

## Optical Absorption and Photoconductivity in the $K$ Band of Some Colored Alkali Halides\*

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The optical absorption of various alkali halides colored by different methods was measured in the  $K$ -band region at liquid-nitrogen and liquid-helium temperatures. Particular attention was devoted to RbCl, in which the  $K$  band is well resolved at liquid-helium temperature. It was found that the  $K$  band in RbCl is neither symmetric nor Gaussian and that the band has a relatively long high-energy tail. Photoconductivity studies on RbCl demonstrated that there is appreciable photoconductivity only in this high-energy tail. It is concluded that these data support the Mott-Gurney model of the  $K$  band which attributes the main part of the  $K$  absorption to allowed transitions of the  $F$  center to a series of bound excited states beneath the conduction band.

### I. INTRODUCTION

THE most prominent feature of the colored alkali halides is the well-known  $F$  absorption band.<sup>1,2</sup> Kleinschrod's high-resolution measurements of this band in KCl disclosed a small additional band toward the high-energy side of the main  $F$  band.<sup>3</sup> This absorption, known as the  $K$  band,<sup>1</sup> has been found in the absorption spectra of colored potassium and rubidium chloride, bromide, and iodide.<sup>3-7</sup> It is best resolved at low temperatures in RbCl, but is obscured by thermal broadening at room temperature. Even at low temperatures no resolved  $K$  bands have been observed in the lithium or sodium salts, although in NaCl the  $F$  band has a long high-energy tail which may be due to the high-energy part of an unresolved  $K$  band.<sup>6</sup>

Following the report of Kleinschrod's observations, Mott and Gurney suggested that the additional absorption was the result of electronic transitions of the  $F$  center to highly excited states.<sup>8</sup> They based their speculation on a hydrogenic model of the  $F$  center and assigned the  $F$  band to the  $1s-2p$  transition and the  $K$  band to the sum of the  $1s-np$ ,  $n \geq 3$ , transitions. Dexter estimated the oscillator strength of the KCl  $F$  band

and several points in the  $K$  band on this model and concluded that it gave reasonable agreement with experiment.<sup>9</sup> Subsequently, doubt was cast on this interpretation by observations of Etzel and Geiger, and Geiger that indicated there was no relation between the  $F$  and  $K$  bands.<sup>10</sup> Similar results were also reported by Konitzer and Markham.<sup>11</sup> However, more recent work using crystals of high purity have re-established a connection between the  $K$  band and the  $F$  center<sup>4,7</sup> and it seems definitely established that at least part of the absorption in the  $K$ -band region is due to transitions of the  $F$  center.<sup>12</sup>

In the last few years there has been considerable speculation as to the nature of the absorption giving rise to the  $K$  band and the present work was undertaken to clarify some features of this band. The optical absorption of various colored alkali halides was measured at liquid-nitrogen and liquid-helium temperatures in both x-rayed and additively colored crystals. Particular attention was devoted to RbCl in which the  $K$  band is well resolved at liquid-helium temperature. In the case of this salt the photoconductivity of the colored crystal was also measured for optical excitation in the  $K$  band.

### II. EXPERIMENTS

The samples used for absorption measurements were made by room-temperature x-ray coloration of hydrided crystals. Additively colored crystals were also used in several comparison measurements of absorption spectra and for the photoconductivity studies. The x-rayed crystals were kept in darkness after coloration

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<sup>1</sup> F. Seitz, *Rev. Mod. Phys.* **18**, 384 (1946); **26**, 7 (1954).

<sup>2</sup> J. H. Schulman and W. Dale Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962).

<sup>3</sup> F. G. Kleinschrod, *Ann. Physik* **27**, 97 (1936).

<sup>4</sup> F. Lüty, *Z. Physik* **160**, 1 (1960).

<sup>5</sup> J. D. Konitzer and J. J. Markham, *J. Chem. Phys.* **32**, 843 (1960).

<sup>6</sup> J. J. Markham and J. D. Konitzer, *J. Chem. Phys.* **34**, 1936 (1961).

<sup>7</sup> G. E. Stungis, J. J. Markham, and G. A. Noble, *J. Chem. Phys.* **40**, 3634 (1964).

<sup>8</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 114.

<sup>9</sup> D. L. Dexter, *Phys. Rev.* **83**, 435 (1951).

<sup>10</sup> H. W. Etzel and F. E. Geiger, Jr., *Phys. Rev.* **96**, 225 (1954); F. E. Geiger, Jr., *ibid.* **97**, 560 (1955).

<sup>11</sup> J. D. Konitzer and J. J. Markham, *Phys. Rev.* **107**, 685 (1957).

<sup>12</sup> D. Y. Smith and G. Spinolo, following paper, *Phys. Rev.* **140**, A2121 (1965).

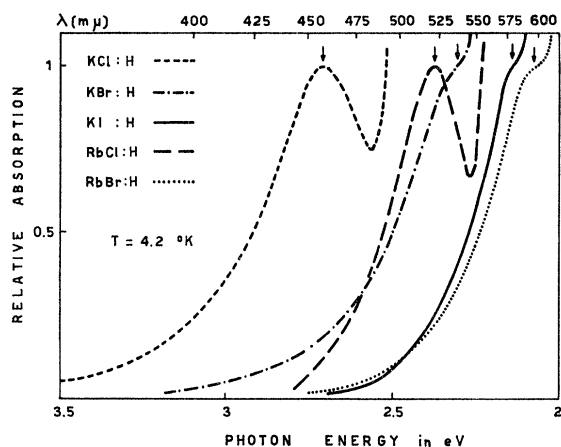


FIG. 1. Absorption spectra in the  $K$ -band region of various colored alkali halides at liquid-helium temperature.

and the additively colored ones were mounted on the optical cryostat under faint illumination.

All optical-absorption measurements were made with either a Cary 14 or Cary 15 spectrophotometer. The photoconductivity measurements were performed with apparatus described by Tippins and Brown<sup>13</sup> and care was taken to avoid polarization effects. All photoconductivity measurements were made with a constant-slit-width monochromator and the amount of light falling on the specimen was determined by calibration with a cesium-antimony photocell.

Figure 1 shows the  $K$  bands for x-ray colored samples of KCl, KBr, KI, RbCl, and RbBr as measured at liquid-helium temperature. The optical densities at the

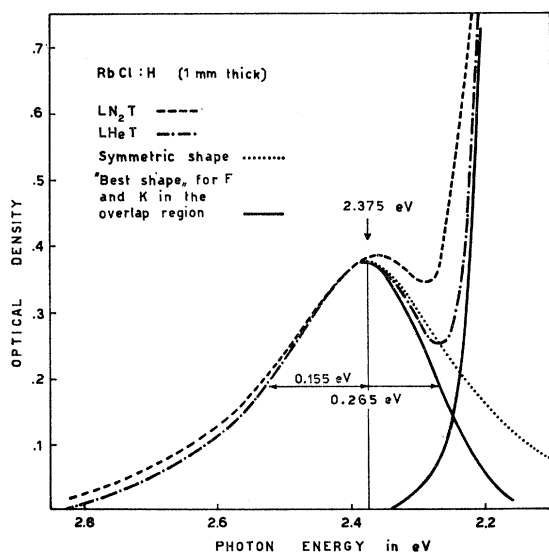


FIG. 2. Absorption spectra of colored RbCl:H at liquid-helium and liquid-nitrogen temperatures. The dotted "symmetric shape" curve is the reflection of the high-energy side of the liquid-helium temperature  $K$  band about the peak of the band.

<sup>13</sup> H. Tippins and F. C. Brown, Phys. Rev. **129**, 2554 (1963).

peaks of the bands have been normalized to one and the  $L$  bands have been suppressed in drawing these curves to show the  $K$  bands more clearly.<sup>14</sup> The absorption spectra of additively colored KCl and RbCl were measured for comparison and they showed no significant differences from those of the x-rayed crystals.

The  $K$  band in RbCl is the best resolved and the present RbCl measurements are reproduced on an expanded scale in Fig. 2. In the past it has been customary to assume that the  $K$  band is symmetrical.<sup>4,5,15</sup> A symmetric reflection of the high-energy side of the liquid-helium temperature  $K$  band about its peak is shown by the dotted curve in Fig. 2. This curve passes above the actual absorption on the low-energy side indicating that the  $K$  band cannot be symmetric. Furthermore, because of the good separation of the  $F$  and  $K$  bands, it seems improbable that there is appreciable  $F$  absorption near the peak of the  $K$  band in RbCl. A possible decomposition of the overlap region which we believe to be reasonable is shown by the solid curves.

Another characteristic shown in Fig. 2 is that there is very little variation in the peak position of the  $K$  band or in the semi-half-width of the high-energy side for a change from liquid-helium to liquid-nitrogen temperature. This property has also been observed in a variety of salts by Lütty.<sup>4</sup>

The results of the photoconductivity measurements on RbCl are summarized in Fig. 3. Here the wavelength dependence of the photoconductivity of additively colored RbCl at 4.2°K is shown for the  $F$ -,  $K$ -, and  $L$ -band regions of the spectrum. When corrected for optical absorption, the photoconductivity exhibits a maximum in the extreme tail of the  $K$  band, but relatively little photoconductivity in the  $F$  band, the low-energy side of the  $K$  band, or in the peak of the  $K$  band. This is in substantial agreement with previous studies of the  $K$  band in KCl<sup>16</sup> and KBr.<sup>17</sup>

### III. DISCUSSION

The results of the optical-absorption measurements on the  $K$  band in RbCl at liquid-helium temperature show that the band is asymmetric. On the basis of a reasonable decomposition of the overlap region of the  $F$  and  $K$  bands, the semi-half-width of the low-energy side of the  $K$  band is 0.11 eV. The semi-half-width of the high-energy side is 0.155 eV or 1.4 times that of the

<sup>14</sup> In the course of this work the absorption of NaCl:H colored by room x irradiation was measured. No  $L$  bands were found even for crystals with an optical density in the  $F$  band of approximately ten. The minimum optical density that could be observed in the experiments was 0.01, but uncertainties in the background made it difficult to distinguish broad bands with optical densities less than 0.05. In all other hydrided alkali halides that were studied, the  $L$  bands appeared in their normal positions and with the usual relative heights.

<sup>15</sup> F. Lütty, in *Halbleiterprobleme*, edited by F. Sauter (F. Vieweg und Sohn, Braunschweig, 1961), Vol. 6, p. 238.

<sup>16</sup> R. L. Wild and F. C. Brown, Phys. Rev. **121**, 1296 (1961).

<sup>17</sup> R. S. Crandall, Ph.D. thesis, University of Illinois, 1964 (unpublished); R. S. Crandall and M. Mikkor, Phys. Rev. **138**, A1247 (1965).

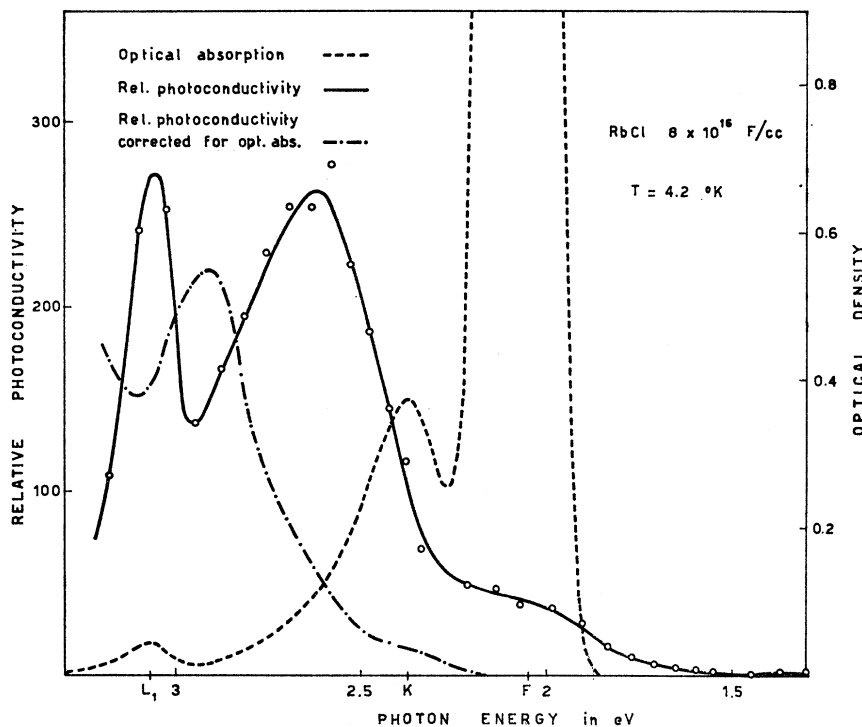


FIG. 3. A comparison of the optical absorption (scale on the right), relative photoconductivity corrected for variations in exciting light intensity, and relative photoconductivity corrected for optical absorption for colored RbCl at liquid-helium temperature.

low-energy side. This is in contrast to the more symmetric *F* band for which this ratio is of the order of 1.1.<sup>7</sup> More striking, though, is the long high-energy tail which extends over half an electron volt beyond the peak of the band.

To see if the high-energy side of the *K* band has a simple shape, the normalized absorption coefficient for the KCl and RbCl *K* bands was plotted versus  $(E-E_0)^2$  as shown in Fig. 4. Here  $E_0$  is the energy at the peak of the band. The resulting curves are not straight lines indicating that the high-energy side is not Gaussian. A further test is afforded by a comparison of the high-energy tail with reasonable predictions for RbCl based on the method of Klick, Patterson, and Knox.<sup>18</sup> This is also shown in Fig. 4. In making these predictions it was assumed that the *K* and the *F* bands have the same ground state and that the effective vibrating masses are equal in the ground and excited states. A value of 0.265 eV was used for the half-width and the vibrational frequency in the ground state  $\nu_g$  was assumed to be  $2.45 \times 10^{12} \text{ sec}^{-1}$ .<sup>19</sup> Three curves are shown for different values of the ratio of ground- to excited-state shape parameters,  $K_e/K_g$ . From the poor agreement we have concluded that no other reasonable choices of half-width or higher ratio of  $K_e$  to  $K_g$  would appreciably reduce the mismatch.

If the *K* band is assumed to arise from a single *F*-center transition, the asymmetry of the band and the long high-energy tail imply that the interaction of the lattice and the excited state involved is significantly different from its interaction with the excited state re-

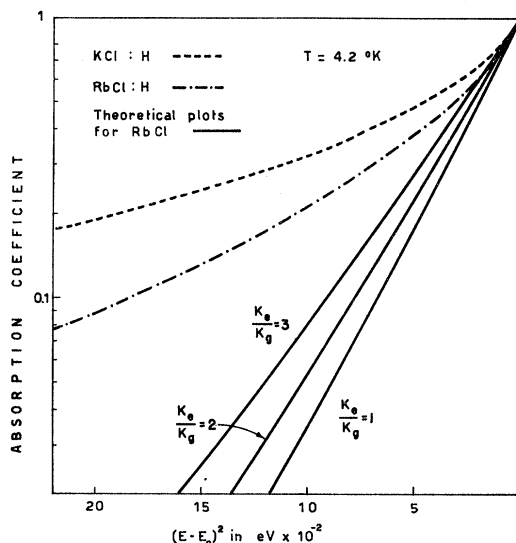


FIG. 4. The absorption coefficient of the high-energy side of the *K* bands in KCl and RbCl plotted versus the square of the energy separation from the peak of the bands. The "theoretical plots" are predicted band shapes found by the method of Klick, Patterson, and Knox from reasonable estimates of the vibrational frequencies and ground- and excited-state shape parameters  $K_g$  and  $K_e$ .

<sup>18</sup> C. C. Klick, D. A. Patterson, and R. S. Knox, Phys. Rev. 133, A1717 (1964).

<sup>19</sup> The half-width is estimated from Fig. 2. The value of  $\nu_g$  was reported by W. Gebhardt and H. Kühnert, Phys. Letters 11, 15 (1964).

sponsible for the  $F$  band. Since these two excited states differ by only a few tenths of an electron volt, a large difference in the interaction with the lattice would seem improbable unless the states were of different symmetry. Since the  $F$  band arises from an allowed  $1s-2p$  transition, this would be in line with Wood's suggestion that the  $K$  band arises from a transition to a state of even parity that is made allowed by lattice vibrations.<sup>20</sup> On the other hand, there is relatively little variation of the area under the  $K$  band when the temperature is changed from that of liquid helium to that of liquid nitrogen. If lattice vibrations were involved in making the transition allowed, there should be a larger increase in area for this temperature change.<sup>21</sup> It therefore seems possible to rule out models in which the  $K$  band arises from a single  $F$ -center transition. This leaves the original Mott-Gurney suggestion as the most probable explanation of the  $K$  band.<sup>8</sup> This model is investigated in detail in the following paper.<sup>12</sup>

The results of the present photoconductivity experiments on RbCl and previous work on KCl<sup>16</sup> and KBr<sup>17</sup> show very low photoconductivity in the  $F$  band and the low-energy side of the  $K$  band, but appreciable photoconductivity in the high-energy tail of the  $K$  band. This indicates that absorption in the  $F$  band and in the low-energy tail of the  $K$  band is to states below the conduction band and suggests that absorption in the high-energy tail may be to states in or near the conduction band. It is, however, difficult to interpret the meaning of the high photoconductivity in the tail of the  $K$  band because of the various mechanisms for excitation into the conduction band.<sup>22</sup>

Transitions directly into conduction-band states are allowed and no doubt account for some photoconductivity in the very high-energy tail of the  $K$  band.<sup>17</sup> Phonon-assisted transitions are also possible so that an elec-

tron excited into a state bound to the  $F$  center may be promoted to a conduction state provided phonons are present. Another mechanism which may give rise to photoconductivity is the relaxation of ions surrounding the  $F$  center after excitation. After absorption the ions around the defect move to new positions and the potential experienced by the  $F$ -center electron is changed. Consequently the electronic wave functions and energy levels are altered. The electronic states of the relaxed system are linear combinations of the states of the unrelaxed system so that a conduction-band state of the relaxed system contains components of both bound and band states of the unrelaxed system. Thus, on relaxation there is a certain probability that an electron excited to a bound state of the  $F$  center may be in a conduction state.

This is not to say that the excited levels of the  $F$  center move into the conduction band on relaxation.<sup>23</sup> In the following paper it is argued that at large distances the effective potential fall-off experienced by the  $F$ -center electron is proportional to  $1/r$ .<sup>12</sup> This holds for both the relaxed and the unrelaxed system and the resulting energy-level spectra have an infinite number of bound states beneath the conduction band.<sup>24</sup> The bound states very near the conduction band in the unrelaxed system will mix significantly with band states on relaxation. However, states well separated from the band go over largely to bound states in the relaxed system.

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<sup>20</sup> R. F. Wood, Phys. Rev. Letters **11**, 202 (1963).

<sup>21</sup> S. F. Schnatterly, Ph.D. thesis, University of Illinois, 1965 (unpublished); Phys. Rev. **140**, A1364 (1965).

<sup>22</sup> See concluding paragraph of D. L. Dexter, C. C. Klick, and G. A. Russel, Phys. Rev. **100**, 603 (1955).

<sup>23</sup> This point is also relevant to the exciton problem. R. F. Wood, Bull. Am. Phys. Soc. **10**, 307 (1965); Solid State Commun. **3**, 39 (1965).

<sup>24</sup> See the discussion starting on p. 80, Ref. 8.