure crystals, including the exciton region, with the exception that at the absorption peaks there are sharp minima of the excitation efficiency; a kind of "self-reversal." The temperature dependence is pronounced: The emission is only observable at low temperature. Different models have been proposed for the mechanism of the emission.

More recently there have been several reports of photoconductivity[9] at the step in the absorption spectrum. These experiments strengthen the original hypothesis of Taft and Philipp.

EXPERIMENTAL TECHNIQUES

A hydrogen lamp in conjunction with a vacuum monochromator was used for excitation. The system described in detail by Hartman[10] gives a many-line spectrum below 160 mμ and a continuum above 160 mμ. The photon flux at the exit slit is between 10^8 and 10^{10} photons/sec with 20 Å resolution. The emission spectra were measured with 10.2-eV (Lyman-α) excitation. The detection system was in line with the incident beam behind the crystal.

[4] M. Ueta and T. Ishii, J. Phys. Soc. Japan **14**, 857 (1959).
[5] I. V. Yaek and G. G. Liidya, Optika i Spektroskopiya **8**, 142 (1960).
[6] K. Aoyagi and G. Kuwabara, J. Phys. Soc. Japan **15**, 2334 (1960).
[7] H. Enz and J. Rossel, Helv. Phys. Acta **31**, 25 (1958).
[8] K. J. Teegarden and R. Weeks, J. Phys. Chem. Solids **10**, 211 (1959).
[9] Y. Nakai, K. J. Teegarden and G. Kuwabara, K. Aoyagi, reported at the 1961 International Conference on Photoconductivity, Cornell University [J. Phys. Chem. Solids **22**, 327, 333 (1961)].
[10] P. L. Hartman, J. Opt. Soc. Am. **51**, 113 (1961).

Due to the low efficiency of the luminescence, scattered light problems were serious. They were minimized by means of baffles and filters but since all optical materials luminesce when irradiated by vacuum ultraviolet, care had to be taken to use materials of lowest luminescence efficiency[11] and to position them at the optimum.

The intensity of the luminescence was measured photoelectrically. Photomultipliers with S11 response were used: the RCA 5819, or the EMI 6097S and the EMI 6255S. The latter has a quartz envelope. The EMI tubes have orders of magnitude lower dark current at room temperature than other types and upon cooling to dry ice temperature signals of 100 photons/sec were measurable. All the tubes used had been selected for low dark current. The photomultiplier currents were amplified with a Cary vibrating-reed electrometer and recorded with a potentiometer-type recorder. To smooth out fluctuations time constants up to 8 sec were used.

The crystal holders used at room temperature were quite simple; more elaborate ones were needed at low temperature. Thermocouples, heaters, and small light bulbs for bleaching were attached on the crystal holders at various times. The low-temperature crystal holder (Fig. 1) had places for four crystals (one of these was the standard phosphor) which could be brought in turn to the monochromator slit, which was horizontal. The
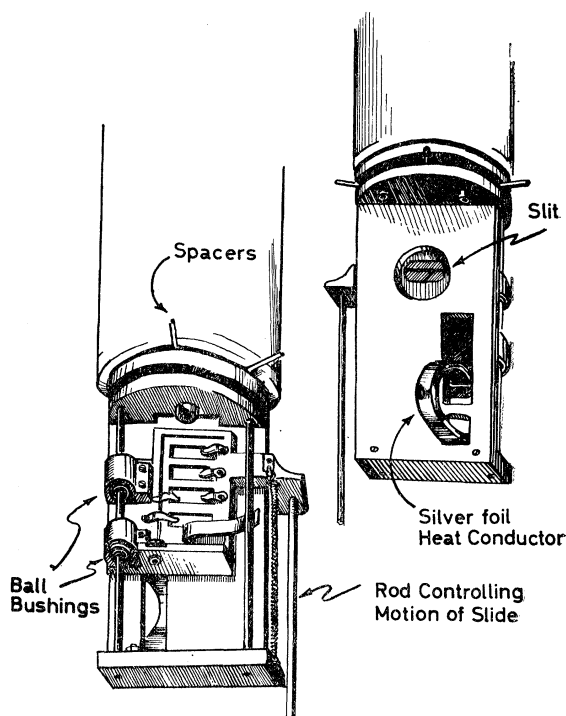

FIG. 1. The low-temperature crystal holder. It employs ball bushings to move four crystals in turn to the slit of the monochromator.

[11] Corning glass filter 6090 is good in this respect. It limits the spectrum to wavelengths above 380 mμ.

in-line motion of the crystal holder was guided by ball bushings.[12] The moving crystal holder made thermal contact with the liquid nitrogen container by means of a pack of 100 thin silver bands.

CRYSTALS

Crystals from the Harshaw Chemical Company were used for many measurements. They had been ordered as "random sizes" and were cleaved just before measurement. Samples from different batches showed no large-scale variations in luminescence properties. The purity of the crystals was determined by optical absorption measurements with the Cary Model 14 spectrophotometer.

The Harshaw KCl and NaCl had the well-known OH^- bands in the ultraviolet. To determine the effect of the impurities associated with this band, crystals that were free of the OH^- band were used in some measurements.[13] In general these behaved like the Harshaw material.

Another impurity known to be present in Harshaw crystals is thallium.[8] The KI used by us had a measurable thallium A band (0.014 cm^{-1}). The nominally pure KCl contained less than 0.03 ppm Tl. The lowest thallium concentration, obtained by deliberate doping and just measurable, was 0.07 ppm Tl. This crystal behaved like the Harshaw material except for a small thallium emission at 305 mμ. With higher concentrations of thallium the 305 mμ emission became more prominent but the pure-crystal luminescence was changed only a little.

RESULTS

A. Excitation Spectra

The quantum efficiency of the luminescence η, as defined by

$$\eta = \frac{\text{rate of emission of photons by the crystal}}{\text{rate of absorption of photons by the crystal}},$$

plotted as a function of exciting photon energy, gives the excitation spectrum. In the fundamental absorption region all the incident light is absorbed (neglecting reflection) and the rate of absorption equals the incident flux. The incident flux was measured by means of a standard phosphor of quantum efficiency independent of exciting energy.[14] Provided the crystal emission does not differ greatly in wavelength from the phosphor emission the quantum efficiency is then given approximately by

$$\eta = \frac{\text{photomultiplier signal with crystal}}{\text{photomultiplier signal with phosphor}} \times 0.10,$$

which is the quantity plotted in the figures.

Figure 2 shows the excitation spectra of four alkali halides at room temperature on a logarithmic scale. It is significant to compare these with the corresponding optical absorption spectra shown as a dotted line below the luminescence spectra.[15] The approximate position of the absorption shoulder is shown by a small arrow.

We note that where the step occurs in the absorption there is a sharp increase in the efficiency of the luminescence. It rises about two orders of magnitude in the immediate vicinity of the step. In KBr and KI the rise in efficiency could change by an even larger factor but it is difficult to determine the lowest efficiencies accurately in the spectral region.[16] Above the step the luminescence efficiency follows the optical absorption: for each maximum in optical absorption there is a minimum of luminescence. This effect is observed in general in the fundamental absorption band luminescence.[5-8] At its highest the quantum efficiency has a value of the order of 1%.

That the threshold of luminescence is real and not connected with the rising optical absorption of the exciton peak can be seen as follows: First, the depth of the threshold is large compared to the other minima associated with peaks comparable in absorption. If the luminescence is only a function of the absorption constant similar peaks should give similar minima. Second, the main decrease of the luminescence occurs in a region where the absorption is nearly constant, or slightly decreasing. Finally, in the exciton region of KBr the exciton peak is a doublet, resolved at room temperature. The corresponding luminescence minimum has no structure.[17] Thus in the exciton region the depression of luminescence is caused not by the high optical absorption but simply by the low efficiency of luminescence processes involving the exciton peaks.

Nevertheless, there is a definite though very low luminescence on the long-wavelength side of the threshold. This effect can be seen in all the curves given.

B. Kinetic Effects

In contrast to the excitation spectra which vary little from crystal to crystal, the kinetic effects of the luminescence, to be described below, are more structure sensitive. We briefly enumerate the effects observed at room temperature.

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[12] These were Thompson's $\frac{1}{8}$-in. size. The shaft had to be ground 0.002-in. undersize and the whole assembly was degreased completely to operate at low temperature.

[13] The OH^--free crystals were grown from chlorine-treated starting material in an atmosphere of argon. We are indebted to M. Klein and J. Ashe for these crystals.

[14] Sodium salycilate was used. Its quantum efficiency was estimated to be 10% using a calibrated photomultiplier-monochromator.

[15] The absorption curves are linear in optical density and are taken from the paper by Eby, Teegarden, and Dutton, reference 1.

[16] Small differences in the low efficiency region between the curves given in reference 3 and here are due to this effect. The newer curves are better.

[17] A dotted line is given in the figure because of uncertainties due to zero-line corrections, which contribute an unknown constant part to the luminescence at very low levels. Any structure in this region is small ($\eta \leqslant 10^{-4}$).
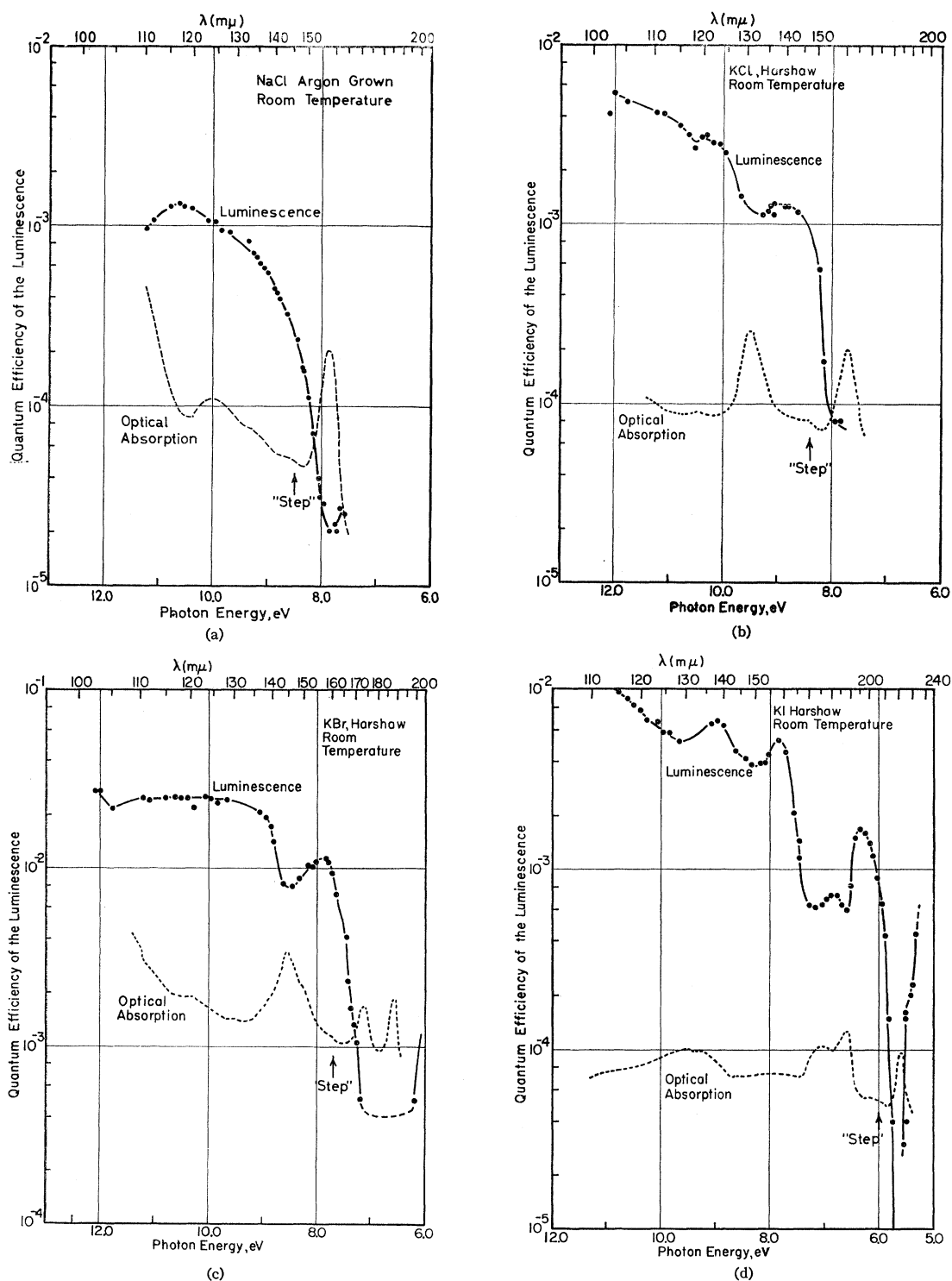
Fig. 2. Excitation spectra of (a) NaCl, (b) KCl, (c) KBr, and (d) KI. The dotted line shows the optical absorption in the same spectral region and the small arrow marked "step" is the point where band-to-band transitions according to Taft and Philipp (reference 2) set in. There is a sharp increase in the efficiency of the luminescence at the step.

1. There is a period of "induction" when, after the ultraviolet is turned on, the luminescence rises from a very low value to the saturation efficiency with a time scale of the order of a minute. Figure 3, curve (a) shows this effect. (The excitation spectra were measured when the saturation was reached.)
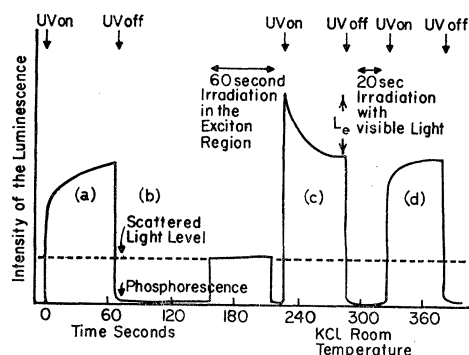
FIG. 3. Kinetic effects of the luminescence. At $t=0$ a freshly cleaved crystal is exposed to the ultraviolet (10.2 eV). As the concentration of carrier traps (recombination centers) rises the luminescence increases in intensity (a). Pre-irradiation in the region of the exciton absorption increases the luminescence (c), while visible light reduces it (d).

2. If after saturation the excitation is turned off, there is a weak phosphorescence [Fig. 3(b)].

3. The luminescence can be enhanced beyond saturation by pre-irradiation in the exciton region. This increase is temporary; irradiation in the band-to-band transition region destroys the extra luminescence [Fig. 3(c)].

4. The luminescence can be reduced to zero and the period of induction can be repeated if the crystal is irradiated with visible light [Fig. 3(d)].

The temporarily enhanced efficiency due to pre-irradiation, quantity L_e in Fig. 3, is plotted in Fig. 4 for KBr as a function of the energy of the photons used for pre-irradiation. The luminescence was measured with 10.2 eV excitation. The dotted curve shows the optical absorption in the same spectral region. It will be noted that the KBr exciton doublet just covers the range of effective pre-irradiation wavelengths. It is reasonable to conclude that the effect described here is directly connected with excitons.

This general behavior contrasts with the behavior of KI at liquid nitrogen temperature where there is strong
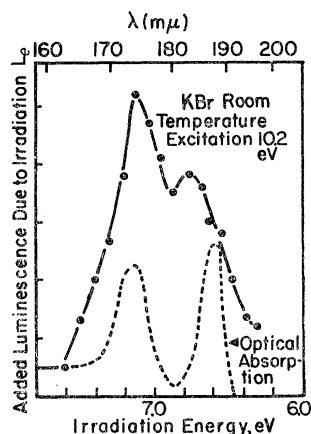

FIG. 4. The enhanced efficiency due to pre-irradiation in the exciton region of KBr (quantity L_e in Fig. 3) plotted as a function of pre-irradiation photon energy. We note that the two components of the exciton peak can be resolved.

luminescence even in the exciton region. This emission is probably the same type as that reported by Teegarden. It differs from the emission at room temperature in that irradiation with visible light does not affect the level of the luminescence. This behavior is confined to the exciton region. At 6.22 eV, energy just higher than that at the step, the luminescence level can be reduced by irradiation with visible light at low temperature as well as at room temperature, and regrown with ultraviolet irradiation. The step marks the change-over point.

C. The Effect of Doping

The time-dependent behavior of the luminescence suggests that the concentration of some center is changing during the irradiation. To investigate the nature of this center we tried to change the luminescence properties by various pretreatments of the crystals.

Most of this work was done on KCl. The addition of known impurities produced in general no large effects. Thus doping with thallium and $CaCl_2$ produced (apart from the 305-mμ Tl emission) only small increases in the level of the pure-crystal luminescence. Crystals heated in air with exposed cleavage faces showed no large-scale changes in luminescence behavior. In general crystals that had received any treatment (the common denominator in most cases is a rapid quenching after heating) showed a slight increase in luminescence level probably associated with mechanical damage. In support of this view, a tenfold increase in the luminescence efficiency was observed when the crystal surface was abraded with silicon carbide paper.

The rate of rise of the luminescence was variable to a slight extent. Taking a pure argon-grown crystal as a standard it was observed that although the final luminescence levels were comparable, the buildup to saturation was rapid in air-grown crystals and particularly slow in crystals doped with $CaCl_2$.

D. The Emission Spectra

In KCl the emission consists of a broad band centered at 430 mμ at room temperature, as shown in Fig. 5. The intensity of the emission ($dN/d\lambda$, the number of photons per wavelength interval) is plotted as a function of photon energy at constant excitation at 10.2 eV. No correction is applied for photomultiplier-monochromator response which is roughly constant and without structure between 250 and 450 mμ. (EMI 6255 A, Bausch & Lomb grating monochromator.) Below 350 mμ the corrections due to scattered light become large and the measurements more uncertain.

The band at 430 mμ is seen in all crystals of KCl at room temperature. Figure 5 also shows a crystal with a mechanically damaged surface—it was abraded with silicon carbide paper. Here the band is slightly broader but again the approximate position is the same.
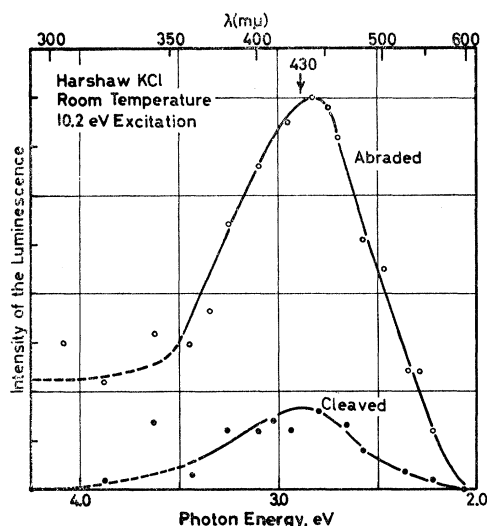
FIG. 5. The emission spectrum of KCl crystals. There is a prominent emission band at 430 mμ. A cleaved and an abraded crystal are compared.
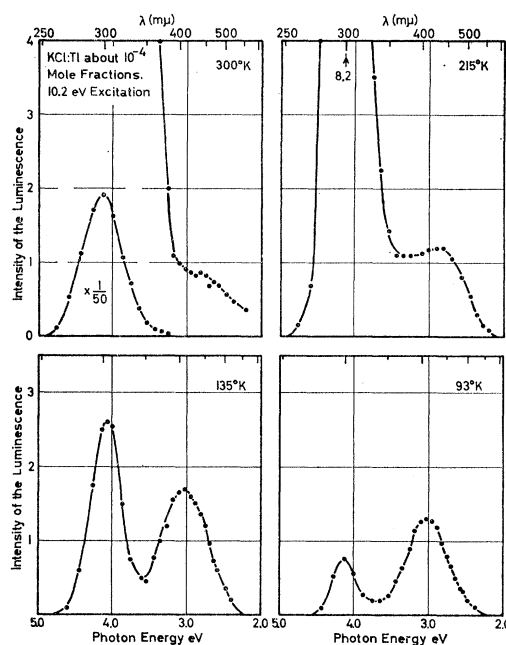

FIG. 6. Emission spectra of a crystal of KCl:Tl at different temperatures. We attribute the band at 410 mμ to the same recombination process that is observed in pure crystals—the shift in wavelength from 430 to 410 mμ could be due to perturbations by nearby thallium ions. We note the insensitivity of the pure crystal emission to temperature, in contrast to the thallium band at 305 mμ.

Figure 6 shows the spectrum of a crystal doped with about 10^{-4} mole fraction of thallium. Luminescence spectra at four different temperatures are given. At room temperature the 430-mμ emission can only be resolved as a long wave tail of the 305-mμ thallium emission. As the temperature is lowered we note the sharp decrease in the thallium luminescence while the pure crystal luminescence changes very little in intensity. But the peak is shifted slightly to higher energies.

In the pure crystals at room temperature the band is centered at 430 mμ while in abraded crystals it is at 440 mμ and in crystals that have not been annealed well or have been doped with thallium the band appears at 420 or 410 mμ. This last effect could either be associated with the copper ion luminescence at 392 mμ[18] or with a changed environment for the recombination centers. We have taken 430 mμ as a mean value for the maximum of the emission band. A correction for photomultiplier sensitivity will shift the peak slightly towards higher wavelengths. The emission band for KBr is at 510 mμ (measured with a calibrated photomultiplier).

DISCUSSION

The discussion can be divided conveniently into two parts. The excitation spectra are connected with the electronic excitations in the fundamental absorption and give information about band structure. The value of the band gap and the electron affinity can be obtained.

The emission spectra and the kinetic properties of the luminescence on the other hand depend on the particular center involved in the recombination process.

A. Excitation Spectra

The excitation spectra, as well as some of the kinetic effects discussed, single out the step as the onset point of recombination luminescence. The sharp rise in efficiency near the step in the optical absorption, we suggest, is a result of the onset of band-to-band transitions at this point. This is in agreement with the hypothesis of Taft and Philipp.

In Fig. 7 we have plotted both the luminescence and the external photoelectric emission[19] on the same graph as a function of photon energy. The units have been chosen to place the two curves parallel. The electron affinity then is the difference between the two curves along the energy axis. In Table I we give the thresholds and the electron affinities obtained from these curves. The numerical values deviate slightly from those in our original report mostly because of the use of a different definition of the threshold. Their uncertainty should be less than 0.2 eV.

The electron affinities given are quite reasonable. For NaCl there is a semiclassical calculation by Seitz.[20] He assumes that an electron coming in from vacuum is

[18] The importance of the copper ion luminescence in commercial crystals has been pointed out by J. Rolfe, R. R. Lipsett, and W. J. King, Phys. Rev. **123**, 447 (1961).

[19] The photoemission data has been taken from the work of Taft and Philipp, reference 2, for KCl, KBr, and KI, and from the paper by Taylor and Hartman, Phys. Rev. **113**, 1421 (1959) for NaCl.

[20] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 400.
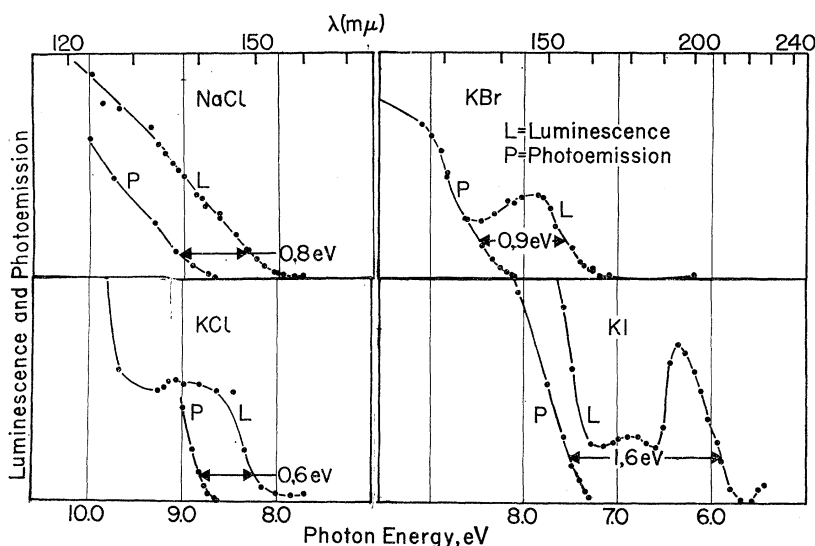
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Fig. 7. Excitation spectra of recombination luminescence compared to photoemission spectra on a linear scale. The difference in the two thresholds is the electron affinity of the crystal.

distributed on the sodium ion much like in metallic sodium. The electron affinity, φ, is then given by

$$\varphi = \alpha(e^2/r_0) - I - \epsilon$$

where the first term is the Madelung energy, I the ionization energy of the sodium, and ϵ the energy due to the development of band structure by the conduction electrons. This last term Seitz assumes to be the same as in metallic sodium. From these assumptions he finds the electron affinity to be 0.8 eV, certainly a fortuitous agreement with our experimental value of 0.8 eV. Mott,[21] comparing photoelectric emission from sodium with photoconductivity from colloidal sodium in NaCl, obtained an affinity of 0.5 eV.

For the potassium salts no comparable data exist. We note however that the Madelung energies for KCl, KBr, and KI are 8.00, 7.62, and 7.10 eV, and that the electron affinities are 0.6, 0.9, and 1.6 eV. Thus, going from the chloride to the bromide the coulomb term changes by 0.4 eV while the observed electron affinity changes by 0.4 eV. From the chloride to the iodide the coulomb term changes by 0.9 eV and the affinity by 1.0 eV. In all these cases the metal ion is the same and it seems that terms such as polarization energy and energy due to

TABLE I. Thresholds of luminescence and photoemission. We associate the thresholds of luminescence with the onset of band-to-band transitions.

Crystal	A Threshold for luminescence (eV)	B Threshold for photoemission (eV)	B−A (electron affinity) (eV)
NaCl	8.0	8.8	0.8
KCl	8.1	8.7	0.6
KBr	7.3	8.2	0.9
KI	5.8	7.4	1.6

[21] N. F. Mott, Trans. Faraday Soc. 34, 500 (1938).

band formation will not be affected by the interchange of the halide. Naively we might say that the main part of the energy gained by electrons going into crystals of increasing ionic radius is simply due to the lower coulomb repulsion of the negative ions.

Returning to the excitation spectra we have still to consider the sharp minima at the inner absorption peaks as well as the question of the slight residual luminescence in the exciton region. We will attempt to explain these in connection with the model for the emission center.

B. The Emission Center

To explain the observed emission we will use the simplest possible model: A vacancy first captures an electron to form an F center and the F center then captures a hole. The net result of the cycle is the destruction of the electron-hole pair at the vacancy. We will show that this model is consistent with most of the observed effects. The model involves centers with relatively well-understood properties and for this reason a prediction can be made about the position of the emission band.

Two photons should be emitted in the recombination cycle. First, when the vacancy captures the electron the normal infrared luminescence of the F center should be observable. Our measurements do not extend to this region. Second, when the hole is captured another photon is emitted and we propose that this is the 430-mμ emission that we have described.

To observe this emission at room temperature it is necessary to have a supply of F centers. We assume they are produced photochemically by ultraviolet irradiation. That F centers are formed by hard ultraviolet has been known since the early work of Smakula.[22] Apker and

[22] A. Smakula, Z. Physik 63, 762 (1930).

Taft[23] and more recently Parker[24] have shown that very high concentrations of the centers can be achieved in thin surface layers. Our induction period then corresponds to the rise in the F-center concentration. The quenching effect of visible light results from the bleaching of the F centers.

Pre-irradiation with light absorbed in the exciton peak increases temporarily the level of the luminescence. This effect can be understood if we accept the view that excitons liberate their energy to form F centers, a theory suggested by many experiments starting with those of Smakula. Thus it is not unexpected that the equilibrium level of the luminescence is shifted to higher values of efficiency on pre-irradiation in the exciton band: new F centers are produced by the excitons. Our curve in Fig. 4 implies that in the valley of the doublet exciton peak a higher concentration of F centers can be reached than in the wings. This observation is in agreement with Parker's data which shows that the concentration of F centers that can be achieved on irradiation in the exciton band depends in the same way on the photon energy.

Unfortunately many of the effects observed become tied up with the general problem of the colorability of the alkali halides, a problem that is not well understood at the present time. It suffices to point out, however, that treatments that are known to enhance the colorability such as heat treatment in air, mechanical damage, doping with $CaCl_2$ or with $TlCl$ and with oxygen (OH^- band) also enhance the luminescence.

The 430-mμ emission, arising as we have suggested from the capture of a hole by an F center, should also be observed when a crystal is irradiated in the α band. The optical excitation of the α center corresponds to the excitation of the negative ions surrounding a negative ion vacancy. But the excited state can also be looked upon as an F center and a hole in a bound state. When the excited center decays to the ground state the process is equivalent to the recombination of a hole with an F center.

This is, in fact, what is observed. We give in a separate paper[25] the positions of the α-center emission bands in KCl and KBr at 440 and 480 mμ, respectively. Within experimental error these figures are in agreement with the recombination emission bands at 430 and 510 mμ. The half-widths and the temperature dependences confirm this view.

On the basis of this model the slight residual luminescence in the exciton band can be explained in terms of a direct excitation of small equilibrium concentrations of α centers present at room temperature.

ACKNOWLEDGMENTS

[23] L. Apker and E. A. Taft, Phys. Rev. **79**, 964 (1950); **81**, 698 (1951); **82**, 814 (1951).
[24] J. Parker, Phys. Rev. **124**, 703 (1961).

[25] To be published. A preliminary report of this work was given. Bull. Am. Phys. Soc. **1**, 38 (1962).