which is in agreement with Fig. 1 (i.e., $\omega_{B_1}''=2\omega_{B_1}$). For this displacement, the potential energy should be $(5/4)\hbar(2\omega_{B_1})$ and therefore, we have the requirement

$$\tfrac{1}{2}\omega_{B_1}^2\langle q_{B_1}^2\rangle_{\text{av}}+\tfrac{1}{2}[(E_2-E_1)^2+4|V_{12}^{(B_1)}|^2\langle q_{B_1}^2\rangle_{\text{av}}]^{1/2} -\tfrac{1}{2}(E_2-E_1)=(5/4)\hbar(2\omega_{B_1}) \quad (55)$$

which follows from Eq. (40). Furthermore, we may take the value

$$E_2-E_1\approx\hbar\omega_{B_1} \quad (56)$$

which is a lower limit of our postulate (20). Thus we get from (54) and (55)

$$|V_{12}^{(B_1)}|^2/(\hbar\omega_{B_1})^2=4.5(\omega_{B_1}/\hbar)\,. \quad (57)$$

The position $q_{B_1}=a_{B_1}$ of the minimum for the lower excited state is given by

$$a_{B_1}=V_{12}^{(B_1)}/\omega_{B_1}^2 \quad (58)$$

or, using (57)

$$a_{B_1}^2=4.5(\hbar/\omega_{B_1})\,. \quad (59)$$

Using the Eqs. (54) to (59) and (43), we have

$$|C_2^{(-)}(a_{B_1})|^2=0.39\,, \quad (60)$$

and consequently

$$\frac{P_{E^{(0)},0,0;E^{(-)},0,0}}{P_{E^{(0)},0,0;E^{(+)},0,0}}\approx\frac{1}{40}\,. \quad (61)$$

Hence, the lines of the transition $E^{(0)}\rightarrow E^{(-)}$ are much weaker than those of the transition $E^{(0)}\rightarrow E^{(+)}$ and this explains why they do not appear in the absorption spectra of Fig. 1. A similar, though more involved, argument shows that the transition probability for the emissive transitions from $E^{(-)}$ to $E^{(0)}$ are much weaker than those from $E^{(+)}$ to $E^{(0)}$.

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Intrinsic Luminescence of RbI and KI at 10°K*

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Emission and excitation spectra for the intrinsic luminescence of RbI and KI have been measured at 10°K and compared with the exciton spectra of the two materials. Two emission bands appear at 3.31 and 4.15 eV for KI, and three for RbI at 2.64, 3.15, and 3.95 eV. Each band has a distinctive excitation spectrum. The high-energy band in each material appears to be connected either with interband transitions or excitation of the $n=2$ Wannier exciton line, while the low-energy emission is associated with absorption in or near the first exciton line. Evidence is given for the existence of a third component of the Wannier exciton series observed recently by Fischer and Hilsch.

INTRODUCTION

IT is known that transitions to exciton states and the conduction band of the alkali iodides result in efficient luminescence at low temperatures.[1] Initial investigations on this intrinsic luminescence have shown that the emission is associated with the recombination of an electron with a trapped hole.[2] Recently, Kabler,[3] and Murray and Keller[4] have presented evidence that the hole trap involved in the luminescence of KI is the well-known V_k center[5] or I_2^--molecule ion. In the present paper some details of the excitation and emission spectrum of the intrinsic luminescence of both KI and RbI are presented. An attempt is made to relate the excitation spectra with specific electronic transitions known to occur in these crystals.

For the purposes of this discussion, a brief description of the absorption spectra of KI and RbI is necessary. The absorption spectrum of a thin film of RbI at 10°K is shown in Fig. 1.[6] According to one interpretation,[7] the sharp lines at 5.74 and 6.65 eV are probably due to transitions from the p^6 ground-state configuration of the iodide ion to a configuration in which the excited electron has a wave function with cubic symmetry. Using atomic notation, we may designate this as a suitably modified p^5s configuration. Two lines appear because of the spin-orbit interaction of the hole in the p^5 core of the iodide ion. The two additional lines at 6.49 and 6.98 eV probably occur because of transitions to a p^5d-like configuration which may be split into several states because of the cubic crystal field. Spin-orbit splitting would further increase the number of possible states due to this configuration. These strong absorption

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* Supported in part by the U. S. Army Research Office, Durham, North Carolina.

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

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

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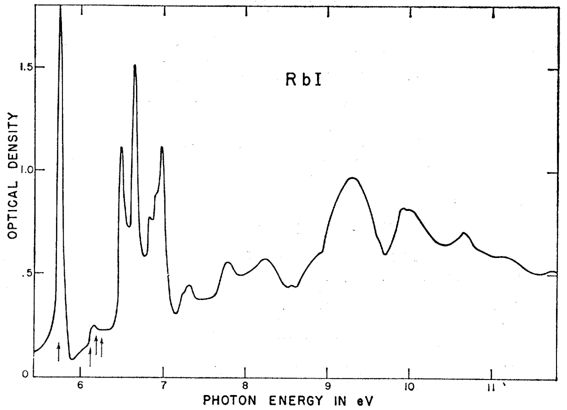

FIG. 1. The absorption spectrum at 10°K of a film of RbI about 1000 Å thick. The positions of exciton lines belonging to the Wannier series discussed in the text are indicated by arrows, as is the series limit.

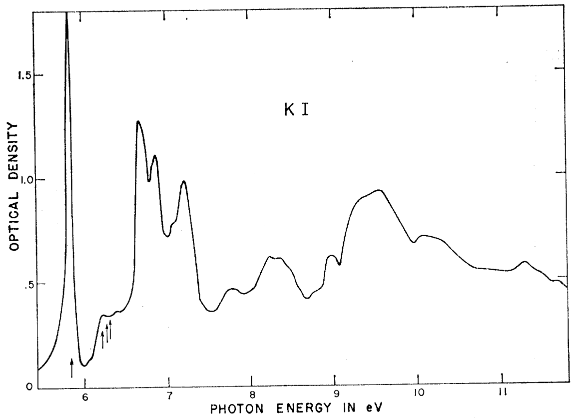

FIG. 2. The absorption spectrum at 10°K of a film of KI about 1000 Å thick. The positions of exciton lines belonging to the Wannier series discussed in the text are indicated by arrows, as is the series limit.

lines may be called exciton lines according to the Frenkel[8] model, in which the excitation is closely confined to a unit cell. Fischer and Hilsch[9] have shown that the shoulder at 6.1 eV is made up of one or more weak absorption bands, not shown clearly in Fig. 1. Fischer and Hilsch suggest that these bands may be due to transitions from the p^6 configuration to diffuse effective mass states in which the electron experiences an essentially coulombic potential. Such states, which occur in the Wannier[8] exciton model, have also been observed in the solid rare gases by Baldini.[10] They would give rise to a hydrogenic-like series of bands if the effective mass approximation was strictly valid. If we call the peak at 5.74 eV the $n=1$ line of this hydrogenic-like series, then the $n=2$ line appears at 6.12 eV, according to Fischer and Hilsch.[9] The $n=3$ and higher lines are not resolved in their absorption data, however. In RbI a photoconductive threshold occurs at 10°K near the expected value of the limit of this Wannier series, that is, at about 6.25 eV.[11] Thus the lines at 6.49, 6.65, and 6.98 eV lie in the Wannier continuum.

The absorption spectrum of KI shown in Fig. 2 has a similar character and presumably can be interpreted in the same way. In addition to the strong Frenkel exciton lines in this spectrum, Fischer and Hilsch[9] have identified a weak line at 6.24 eV which they designate as the $n=2$ Wannier line, in analogy with the result obtained for RbI. The series limit of these lines and hence the expected threshold for photoconductivity lies at 6.31 eV in KI.

It should be noted that other descriptions of the exciton states are possible. For example, Phillips[12] has discussed the absorption lines described above in terms of the band structure of the alkali halides. For our purposes the important point is that one Frenkel exciton line in the absorption spectra of KI and RbI lies below the photoconductive threshold, while the others lie above this threshold. The $n=2$ Wannier line lies, however, below but very close to the photoconductive threshold, since this threshold coincides with the series limit.

EXPERIMENTAL

The monochromator used for exciting the crystals was a small version of the one used by Eby, Teegarden, and Dutton.[13] The light source was a Tropel BNH-1 discharge tube filled with hydrogen. The monochromator used for analyzing the emission was a Bausch and Lomb grating monochromator, No. 33-85-40. An EMI 9526B photomultiplier tube was used to detect light at the exit slit of the emission monochromator. A sodium salicylate photomultiplier combination was used to monitor the spectrum and intensity of the source. The output of the photomultiplier tubes was recorded on a Brown recording potentiometer.

Freshly cleaved samples of size 2.0×1.5×0.2 cm were mounted on an off-center sample holder of a metal cryostat of standard design. The cryostat contained a rotating O-ring seal by means of which the sample could be rotated out of the beam to scan the spectrum of the source directly. The emission was focused by a quartz lens on the entrance slit of the B & L monochromator. The emission spectra were recorded by keeping the excitation monochromator slits open to a band pass of 41 Å and by scanning with the emission monochromator, with a band pass of 66 Å. The excitation spectra for each emission band was obtained by setting the emission monochromator at one wavelength and changing the excitation wavelength. In this case the band pass of the

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[8] For a review of exciton models, see R. S. Knox, *Solid State Physics Supplement 5* (Academic Press Inc., New York, 1963).

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

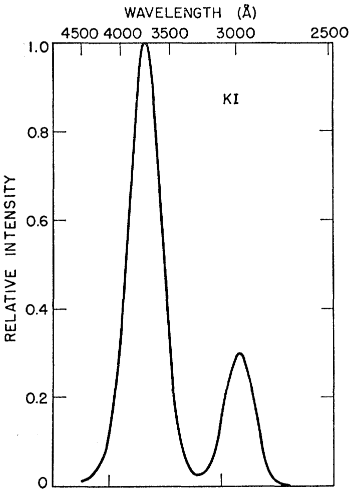

FIG. 3. The emission spectrum of a single crystal of KI at 10°K during excitation with 7.7-eV photons. The band pass of the emission monochromator was set at 66 Å.

emission monochromator was 250 Å and the excitation band pass was 16 Å or 8 Å. The excitation spectrum for the total emission was obtained by setting the emission monochromator with zero order focused on the exit slit, so that all the light emitted by the crystal, undispersed, was incident on the photocathode. Excitation spectra were normalized to correct for changes in the spectral output of the source. Corrections were not made for the spectral response of the photomultiplier, or the transmission of the monochromator used to measure emission spectra, since experience has shown that such corrections do not alter the data significantly.

Crystals of KI and RbI were obtained from several sources. All contained thallium to a greater or lesser degree. The purest crystals of KI were obtained from the Harshaw Chemical Co., while quite pure RbI crystals were supplied by Dr. Karl Korth of Keil, Germany. Only emission which was independent of the source of the crystal is discussed in this paper.

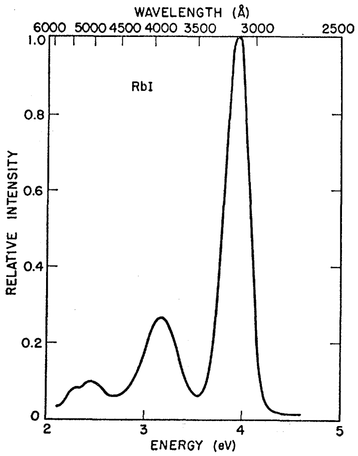

FIG. 4. The emission spectrum of a single crystal of RbI at 10°K during excitation with 7.7-eV photons. The band pass of the emission monochromator was set at 66 Å.

RESULTS

The results of the measurements of the emission and excitation spectra of RbI and KI may be summarized in the following way. Two emission bands appear in the case of KI, at 10°K. These lie at 3.31 and 4.15 eV. At excitation energies significantly greater than the band gap, these two emission bands have about the same relative intensities and positions as those observed at 4°K by Kabler,[3] and Murray and Keller[4] using x rays for stimulation, and are the same bands observed at 80°K by Teegarden,[1] Weeks,[2,14] and Edgerton.[15] This is shown in Fig. 3. In the case of RbI, two strong bands previously observed by Weeks[2,14] and by Edgerton,[15] at 80°K, also appear for 7.7-eV excitation at 10°K. These lie at 3.15 and 3.95 eV as shown in Fig. 4. It is to be noted that the relative intensities of these two lines are different in the two iodides. In RbI the high-energy band is stronger at this excitation energy. In addition, two other weak bands appear for the case of RbI, at 2.27 and 2.44 eV. The origin of these bands is not known. It is possible that they are an intrinsic effect, or are due to some unknown impurity. They are not emphasized in the present discussion. Excitation spectra for the emis-

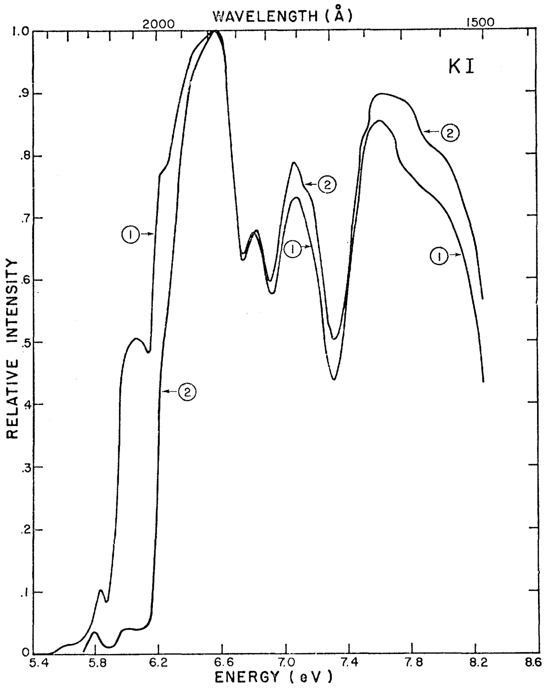

FIG. 5. ① The excitation spectrum of the 3.31-eV emission band of KI at 10°K. ② The excitation spectrum of the 4.15-eV emission band of KI at 10°K. In both cases the band pass of the exciting monochromator was 16.4 Å.

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[14] R. Weeks, Ph.D. thesis, University of Rochester, 1958 (unpublished).

[15] R. Edgerton, Ph.D. thesis, University of Rochester, 1962 (unpublished).

sion bands of KI and the 3.15 and 3.95 eV bands of RbI are shown in Figs. 5 and 6. These spectra show that the low-energy band is excited in the high-energy tail of the lowest lying exciton band, while the high-energy band is stimulated in the region of the shoulder and at higher energies in each material.

A third strong emission band appears in the case of RbI for 6.05-eV excitation. This band has its maximum at 2.64 eV as is shown in Fig. 7. An excitation spectrum for emission at 2.64 eV is shown in Fig. 8. In this spectrum the quantum efficiency has maxima on the long and short-wavelength tails of the first exciton peak, and decreases abruptly at about 6.05 eV, very near the high-energy tail of the $n=2$ line in RbI at 10°K. The excitation spectrum of this band is qualitatively similar to the excitation spectrum of the 3.15-eV band in RbI.

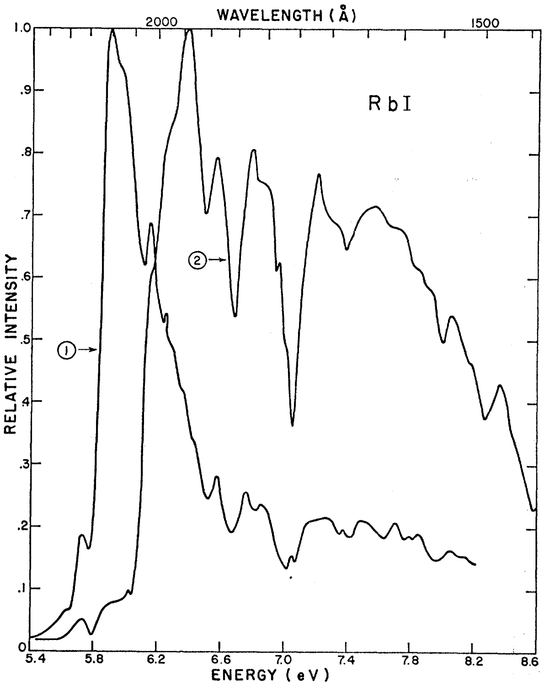

FIG. 6. ① The excitation spectrum of the 3.15-eV emission band of RbI at 10°K. ② The excitation spectrum of the 3.95-eV emission band of RbI at 10°K. In both cases the band pass of the exciting monochromator was 16.4 Å.

The excitation spectra shown all exhibit minima at the peaks of the strong exciton lines, and even at the known position of the $n=2$ Wannier line. This is most easily seen in excitation spectra for the total luminescence of the crystals; that is, spectra taken under conditions where the luminescence is not dispersed before reaching the detecting photomultiplier. Such spectra are shown in Figs. 9 and 10. The one to one correspondence between minima in the excitation spectra and exciton lines provides a somewhat clearer picture of the weak members of the Wannier series than has been obtained from absorption data up to now. For example, in RbI lines are indicated not only at 5.76, 6.12, but also at 6.20 eV as shown by the arrows in Fig. 9. In the case of KI an analogous series of lines occurs at 5.87, 6.22, and also 6.27 eV as is shown in Fig. 10.

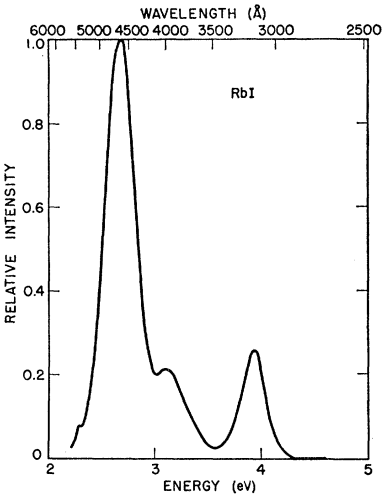

FIG. 7. The emission spectrum of a single crystal of RbI at 10°K during excitation with 6.05-eV photons. The band pass of the emission monochromator was set at 66 Å.

DISCUSSION

The excitation spectra shown above indicate that the low-energy emission band of KI at 3.31 eV, and the 3.15-

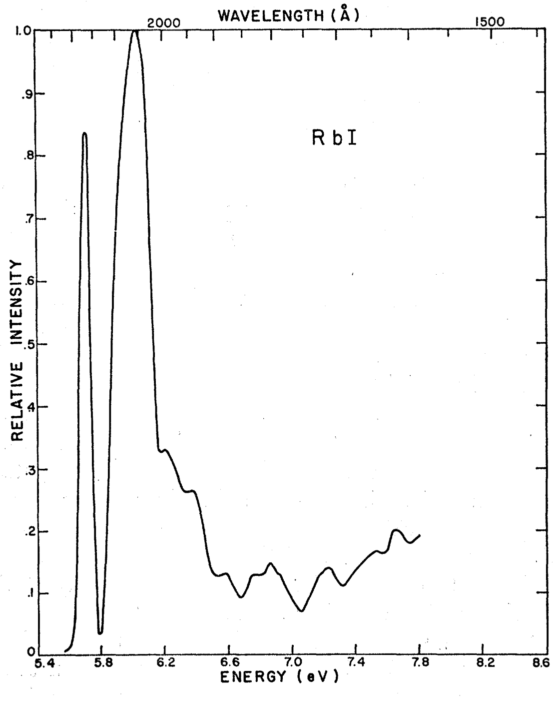

FIG. 8. The excitation spectrum of the 2.64-eV band of RbI at 10°K. The band pass of the exciting monochromator was 16.4 Å.

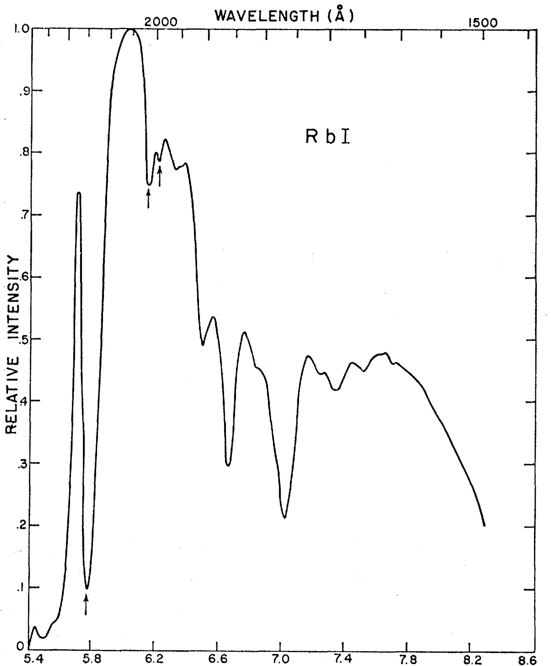

FIG. 9. The excitation spectrum of the total emission of RbI at 10°K. The band pass of the exciting monochromator was 8.2 Å. Arrows indicate the positions of $n=1$ exciton line and the $n=2$ line according to Fischer and Hilsch. The minimum corresponding to a line which may be $n=3$ is also indicated.

and 2.64-eV bands of RbI are connected with excitation in the first exciton band of these materials. This statement has to be qualified by the fact that the emission is quenched by some mechanism when light is absorbed near the surface of the crystals. The high-energy emission in each material (3.95 in RbI and 4.15 in KI) seems to be connected with absorption either in the $n=2$ Wannier line or interband transitions. It is difficult to differentiate between these two possible transitions because of the proximity of the $n=2$ line to the photoconductive threshold.

The two emission bands which characterize the intrinsic luminescence of KI have been observed during excitation with x rays by Kabler,[3] and Murray *et al.*[4] The relative heights of the emission bands is the same as that presented above for 7.7-eV excitation (Fig. 3). Kabler[3] has shown that if V_k centers in x-rayed crystals of KI are oriented with polarized light, and the crystals subsequently irradiated with light absorbed in the *F* band, the 3.31-eV emission appears partially polarized with the electric vector of the emitted radiation perpendicular to the axis of the V_k center. Murray *et al.*[4] have shown that a similar result occurs for the case of the 4.15-eV band, except that the emission is polarized parallel to the molecular axis. The emission is thus to be associated with the presence of V_k centers or halide-molecule ions in the crystals. The similarity between the emission spectra of KI obtained with 7.7-eV excitation and the spectrum observed with x irradiation clearly indicates that the origin of the emission is the same with either excitation.

It is tempting to attribute some of the emission bands of RbI to the same cause; namely, the recombination of an electron with the halide-molecule ion. The most obvious choices are the bands which appear for 7.7-eV excitation, that is, the 3.15- and 3.95-eV bands. The origin of the band at 2.64 eV is as yet unknown, although for the reason stated in the section on experimental technique, this emission is probably not due to an impurity. It is possible that the band originates from the same center as the other two, or that an entirely different hole trap is involved. A more positive identification of the emission bands of RbI could be made by using the technique Kabler[3] employed for KI.

Kabler[3] has suggested that the electronic levels possible in the field of a self-trapped hole or halide-molecule ion (I_2^-) may be considered as the excited states of a halide-ion molecule (I_2^{--}) which has the same electron configuration as a rare-gas molecule. The ground-state configuration of such a molecule may be taken as $(\sigma_g p)^2(\pi_u p)^4(\pi_g p)^4(\sigma_u p)^2$ if we consider only the electrons from the filled p shells of the isolated atoms. This configuration gives rise to a $^1\Sigma_g{}^+$ ground state. Presumably, excitation of a negative ion by absorption in one of the exciton bands can result in an excited state of such a molecule after the lattice relaxes. Thus Kabler[3]

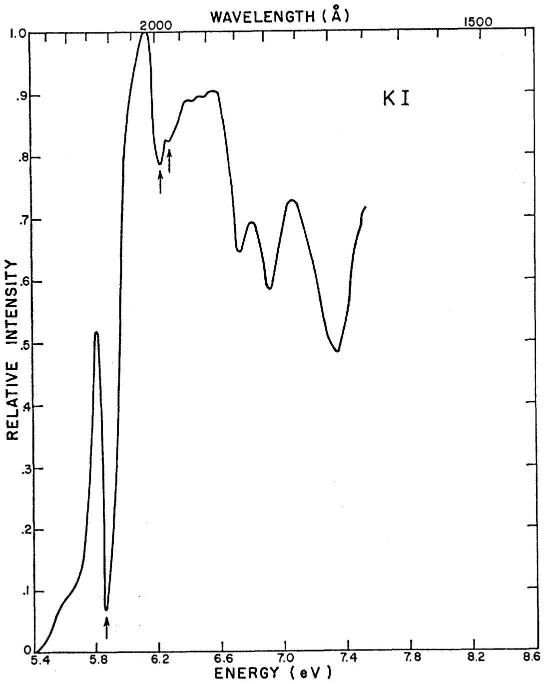

FIG. 10. The excitation spectrum of the total emission of KI at 10°K. The band pass of the exciting monochromator was 8.2 Å. Arrows indicate the positions of the $n=1$ exciton line and the $n=2$ line according to Fischer and Hilsch. The minimum corresponding to a line which may be $n=3$ is also indicated.

TABLE I. The values of the band gap E_G and exciton binding energy G for RbI and KI calculated from the $n=2$ and $n=3$ Wannier exciton lines as discussed in the text. For comparison, the values of E_G and G calculated by Fischer and Hilsch[a] using the $n=1$ and $n=2$ lines are also given. The position of the first line, $h\nu_1$, of a true hydrogenic series has also been calculated from the measured positions of $n=2$ and $n=3$ and is compared with the position of the first exciton line in RbI and KI. The calculated values of the effective exciton mass, μ, are listed.

			(calc)	(obs)			From Fischer and Hilsch	
Crystal	E_G (eV)	G (eV)	$h\nu_1$ (eV)	$h\nu_1$ (eV)	ϵ	μ	E_G (eV)	G (eV)
RbI	6.26	0.58	5.68	5.74	2.72	0.32	6.24	0.50
KI	6.31	0.36	5.95	5.85	2.82	0.21	6.32	0.45

[a] Reference 9.

suggests that the 3.31-eV band of KI is due to a $\Pi_u \rightarrow {}^1\Sigma_g^+$, because of the π polarization observed in the case of this emission. For similar reasons, the 4.15-eV band may be due to a $\Sigma_u \rightarrow {}^1\Sigma_g^+$ transition.

Data presented in the present paper indicates that the high-energy band in both crystals is stimulated either by transitions to a higher lying exciton state, namely the $n=2$ line, or by band-to-band transitions. In the first case, the appearance of the high-energy band could be explained by assuming that the higher energy exciton state relaxes into a higher excited state of the molecule, which seems to be entirely possible. In the second case, the role of free electrons in the preferential stimulation of the high-energy emission may be understood in the following way. For emission to occur, the electron must be recaptured into one of the excited states of the V_k molecule. The probability of capture is greater the higher the excited state because fewer phonons are involved. However, electronic states of too great an energy are probably unstable because thermal ionization may occur before the radiative transition can take place. Thus there most likely is some intermediate excited state, which represents a deep enough electron trap to prevent thermal ionization, but still not so deep as to have a small probability of capture. This state will be preferentially populated by the production of free electrons and give rise to the high-energy emission. It is not possible to decide between these two cases on the basis of the data presented in this paper.

As pointed out above, an interesting by-product of the excitation spectra we have presented is that they appear to give information about the absorption spectra of KI and RbI. Minima which appear in the excitation spectra coincide with the positions of exciton lines. This fact enables us to resolve one more line in the hydrogen-like series first observed by Fischer and Hilsch; that is, the line corresponding to the principle quantum number $n=3$. If the effective-mass approximation, and the Wannier exciton model is valid, the positions of such lines should be given by the formula

$$h\nu_n = E_G - G/n^2, \qquad n=1, 2, 3\cdots,$$

where E_G is the band gap of the crystal and G is the exciton binding energy. Fischer and Hilsch[9] have used this formula to calculate E_G and G using the two lines $h\nu_1$ and $h\nu_2$. This calculation has been criticized because the $n=1$ line may correspond to an electron orbit too small for the effective mass approximation to be valid. If we recalculate G and E_G using the observed values of the $n=2$, and $n=3$ lines in KI and RbI, the results shown in Table I are obtained for the exciton binding energy and band gap. These results are to be compared with the values obtained by Fischer *et al.*,[9] also shown in Table I. The agreement is good except for the value of the exciton binding energy in KI.

The expected position of the $n=1$ line can also be calculated from the above formula and compared with the observed position of the first exciton line in both materials. It should be noted that the calculated value of $h\nu$ is closer to the observed position of the first exciton line in RbI than in KI, indicating that the effective-mass approximation is somewhat better for RbI than KI. The effective mass of the exciton in electron mass units, μ, is related to the binding energy by $G=13.6\mu/\epsilon^2$ eV, where ϵ is the high-frequency dielectric constant. The value of μ for KI and RbI calculated using the observed $n=2$ and $n=3$ lines is included in Table I.

ACKNOWLEDGMENTS

The authors would like to express their deep appreciation to Professor Robert Knox, Professor Giancarlo Baldini, and Professor Theodore Castner for many discussions of the work presented above.